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Partitioning of Zn, Cd, Pb, and Cu in organic-rich soil profiles in the vicinity of a zinc smelter

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ABSTRACT

A five-step sequential extraction procedure was applied to organic-rich soil samples from five soil profiles situated 1–8 km from a zinc smelter. The partitioning of Zn, Cd, Pb, and Cu into five operationally defined fractions (exchangeable, “carbonate”-bound, reducible, oxidizable, and residual) was studied at different soil depths down to 35 cm. In the surface soil (0–1 cm) a major part of Pb and Cu was extracted in the oxidizable fraction, whereas for Zn and Cd slightly more was extracted in the “carbonate”-fraction than in the other four fractions. Extracted metal proportions in the oxidizable fraction were respectively of the order of 30%, 20%, 50%, and 80% for Zn, Cd, Pb, and Cu in the surface soil for all sites, but these proportions decreased with soil depth. In the surface soil less than 20% of all the elements were extracted in the residual fraction, but the proportions associated with this fraction generally increased with soil depth. In the C-horizon, differences in extracted proportions of Pb and Cu in the residual fraction were probably due to geochemical factors, whereas for Zn the low extracted proportion at a highly contaminated site (20%) may be due to Zn migration to the C-horizon at this site. For Cd the extracted proportions in the C-horizon were lower than for the other elements, generally below 20%, presumably because Cd is weaker in terms of its adsorption to the soil than the other elements studied. Total concentrations of the metals decreased strongly with increasing distance from the smelter, but less systematic differences were observed for their distributions among fractions. Potentially bioavailable metal proportions (exchangeable + “carbonate”-bound fraction) in the surface soil were about 50%, 60%, 20%, and 10% for Zn, Cd, Pb, and Cu, respectively. In C-horizon soil the mobility sequence $Cd > Zn \geq Pb = Cu$ was generally observed. The present results indicate that the concentrations and chemical fractionation of Zn, Pb, and Cd in these soils represent a considerable risk to natural terrestrial food chains.

Keywords: zinc smelter, soil contamination, sequential extraction, bioavailability, cadmium

1. INTRODUCTION

Soil contamination in areas surrounding zinc smelters has been frequently studied (Little and Martin, 1972; Martin and Coughtrey, 1976; Farago, 1979; Martin *et al.*, 1982; Verner *et al.*, 1996; Ullrich *et al.*, 1999; Sterckeman *et al.*, 2000; Goodarzi *et al.*, 2002; Almås *et al.*, 2007). Focus has mostly been on total metal concentrations in the surface soil, but some researchers have also studied vertical distribution of contaminants (Buchauer, 1973; Låg, 1974; McMartin *et al.*, 2002; Scokart *et al.*, 1983; Svendsen *et al.*, 2007). In order to assess the ecological risk associated with soil metal contamination, however, determination of total metal concentrations is not sufficient. Sequential extraction procedures, despite their limitations, yield an assessment of the mobility of metals associated with various solid phases, an approach capable of providing

an estimate of metal bioavailability (Basta and Gradwohl, 2000; Sauvé, 2002). Soluble, exchangeable, and chelated metal species are quite mobile and hence potentially available for plants and further steps in the food chain (Maiz *et al.*, 1997). Many functional fractionation methods have been established (Gatehouse *et al.*, 1977; Hirner *et al.*, 1990; Miller and McFee, 1983; Tessier *et al.*, 1979). The extraction procedure followed in the present work is based on the scheme introduced by Tessier *et al.* (1979), a procedure widely employed on metal contaminated soil and sediment samples (Harrison *et al.*, 1981; Hickey and Kittrick, 1984; Li *et al.*, 1995a; Maiz *et al.*, 1997; Kabala and Singh, 2001). Choosing a well-known procedure is of vital importance for researchers to be able to compare their results with others. Limited attention has been paid in the literature on potential bioavailability of metals in soils surrounding zinc smelters (Scokart *et al.*, 1983; Verner

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Table 1 Characteristics for the five locations where soil profiles were sampled. The locations are numbered from 1 to 5 according to their location in the south–north direction

Site no.	Distance from zinc smelter (km)	Position (UTM coordinates) ^a	Soil type ^b	pH ^c
1	7.7	32V 0364154 6656701	Podzol	4.8
2	4.4	32V 0363449 6659894	Cambisol	4.5
3	3.6	32V 0363003 6660660	Podzol/cambisol	4.8
4	3.0	32V 0364203 6661635	Podzol/cambisol	4.0
5	0.9	32V 0362586 6663290	Cambisol	4.8

^aAccuracy of about 10 m.

^bPodzol/cambisol represents soil with features from both podzols and cambisols.

^cpH measured in a surface soil sample (10 × 10 × 5 cm).

et al., 1996; Ullrich *et al.*, 1999; Basta and Gradwohl, 2000; Horckmans *et al.*, 2006), and no relevant information seems to be available on the organic-rich soils (podzols and cambisols) most commonly present in temperate regions.

In the present study a five-step sequential extraction procedure slightly modified from Tessier *et al.* (1979) has been applied to samples from five natural soil profiles near a zinc smelter at Odda, southwest Norway. A site description and total concentrations of Zn, Cd, Pb, and Cu in a number of soil profiles and additional surface soils are reported elsewhere (Svendsen *et al.*, 2007). In the present paper the partitioning of these elements in a selected number of these soil profiles is studied. The main objectives of the present study were:

1. To study the distribution of Zn, Cd, Pb, and Cu in organic-rich surface soils among the five operational fractions defined by the sequential extraction scheme.
2. To investigate variations in extraction behaviour of Zn, Cd, Pb, and Cu with soil depth for each of the five operational fractions.
3. To discuss the potential bioavailability among elements and locations in terms of the results obtained.

In addition to providing more general information about the bonding properties of these elements in soils near the zinc smelter the results would also indicate the extent of their availability to naturally growing plants in the area serving as feed for several species of wild animals.

2. MATERIALS AND METHODS

2.1 Site description

The Odda zinc smelter, which has been in continuous operation for the last 100 years, is situated at the southern end of a 35-km long fjord in southwest Norway. The fjord is surrounded by steep mountains of 1,200–1,500 m altitude, as is a 15-km long valley extending to the south of Odda. Prevailing winds are from the south and the north and follow the direction of the fjord. A more detailed

description of the site and the associated operations is given elsewhere (Svendsen *et al.*, 2007).

2.2 Soil characteristics

Five soil profiles from the previous investigation (Svendsen *et al.*, 2007) located 0.9–7.7 km from the smelter and representing a range of contamination levels were selected for the present study. Coordinates of these sites, their distances from the smelter, and some characteristics of the soils are shown in Table 1.

2.3 Sample preparation

Samples were dried at room temperature (25°C), disaggregated and passed through a 2 mm sieve. The metals were then separated into five operationally defined fractions as follows: (1) exchangeable, (2) susceptible to changes in pH, (3) thermodynamically unstable under anoxic conditions (*i.e.* low Eh), (4) oxidizable, mainly bound to organic matter, and (5) nitric acid recoverable. This separation scheme is in accordance with Tessier *et al.* (1979) with the exception of the final step.

The first fraction (step 1) was obtained by extraction with NH₄NO₃ adjusted to pH 7.0 with HNO₃. About 1.5 g of dry soil and 20 mL of NH₄NO₃ were added to a 50 mL centrifuge tube and shaken for one hour. Then the mixture was centrifuged, the supernatant liquid was decanted and poured into a 50 mL glass vessel. The remaining soil was washed twice with 10 mL distilled water, and the supernatant liquids were removed and added to the first extract. The extract was then diluted with distilled water to 50 mL.

In the second fraction (step 2) 20 mL of 1 M NaOAc adjusted to pH 5.0 with HAc was added to the residue from the first fraction. The mixture was shaken for 5 hours, and the sample was centrifuged and washed following the same procedure as used for the exchangeable fraction.

In the third extraction (step 3) 20 mL of 0.04 M NH₂OH·HCl dissolved in 25% HAc solution was added to the residue from the second step. This mixture was then allowed to boil for 6 hours in a glass bottle placed in a

Table 2 Percentage recovery of metals in a certified reference material (H3-certified reference sample)

Element	Sum (mg kg ⁻¹) ^a	H3-Humus rich soil ^b (mg kg ⁻¹)	Recovery rate ^c
Zn	38.7	43.7 ± 2.5	88.6%
Cd	0.57	0.69 ± 0.03	82.9%
Pb	33.8	31.9 ± 3.0	106%
Cu	5.42	6.88 ± 0.40	78.8%

^aSum of metal concentrations extracted in the five fractions.

^bCertified total concentrations in H3 from Steinnes *et al.* (1997); concentrations are given with standard deviation.

^cRecovery rate was calculated as; [total concentration from five sequentially fractions/certified total concentration] × 100.

water bath at 96°C with regular agitation. After cooling the sample was centrifuged, washed with distilled water, and the centrifuged solution was diluted to 50 mL in the same manner as described for step 1.

The residue from the third step was passed on to the fourth step (step 4) where 3 mL of 0.02 M HNO₃ and 5 mL 30% H₂O₂ adjusted to pH 2.0 with HNO₃ were added. A glass tube containing this soil mixture was placed in a water bath with the temperature stabilised at 85°C, and the tube was covered with a watch glass to avoid splashing. After 2 hours another aliquot of 3 mL of 30% H₂O₂ was added to the soil mixture, and it was allowed to boil for additional 3 hours. After cooling of the sample mixture, 5 mL of 3.2 M NH₄Ac dissolved in 20% HNO₃ and 4 mL of distilled water was added. The soil mixture was then continuously agitated in a shaking machine for 30 min and then centrifuged, washed with distilled water and diluted to 50 mL as described for step 1. The addition of NH₄Ac is to prevent re-adsorption of the extracted metals onto the oxidized soil.

Finally, for step 5 of the sequential extraction the soil residue from the fourth step was added to a centrifuge tube together with 10 mL of concentrated HNO₃. The tube was placed in a hot block for 6 hours, keeping a constant temperature of 110°C. The soil mixture was then filtered through a filter paper (Schleisser and Schull no. 604) to remove any undissolved material and diluted to 25 mL with distilled water. The samples were stored in polyethylene bottles until the analysis.

2.4 Analytical procedures

Zinc concentrations were determined by flame AAS (Perkin-Elmer 1100B) after appropriate dilution of some samples to fit within the linear area of the instrument. Samples high in Pb (≥ 0.08 mg L⁻¹), Cu (≥ 0.01 mg L⁻¹) and Cd (≥ 0.03 mg L⁻¹) were analysed by flame AAS using Zeeman background correction for the Pb and Cu determination, whereas samples low in Pb (< 0.08 mg L⁻¹), Cu (< 0.01 mg L⁻¹), and Cd (< 0.03 mg L⁻¹) were analysed by graphite furnace AAS (Perkin-Elmer Analyst 600 with Auto sampler AS 800) using Mg(NO₃)₂ as a matrix modifier. The average detection limits (D.L.) for the five extraction steps were calculated to 0.1, 0.001, 0.01, and 0.03 mg kg⁻¹ for Zn, Cd, Pb, and Cu, respectively.

For the determination of loss on ignition (LOI) 0.3–3.0 g of the soil samples was dried at 105°C overnight, followed by ignition at 550°C for 12 hours. As shown by Adamo *et al.* (2002) LOI values can be used as a measure of the organic content of the soil. Soil pH was determined with a pH-meter (744 pH Meter Metrohm) in a slurry of 2 g soil in 20 mL of distilled water.

2.5 Quality control

Accuracy of the employed procedure was checked by calculation of recovery rates [RR, Eqn (1)] from sequential extraction of the international reference sample H3 = Humus rich soil (Steinnes *et al.*, 1997), and were 89%, 83%, 106%, and 79% for Zn, Cd, Pb, and Cu respectively (Table 2). Over-all RR higher than 80% are generally considered as acceptable for most applications of multi-element determinations in sequential chemical extractions (Li *et al.*, 1995b).

$$RR = \frac{\text{Sum of metal concentrations in the 5 sequentially fractions}}{\text{Certified acid extractable metal concentration for H3}} \times 100\% \quad (1)$$

Precision was studied from replicate extractions of one sample ($n = 4$) and the resulting relative standard deviations (RSD) were generally 10% or less for all the elements (Table 3). Concentrations in the reagent blanks were negligible (< 1%) for all four elements.

3. RESULTS AND DISCUSSION

3.1 Nitric-acid recoverable concentrations of metals

HNO₃ recoverable concentrations of Zn, Cd, Pb, and Cu in the present samples (Svendsen *et al.*, 2007), reflecting a wide range in contamination levels, are presented in Table 4. As a measure of the feasibility of the sequential extraction, including the homogeneity of the samples, “recovery percentages” (RP) have been calculated [Eqn (2)]. In the case of Cd, some concentrations in the extracts were below the detection limit (D.L.) of the instrument. The calculation was therefore not carried out for Cd.

$$RP = \frac{\text{Sum of metal concentrations in the 5 sequentially fractions}}{\text{HNO}_3 \text{ recoverable metal concentration}} \times 100\% \quad (2)$$

Table 3 Precision calculated for each of the four metals in each of the five fractions

Fraction	RSD ^a (%) ($n = 4$) ^b			
	Zn	Cd	Pb	Cu
Exchangeable	1.4	2.5	16.6	7.1
Acid	5.3	15.0	6.1	1.4
Reducable	12.2	10.9	2.8	7.3
Oxidizable	8.4	1.6	9.4	6.7
Residual	10.7	5.1	6.3	9.3
Mean RSD (%)	7.6	7.0	8.2	6.4

^aRSD = relative standard deviation.

^bFour parallel extractions of the same soil sample.

The obtained RP values for Zn, Pb, and Cu are shown in Table 5. In some cases the RP values considerably exceeded 100%, which indicates that the amount extracted by HNO₃ in some cases may be enhanced by changes introduced during the preceding extraction steps. Mean RP for Zn, Pb, and Cu based on all five soils at different soil depths were 103%, 114%, and 78% respectively. The low

RP observed for Cu may be related to a difference in extraction time with HNO₃ in the previous investigation (12 h) and in step 5 of the present study (6 h). Extraction time may be a significant factor in this case because Cu in the present samples is presumably mainly of natural origin and thus predominantly included in soil minerals, as opposite to Zn and Pb which are considered to be mainly of anthropogenic origin and hence less strongly bound. RPs differing considerably from 100% have also been reported in other applications of sequential extractions to soils (Ramos *et al.*, 1994).

At four of the five sites (sites 2, 3, 4, 5) the surface soil (0–1 cm) HNO₃ recoverable concentrations of Zn, Pb, and Cu (Table 4) were markedly higher than the regional background range for south-west Norway (Svendsen *et al.*, 2007), whereas at site 1 the levels of Zn, Pb and Cu were within this range. For Cd the surface soil (0–1 cm) levels clearly exceeded the regional background range at three of the five sites (site 3, 4, and 5). The HNO₃-recoverable concentrations of Zn, Pb, and Cu (Table 4) in the surface soil (0–1 cm) generally decreased among the sites in the order 5 > 4 > 3 > 2 > 1, *i.e.* with increasing distance from

Table 4 HNO₃-recoverable concentrations of Zn, Cd, Pb, and Cu for the five soil profiles studied^a; sums of metals extracted in five fractions are given in parentheses

Soil depth (cm)	LOI (%)	Zn (mg kg ⁻¹) ^a	Cd (mg kg ⁻¹) ^a	Pb (mg kg ⁻¹) ^a	Cu (mg kg ⁻¹) ^a
Site 1					
0–1	63.4	551 (330)	1.5 (<d.l.)	43.8 (50.4)	11.6 (9.8)
3–5	10.7	557 (140)	0.3 (<d.l.)	39.1 (47.8)	8.8 (7.2)
7.5–10	6.3	44.2 (68.9)	0.1 (<d.l.)	18.8 (29.1)	5.1 (4.2)
15–20	5.1	33.5 (57.9)	<0.1 (<d.l.)	18.9 (29.3)	5.0 (4.4)
30–35	5.0	25.6 (44.2)	<0.1 (<d.l.)	17.8 (24.6)	4.2 (3.2)
Site 2					
0–1	34.3	736 (822)	3.3 (5.9)	80.0 (84.9)	17.2 (13.1)
3–5	17.2	336 (381)	1.4 (3.6)	74.7 (81.3)	16.1 (13.0)
7.5–10	10.6	118 (145)	0.5 (<d.l.)	34.2 (42.1)	9.4 (7.9)
15–20	2.6	54.2 (53.1)	0.1 (<d.l.)	16.8 (19.9)	3.5 (2.5)
30–35	3.3	91.4 (86.1)	0.1 (<d.l.)	19.2 (22.6)	4.3 (2.4)
Site 3					
0–1	67.3	1315 (1178)	6.0 (8.1)	102 (102)	23.0 (16.6)
1–3	57.9	1167 (1148)	5.8 (8.3)	109 (115)	24.6 (18.3)
3–5	31.4	665 (623)	2.7 (<d.l.)	90.8 (92.8)	22.6 (19.3)
5–7.5	32.9	730 (534)	2.2 (<d.l.)	83.1 (93.7)	20.9 (14.9)
7.5–10	24.5	668 (375)	2.1 (<d.l.)	97.8 (86.3)	21.9 (14.6)
15–20	10.3	59.8 (63.7)	0.3 (<d.l.)	26.9 (29.6)	6.1 (5.5)
30–35	7.5	76.0 (79.5)	0.1 (<d.l.)	22.1 (26.5)	5.8 (3.9)
Site 4					
0–1	71.9	1858 (945)	4.3 (6.7)	134 (146)	37.9 (29.9)
3–5	24.0	1179 (315)	1.0 (<d.l.)	116 (112)	25.7 (20.1)
7.5–10	12.9	72.5 (73.4)	0.3 (<d.l.)	32.8 (37.2)	14.2 (11.2)
15–20	4.8	74.0 (69.2)	0.2 (<d.l.)	20.9 (22.3)	11.1 (7.1)
30–35	3.4	72.3 (79.3)	0.2 (<d.l.)	17.4 (21.4)	9.3 (6.8)
Site 5					
0–1	88.8	5255 (5832)	22.1 (24.4)	238 (228)	49.5 (34.1)
3–5	64.6	5304 (5131)	43.2 (44.0)	657 (672)	134 (108)
5–7.5	12.1	1897 (2262)	15.2 (18.4)	240 (268)	86.7 (74.8)
7.5–10	7.1	1067 (1348)	8.8 (12.3)	61.2 (65.7)	36.6 (30.0)
15–20	4.6	501 (587)	2.1 (4.2)	23.4 (27.4)	13.3 (11.2)
30–35	4.5	166 (206)	0.4 (2.2)	23.4 (27.0)	7.7 (5.7)

^aFrom Svendsen *et al.* (2007).

d.l. = detection limit.

Table 5 Sum of metal concentrations in the five sequentially extracted fractions relative to HNO₃-recoverable concentrations (RP values)

	Site	0–1 (cm)	3–5 (cm)	7.5–10 (cm)	15–20 (cm)	30–35 (cm)
Zn	1	60	25	156	173	173
	2	112	113	123	98	94
	3	90	94	56	106	105
	4	51	27	101	94	110
	5	111	97	126	117	124
Mean ± SD ^a		85 ± 33	71 ± 59	112 ± 33	118 ± 27	121 ± 25
Pb	1	115	122	155	155	138
	2	106	109	123	118	118
	3	100	102	88	110	117
	4	109	104	113	107	123
	5	96	102	107	117	115
Mean ± SD ^a		105 ± 7	108 ± 8	117 ± 21	121 ± 16	122 ± 8
Cu	1	84	82	82	88	76
	2	76	81	84	71	56
	3	72	74	67	90	67
	4	79	78	79	64	73
	5	69	81	82	84	74
Mean ± SD ^a		76 ± 8	79 ± 4	79 ± 9	79 ± 14	69 ± 12

^aSD = standard deviation.

the smelter, whereas the corresponding Cd concentrations generally decreased in the order 5 > 3 > 4 > 2 > 1. The concentration levels among the elements range in the order Zn > Pb > Cu > Cd, and the decrease with distance from the smelter is very distinct for all four elements.

3.2 Distribution of metals between the five operational fractions

The average percentage distribution of metals among the five operationally defined fractions is shown in Figure 1. Mean percentage extraction of the metals in different soil layers at the five sites are shown for each of the operationally defined fractions in Figures 2–6, and the ranges of these values in the 0–1 cm soil layer are listed in Table 6. The distributions of extracted Zn, Cd, Pb, and Cu levels among the five operationally defined fractions generally show quite similar trends at all soil depths for the five soil profiles discussed in this paper, cfr. Figures 2–6. Major parts of Pb and Cu are extracted in Fraction 4, probably as a result of oxidation of organic matter to which these metals are generally very strongly adsorbed (Bunzl *et al.*, 1976).

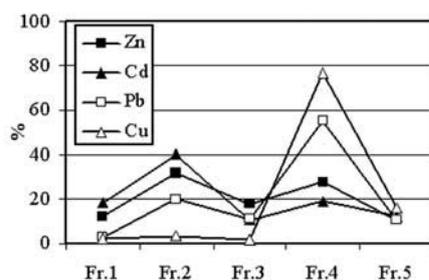


Figure 1 Mean ($n = 5$) percentage distribution of Zn, Cd, Pb, and Cu between the five operationally defined fractions in surface soil (0–1 cm).

Only small amounts of Cu and Pb are extracted in Fractions 1, 2, and 3. Zn and Cd levels are more evenly distributed among the five fractions, but especially for Cd a slightly higher proportion is extracted in the second than in the other fractions.

3.3 Exchangeable concentrations of metals in soil profiles

Element proportions extracted in the exchangeable fraction are likely to be available to plant roots. In the present study 9–16%, 15–21%, 1.5–5%, and 1.0–4% of total Zn, Cd, Pb, and Cu respectively were extracted in this fraction in the surface soil (0–1 cm) at all sites (Figure 1, Figure 2, Table 6). A similar trend was also observed in surface soil samples from the surroundings of a Pb–Zn smelter in Bukowno, Poland, with proportions of exchangeable Zn, Cd, and Pb of about 10%, 40%, and 1–2% respectively (Verner *et al.*, 1996).

Extracted proportions of Pb and Cu did not vary strongly with soil depth at any of the sites, and thus seemed to be independent of the variation in total contamination level (Figure 2). In general exchangeable concentrations of these elements were lower than 5% of the total. At the most heavily contaminated site 5 the exchangeable proportion of Zn and Cd was distinctly higher in deeper soil layers (3–10 cm) than in the surface soil (0–1 cm) and then dropped again at soil depths of 15–35 cm. The levels were stable at about 20% and 40% for Zn and Cd, respectively, in the 3–10 cm soil layer. The HNO₃ recoverable metal concentrations for this soil layer were high (Table 4), but decreased with depth. High proportions of exchangeable elements may indicate that the soil contains elements of anthropogenic origin, even though the anthropogenic metal loadings are subjected to weathering processes presumably making

Table 6 Percentage distribution of metals among the five fractions (range) in the 0–1 cm layer

	F1 ^a	F2 ^b	F3 ^c	F4 ^d	F5 ^e
Zn	9–16	27–35	12–23	19–35	5–18
Cd	15–21	36–51	9–14	11–26	9–15
Pb	1.5–5	16–29	6–16	51–61	7–16
Cu	1.0–4	2–7	0.2–3	67–87	8–23

^aF1 = Fraction 1 (Exchangeable). ^bF2 = Fraction 2 (“Carbonate-bound”). ^cF3 = Fraction 3 (Reducible). ^dF4 = Fraction 4 (Oxidizable). ^eF5 = Fraction 5 (Residual).

the extracted proportions more unavailable with time. This probably explains the high total levels of Zn and Cd observed in the 3–10 cm soil layer at site 5. A similar depth distribution of exchangeable Zn and Cd as for site 5 was observed at site 3. The proportion of extracted Zn and Cd at the least contaminated site 1 decreased markedly between the 0–1 cm and 3–5 cm soil layer, indicating that the surface soil layer contains the highest concentrations of elements of anthropogenic origin (Figure 2). This argumentation is also valid when discussing the behaviour of Zn and Cd at sites 2 and 4. The HNO₃-recoverable concentrations of Zn and Cd at these sites (Table 4) were intermediate the concentrations present at site 1 and 5. The proportions of Zn and Cd extracted from the 3–35 cm soil layers at site 1 were stable at about 1% and 15% respectively.

3.4 “Carbonate”-bound concentrations of metals in soil profiles

Concentrations of Zn, Cd, Pb, and Cu extracted by NaOAc in the 0–1 cm soil layer ranged from 27–35%, 36–51%, 16–29%, and 2–7% respectively of the total extracted metal amounts in the same soil layer among the different sites (Figure 3, Table 6). According to the extraction scheme (Tessier *et al.*, 1979) this fraction should extract metals bound to carbonates in the soil. The carbonate content of the present soils, however, is presumably very low because of generally low pH in the surface soil, and in the discussion this fraction is therefore considered simply as metals extractable with weak acid (pH = 5). There were no systematic trends observed for the variations of extracted proportions of Zn, Cd, Pb, and Cu with soil depth in this fraction for any of the sites.

For all the four metals the percentages of the total levels extracted in this fraction were higher than in the exchangeable fraction (Figures 2 and 3), and among the metals Cd was extracted in the greatest proportion at all five sites (Figure 3). Extracted metal proportions in the surface soil varied much more among the sites in this fraction than for the exchangeable fraction. At the site least contaminated with Cd (site 1) extracted fractions of this element did not vary considerably with soil depth, whereas at sites 2–5 extracted Cd increased with soil depth to some extent. The Zn fraction on the other

hand was seen to be stable with soil depth at sites 3 and 5, whereas extracted fractions decreased with soil depth at the other sites. Extracted proportions of Pb decreased slightly with depth at the two most contaminated sites (sites 4 and 5), but varied little at the other sites. In the case of Cu the extracted proportion was observed to increase slightly with soil depth in all profiles, possibly associated with a higher degree of complexation near the surface where the organic matter content is higher (c.f. Section 3.6).

3.5 Reducible concentrations of metals in soil profiles

Metals extracted in fractions 3 and 4 were by Tessier *et al.* (1979) considered to constitute important sources of potentially available trace metals, which should be considered explicitly when estimating the bioavailability of a particular metal. For this reason we have included extraction data from fractions 3 and 4 in this paper. Metal proportions extracted in the reducible fraction, generally considered to be easily reducible metal forms adsorbed to clays and amorphous Fe and Mn oxides (Scokart *et al.*, 1983), did

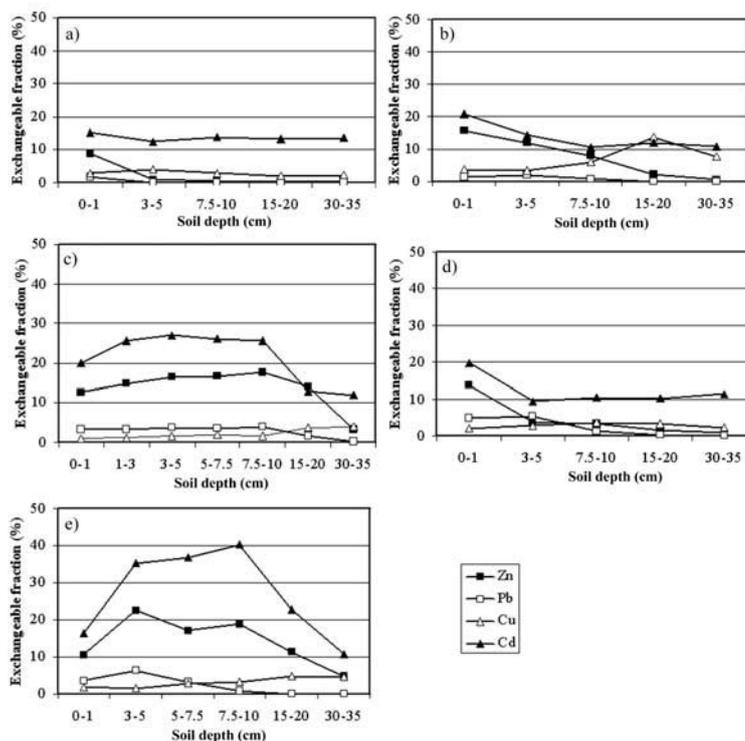


Figure 2 Mean ($n = 5$) exchangeable fractions (%) of Zn, Cd, Pb, and Cu in five soil profiles as a function of soil depth: (a) site 1, (b) site 2, (c) site 3, (d) site 4, and (e) site 5.

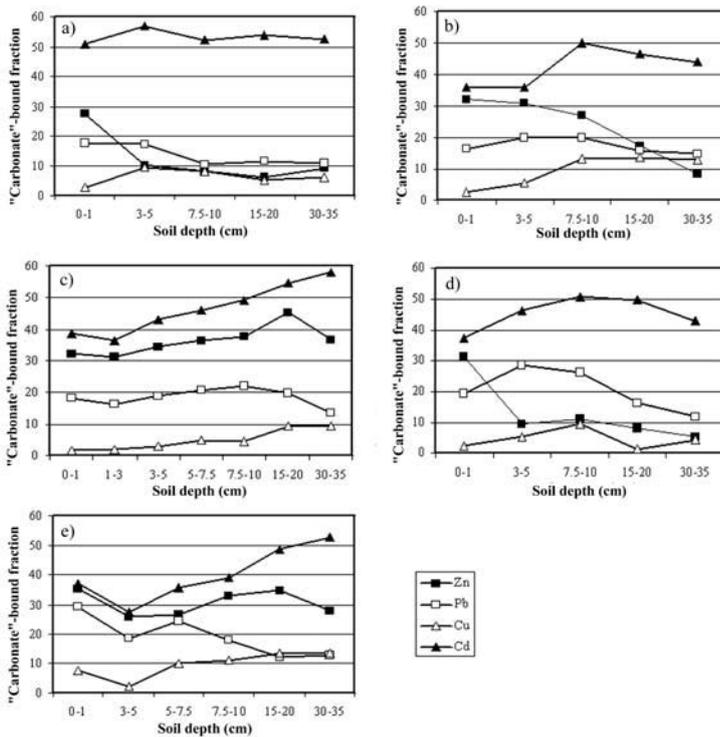


Figure 3 Mean ($n = 5$) "carbonate"-bound fractions (%) of Zn, Cd, Pb, and Cu in five soil profiles are shown as a function of soil depth: (a) site 1, (b) site 2, (c) site 3, (d) site 4, and (e) site 5.

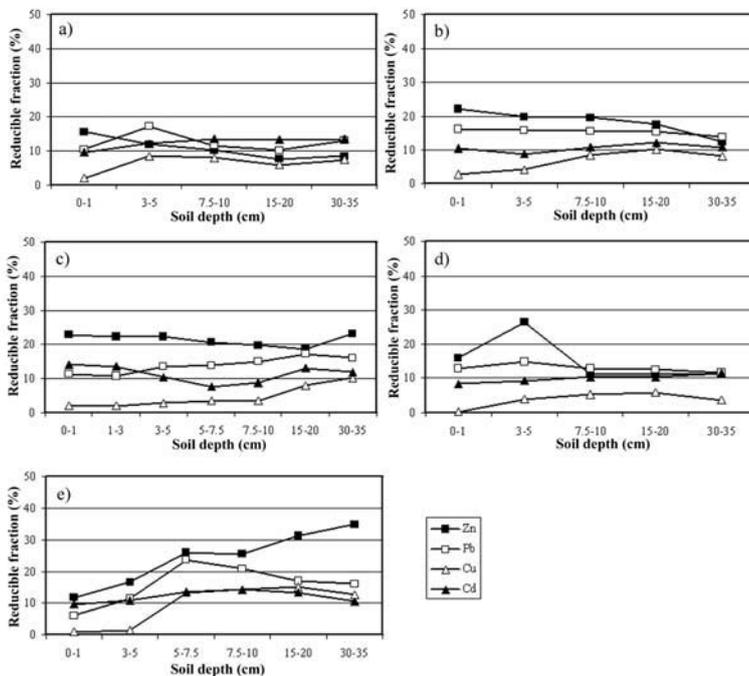


Figure 4 Mean ($n = 5$) reducible fractions (%) of Zn, Cd, Pb, and Cu in five soil profiles are shown as a function of soil depth: (a) site 1, (b) site 2, (c) site 3, (d) site 4, and (e) site 5.

not exceed 40% for any of the metals (Figure 4). Concentrations of Zn, Cd, Pb, and Cu extracted in this fraction in the 0–1 cm soil layer ranged from 12–23%, 9–14%, 6–16%, and 0.2–3% respectively of the total extracted metal amounts (Table 6), and the extracted

metal proportions did not vary appreciably with soil depth at sites 1–4. At the most contaminated site (site 5) the proportions of Zn increased with soil depth, whereas for the other metals the levels only increased slightly. Saturation of the surface layer with Zn from the smelter and subsequent leaching to deeper layers may explain the different behaviour at site 5.

3.6 Oxidizable concentrations of metals in soil profiles

Metals extracted in fraction 4 are considered mainly to constitute metals bound to soil organic matter (Tessier *et al.*, 1979). Organic matter (*e.g.* humic and fulvic acids) is likely to be degraded under oxidizing conditions, leading to a release of soluble trace metals, even though oxidation of all forms of organic matter may not be complete (*op. cit.*). We wanted to test if there was a linear relation in the surface samples (0–1 cm) between the organic matter content (expressed as LOI) and metal levels (mg kg^{-1}) extracted in fraction 4. The organic matter content in the surface soil of the present samples varied from 34.3% at site 2 to 88.8% at site 5 (Table 4). The large spread in organic content at the five sites made the present material well suited for this purpose. Significant linear correlation between oxidizable metal content and LOI values were not found for any of the metals when all the five sites were included. When the site with the lowest organic content (site 2) was removed from the calculation, it appeared that Zn and Cd in the oxidizable fraction showed significant positive linear correlations with LOI ($r = 0.97$ and 0.98 , respectively; $P < 0.05$). Even though significant linear correlations in the surface soil (0–1 cm) were seen between contents of Zn and LOI and between contents of Cd and LOI, the proportions (%) of the same metals in the oxidizable fraction in surface soil did not show any correlation with organic content (LOI%).

In Figure 5 metal proportions extracted in fraction 4 are presented for the five sites as a function of soil depth. Generally about 25%, 20%, 50%, and 80% of Zn, Cd, Pb, and Cu respectively were extracted from the surface layers (0–1 cm), and the relative contribution of this fraction decreased strongly with depth within each profile. This trend is probably related to a decreasing content of soil organic matter with depth (Table 4). The Zn and Cd proportions extracted in the C-horizons (30–35 cm soil depth) were about 10% at all the five sites, whereas C-horizon proportions of Pb and Cu ranged from 20 to 40%. The following extraction efficiency, based on extracted

metal proportions from all the five sites and all soil depths, was observed: $\text{Cu} > \text{Pb} > \text{Zn} > \text{Cd}$, presumably due to the inherent stronger adsorptive behaviour of Pb and Cu towards organic matter in soil relative to that of Zn and Cd (McBride, 1994).

3.7 HNO_3 -recoverable concentrations of metals in soil profiles

The residual fraction extracted with concentrated HNO_3 presumably consists of metal forms extremely strongly bound and thus probably very immobile under soil conditions normally encountered. Variations in residual metal proportions with soil depth at the 5 sites are presented in Figure 6.

In the present surface soils (0–1 cm) less than 20% of all the elements in question were generally extracted in this fraction, but the extracted proportions generally increased with soil depth. This trend is likely to be connected to an increased proportion of mineral material with soil depth. The residual proportion of Pb in the C-horizon was around 40% at sites 2–5, whereas at the least contaminated site 1 it was nearly 60%. Higher extracted Pb proportions at the least contaminated site means that lower Pb proportions have been extracted in the more mobile fractions at this site. This may be due to insignificant migration of anthropogenic Pb at this site, or it may be seen as a consequence of local geochemical differences in the soils. Since Pb is normally very immobile in organic-rich soils (McBride, 1994), we believe that the latter explanation best explains the observation. Extracted proportions of Cu in the C-horizon were about 40% at sites 3 and 5, about 50% at site 2, and about 70% at sites 1 and 4. The differences in extracted proportions for Cu are probably not connected to the surface contamination level but probably reflect local geochemical differences in the soils. The extracted proportion of Cd in the C-horizon was generally lower than 20%, whereas for Zn it was of the order of 70% at sites 1, 2, and 4, and 20% and 30% at sites 5 and 3, respectively. The low extracted proportion of residual Zn in the C-horizon at the highly contaminated site 5 and at site 3 was a consequence of higher extracted proportions in the earlier fractions, and interpreted as a sign of anthropogenic Zn in the C-horizon. Zn migration to the C-horizon at the contaminated site 5 was also indicated previously based on total recoverable Zn/Cd ratios in the same samples (Svendsen *et al.*, 2007). It is not clear why the extracted proportion of Zn in the C-horizon at site 4 is so much higher (70%) than at the less contaminated site 3 (30%).

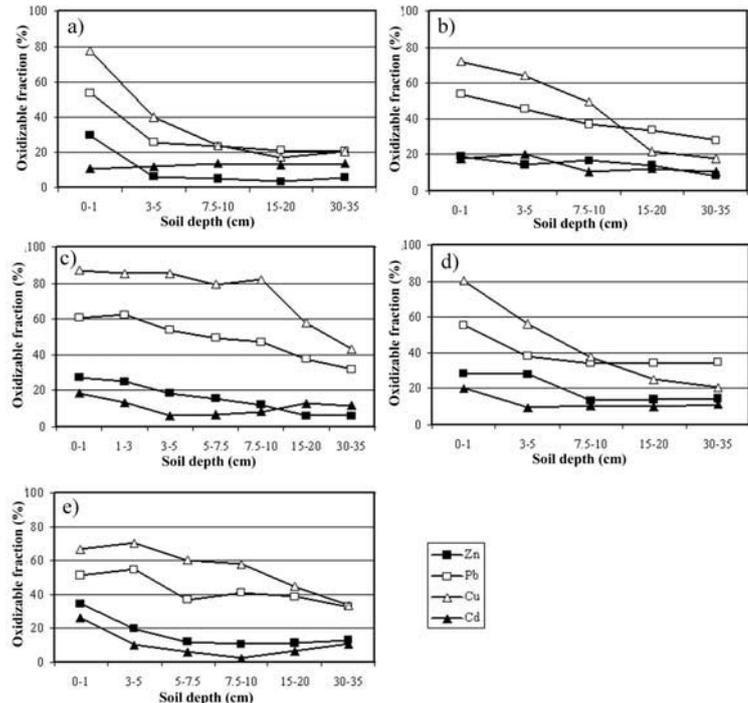


Figure 5 Mean ($n = 5$) oxidizable fractions (%) of Zn, Cd, Pb, and Cu in five soil profiles are shown as a function of soil depth: (a) site 1, (b) site 2, (c) site 3, (d) site 4, and (e) site 5.

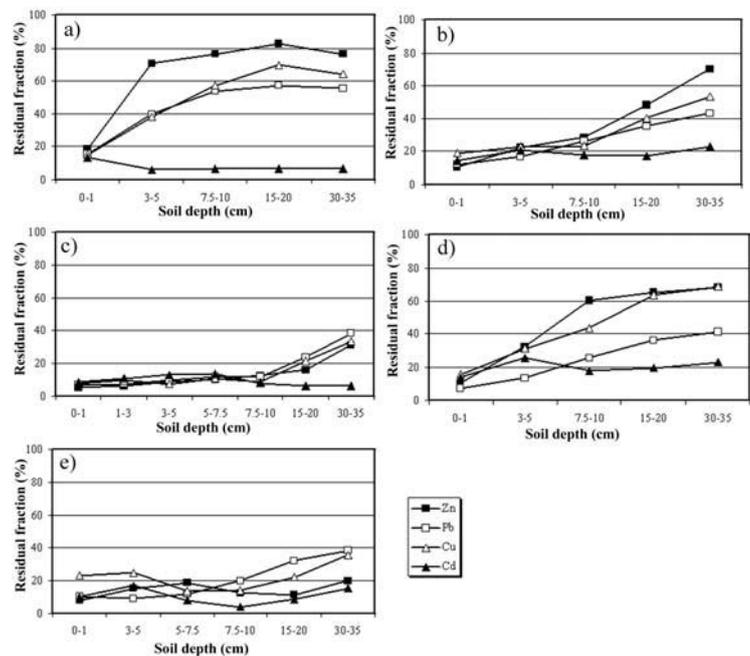


Figure 6 Mean ($n = 5$) residual fractions (%) of Zn, Cd, Pb, and Cu in five soil profiles are shown as a function of soil depth: (a) site 1, (b) site 2, (c) site 3, (d) site 4, and (e) site 5.

3.8 Potential bioavailability of Zn, Cd, Pb, and Cu in soil profiles

Generally the pH dependence of the soil solution concentrations of Zn, Cd, Pb, and Cu shows that the mobility and availability of metals is high at strongly acidic soil reaction

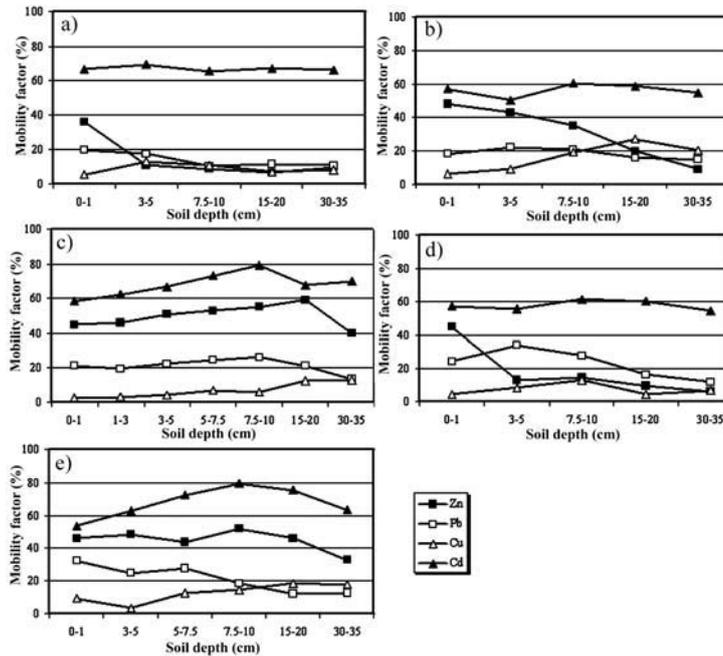


Figure 7 Potentially bioavailable fractions (%) of Zn, Cd, Pb, and Cu in five soil profiles are shown as a function of soil depth: (a) site 1, (b) site 2, (c) site 3, (d) site 4, and (e) site 5.

and increase below that range. Ullrich *et al.* (1999) found that there seemed to be a threshold pH value of about 6, below which a significant increase in the exchangeable fraction of Zn and Pb was observed. In our five soil profiles, the surface pH values were considerably lower than 6.0 (Table 1), and even though site specific soil factors other than pH might control metal mobility in the soil, the low pH values indicate a potential for metal leakage in the studied soil profiles.

Mobility and potential bioavailability of metals extracted from soils by the scheme introduced by Tessier *et al.* (1979) are considered to decrease approximately in the order of the extraction sequence (Harrison *et al.*, 1981). Accordingly metals extracted in the first two extraction steps in this paper, through calculation of “mobility factors”, are considered here as potentially bioavailable [Eqn (3)]. Mobility factors (MF) have been defined as the sum of metals extracted in fraction 1 and 2 as percentage of the cumulative total extracted amounts (Kabala and Singh, 2001). We believe this sum represents a reasonable estimate of the bioavailable pool, since the surface pH values at all the five locations are lower than the pH values of the extraction agents used in steps 1 and 2. Potentially bioavailable metal proportions (percentage mobility factors) at the five sites at selected soil depths are presented in Figure 7.

(Brummer *et al.*, 1986). They found that the concentrations of Zn and Cd in soil solution are generally low at pH 7–8 but increase strongly below pH 6, whereas the Cu and Pb concentrations show distinct minima between pH 5 and 6

$$MF = \frac{(F1 + F2)}{(F1 + F2 + F3 + F4 + F5)} \times 100\% \quad (3)$$

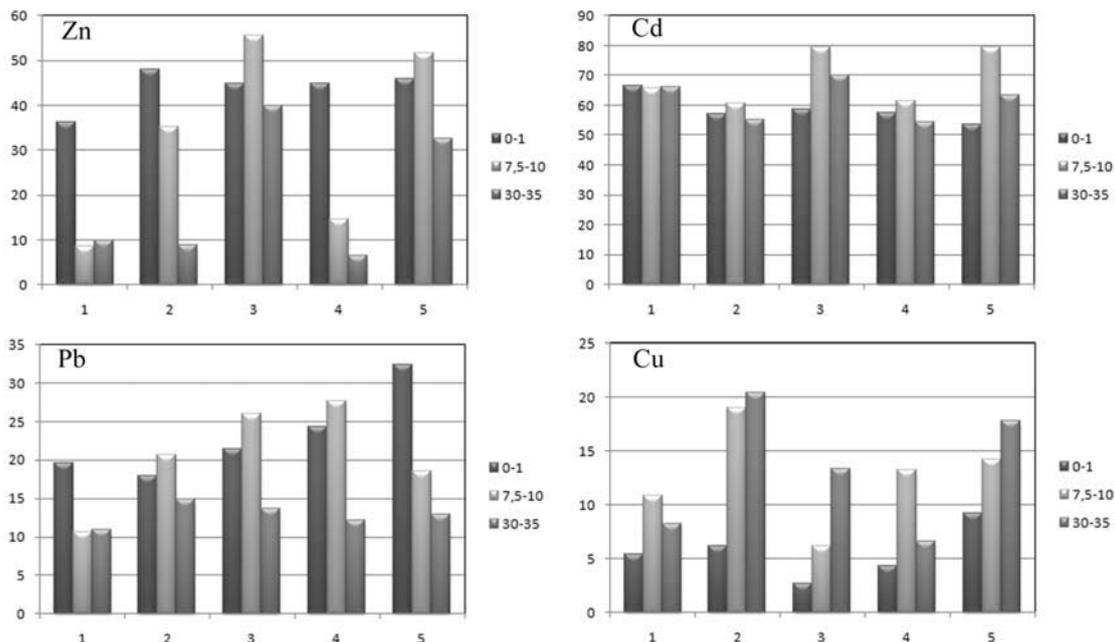


Figure 8 Mobility factors (%) of Zn, Cd, Pb, and Cu in different soil layers at the five sites.

Table 7 Metal concentrations in sequentially extracted fractions in the 0–1 cm soil layer (mg kg⁻¹)

	Site	F1 ^a	F2 ^b	F3 ^c	F4 ^d	F5 ^e
Zn	1	29.1	90.6	51.6	98.3	60.5
	2	130	265	182	159	85.7
	3	148	380	268	324	57.4
	4	129	295	151	269	100
	5	608	2062	689	2023	449
Cd	1	0.48	1.60	<0.30	0.35	0.43
	2	1.24	2.13	0.62	1.06	0.86
	3	1.61	3.11	1.15	1.51	0.71
	4	1.33	2.52	0.57	1.36	0.93
	5	3.99	9.07	2.39	6.44	2.49
Pb	1	0.91	8.94	5.27	27.2	8.06
	2	1.25	14.0	13.6	45.8	10.3
	3	3.33	18.6	11.6	62.0	6.82
	4	6.87	28.6	19.0	81.6	10.2
	5	7.82	65.9	13.7	116	23.5
Cu	1	0.27	0.26	0.21	7.59	1.47
	2	0.49	0.32	0.39	9.44	2.49
	3	0.16	0.29	0.34	14.5	1.36
	4	0.59	0.70	0.06	23.9	4.61
	5	0.63	2.52	0.27	22.7	8.00

^aF1 = Fraction 1 (Exchangeable). ^bF2 = Fraction 2 ("Carbonate-bound"). ^cF3 = Fraction 3 (Reducible). ^dF4 = Fraction 4 (Oxidizable). ^eF5 = Fraction 5 (Residual).

Where MF = mobility factor of the metal; F1 = fraction 1; F2 = fraction 2; F3 = fraction 3; F4 = fraction 4; F5 = fraction 5, all fractions in mg kg⁻¹ (Table 7).

In the 0–1 cm soil layers MFs of about 40–50%, 60%, 20–30%, and 10% were observed for Zn, Cd, Pb, and Cu, respectively (Figure 8). This corresponds to a general mobility sequence of Cd > Zn > Pb > Cu in these organic-rich surface samples, and may indicate high potential biological availability of Zn and Cd in particular. The MFs for Pb in the 0–1 cm soil layer correlated significantly and positively with the total HNO₃-extractable metal levels ($r = 0.96$; $P < 0.01$), whereas corresponding correlations for the other metals in question were insignificant at this soil depth. This finding may indicate that the anthropogenic Pb added to the soil partly remains in relative weakly bound forms potentially available for plant uptake.

In the C-horizon of the soils two different mobility sequences were observed, one for sites 3 and 5 (Cd > Zn > Pb = Cu), and another for sites 1, 2, and 4 (Cd ≫ Zn = Pb = Cu). These sequences are in generally good agreement with results from an investigation of acidic soils from near Hamburg (Bruemmer *et al.*, 1986) where a metal mobility sequence of Cd > Zn > Cu > Pb was observed, and with results from an investigation of soils from near a Zn-smelter in Belgium (Huckmans *et al.*, 2006) where the corresponding metal mobility sequence was Cd > Zn > Pb > Cu.

For comparison between the sampling sites mobility factors of the four metals in the 0–1 cm, 7.5–10 cm, and 30–35 cm soil layers are shown in Figure 8. It appears that the mobility of Cd is consistently high (MF around 60%) at all sites and all soil depths. In the case of Zn the MF is around 40% in the surface layer all over, whereas in the C-horizon soils it was around 40% at sites 3 and 5, but only

around 10% at the other three sites. This supports a previous mobility of Zn to the C-horizon soil at sites 3 and 5 as discussed above. Generally, proportions of Cd, Pb, and Cu in the C-horizon of 60%, 10%, and 10% respectively were observed at all five sites.

4. CONCLUSIONS

Mean recovery percentages of Zn, Pb, and Cu from the five-step sequential extractions of soils contaminated by a zinc smelter were 103%, 114%, and 78% respectively (see Section 3.1), where recovery percent means the sum of an element extracted in the five fractions relative to HNO₃-extractable levels of the same element.

In the surface soil (0–1 cm) a major part of Pb and Cu was extracted in the organic fraction, whereas for Zn and Cd slightly greater amounts were extracted in the "carbonate"-fraction than in the other four fractions (see Section 3.2). In the exchangeable fraction about 9–16%, 15–21%, 1.5–5%, and 1.0–4% of Zn, Cd, Pb, and Cu, respectively, was extracted from the surface soil (0–1 cm) at all sites (Figures 1 and 2, Table 6). The exchangeable Pb and Cu proportions were generally lower than 5% at all soil depths. For Zn and Cd the exchangeable proportions appeared to increase in the 3–10 cm soil depth interval at the most contaminated site, and then decreasing again at greater soil depth. This distribution appeared to follow the distribution of total metal concentrations in the same profiles. No systematic variation with soil depth was observed for Zn and Cd at the less contaminated sites.

In the "carbonate"-fraction higher proportions were extracted of all metals than in the exchangeable fraction, and for Cd this was the fraction generally showing the highest abundance at all soil depths in the five profiles.

Metal proportions extracted in the reducible fraction did not exceed 40% for any of the elements. At the most contaminated site (site 5) reducible proportions of Zn increased notably with soil depth, whereas at the other four sites the variations in reducible metal proportions with soil depth were small.

The oxidizable fraction of Zn, Cd, Pb, and Cu in the surface soil generally amounted to about 25%, 20%, 50%, and 80% respectively. Based on data from four of the 5 five sites it appeared that oxidizable metal content of Zn and Cd in the surface soil showed significant positive correlations with LOI values ($r = 0.97$ and 0.98 ; $P < 0.05$). The contribution from this fraction decreased with soil depth. In the C-horizon, about 10% of Zn and Cd were extracted, and between 20 and 40% of Pb and Cu.

In the residual fraction, less than 20% of all the elements were extracted in the surface soil, but the contribution of this fraction generally increased with soil depth. In the C-horizon, differences in extracted proportions of Pb and Cu in the residual fraction were probably due to geochemical factors, whereas for Zn the low extracted proportions at one highly contaminated site (20%) may be due to migration of anthropogenic Zn to the C-horizon at this site. At the less contaminated sites the extracted proportions of Zn were as high as 70–80% in the C-horizon. For Cd, the extracted proportions in the C-horizon were lower than for the other elements, generally below 20%.

Potentially bioavailable metal proportions were defined as the sum of metals extracted in the exchangeable fraction and the “carbonate”-fraction. Accordingly about 50%, 60%, 20%, and 10% of Zn, Cd, Pb, and Cu, respectively were potentially bioavailable in the surface soil, yielding the mobility sequence $Cd > Zn > Pb > Cu$. Potentially available proportions of Pb in the surface soil at the five sites correlated significantly with the surface contamination level of Pb ($r = 0.96$; $P < 0.01$), indicating that anthropogenic Pb was relatively weakly bound in the soil. In the C-horizon about 60% of Cd was potentially bioavailable, as opposite to only around 10% of Pb and Cu. For Zn about 40% in the C-horizon was potentially bioavailable at the most contaminated site, decreasing to around 10% at the least contaminated site.

Although a discussion of ecological effects related to the present results is beyond the purpose of this paper, a few comments may be made, considering the upper 10 cm of the soil from where most uptake of metals to plants is likely to occur. The present results generally indicate that for Pb and Zn, the two metals representing the highest environmental burden, the potentially plant-available fraction is of the order of 20–40%, varying only moderately with distance to the smelter. With the high total surface concentrations of these metals in the soil there appears to be a considerable risk associated with transfer to terrestrial food chains. In the case of Cd the surface soil concentrations are 1–2 orders of magnitude lower than those of the other metals but the potentially plant-available fraction is as high as 60–80%, placing this highly toxic metal in the risk group along with Zn and Pb. For Cu, with a moderate

total content and a bio-available fraction of only a few percent, the risk potential appears much lower, than for the other elements.

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