CHAPTER 12

Distribution of Ecologically Significant Fractions of Selected Heavy Metals in the Soil Profile

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INTRODUCTION

The amount of wastes, wastewaters, and sewage sludges produced by agricultural, industrial, and municipal activities is rapidly increasing worldwide. In the developing regions of the world this may be simply the result of the improving supply of clean tap water and canalization. Because of increasing environmental awareness, dumping of sewage into surface waters is subject to more strict regulations, thus the amount of wastewaters subjected to treatments is also increasing in nonindustrialized countries. In consequence, a large growth in sewage sludge production may be expected, especially when taking into account the higher requirements and standards for wastewater treatment.

In Hungary approximately 1000 million cubic meters (m^3) of wastewater were produced per year in the middle of the '80s, of which only 187 million m^3 were sufficiently treated, the majority only partially treated, and 173 million m^3 not treated at all. At that time, there was an increasing gap between the development of municipal water supply and of sewage systems, with the latter lagging behind the substantial improvements in the water supply. To develop the collection and proper treatment of liquid wastes is still a problem for many smaller municipalities. According to recent data, the amount of sewage sludges in Hungary was above 1 million m^3 per year. About 40% of these sludges were deposited on agricultural fields and on forest plantations.

One reasonable and economic way to dispose of wastewaters and sludges is to apply them to agricultural fields, thereby exploiting their water and nutrient content. Currently, this practice is becoming increasingly important in many countries. In the early nineties about 30–50% of the sewage sludges were disposed by land application in the majority of the industrialized European countries, which compares to 33% of the annual sludge production in the United States (McGrath et al., 1994).

Sludge Application

Excessive application of wastewater and sewage sludge to agricultural land may cause soil and groundwater pollution problems, since heavy metals and other, potentially toxic elements may be regarded as characteristic contaminants of sewage sludges and waste-waters. These elements often occur in large amounts in these wastes, limiting their applicability in agriculture (Chang et al., 1984; Juste and Mench, 1992).

Sludge application in Hungary is officially regulated in order to prevent or limit the pollution of soils, surface waters and groundwater (Hung. Techn. Dir., 1990; Molnár et al., 1995). The regulations use a 3-step system in which water and nitrogen content of the sludge, and the concentration of any toxic element in the sludge and in the sludge-treated soil are the limiting factors. Also, limiting conditions have been defined for each soil factor related to the application of wastewaters and sewage sludge on a specific agricultural field. Taking into consideration the hazard of contamination of surface and subsurface waters, a permanent monitoring is required on fields where these materials are used, in order to control the load effect. The upper limits for the toxic elements used in the case study discussed in later sections are 15 mg Cd, 1000 mg Cr, 200 mg Ni, 1000 mg Pb, and 3000 mg Zn per kg sludge dry matter (Hung. Techn. Dir., 1990). Assuming average sludge application practices (i.e., incorporating 500 t/ha sewage sludge containing 5% dry matter into a 20-cm surface soil layer), these limits are equal to loadings of 0.375 kg Cd, 25 kg Cr, 5 kg Ni, 25 kg Pb, and 75 kg Zn per hectare. The cumulative amounts of the toxic elements after prolonged application of sludge or of any other contaminant sources must not exceed their maximum acceptable concentrations in the soil, which for the metals selected for the present study are the following: 6.4 kg Cd, 320 kg Cr, 64 kg Ni, 320 kg Pb, and 800 kg Zn per ha for soils with an adsorption capacity of 15–25 cmol/kg soil as calculated from maximum allowed limits of soil concentrations.

Although the limit values relating to sludge application practice are generally lower in Hungary than in the European Community or in the United States (Hung. Techn. Dir., 1990; USEPA, 1989; Chang et al., 1992; McGrath et al., 1994), improper or illegal deposition of sludges and industrial wastes may lead to serious contamination of the Hungarian environment with toxic substances.

Adsorption and Mobility

The potential risks for heavy metal contamination in agricultural fields depend on the relative amounts of metals being adsorbed versus amounts in the soil solution. Potentially toxic elements may become especially hazardous to the environment, when they enter the liquid phase of the soil. Soil solution concentrations are regarded to be indicators of the *mobile* pool of metals in soils (Kabata-Pendias and Adriano, 1995). Water-soluble forms of an element may move through the vadose zone (Kabata-Pendias and Pendias, 1992). Although the removal of metals from sludge-treated soils by leaching to the subsurface is normally very small (McGrath et al., 1994; Kabata-Pendias and Adriano, 1995), some literature data indicate that sludge-born metals may get further from the site of contamination under specific circumstances (McBride, 1995).

There are contradictory views in the literature regarding the extent to which sludge-born metals are vulnerable to leaching. Differences among experimental conditions may be one reason for the differences observed in the movement of various metals in the soil.

For instance, Legret et al. (1988) found significant migration of Ni and especially of Cd, but little or no movement of Pb and Cr during a field experiment on a sludge-treated, coarse-textured soil. Dudka and Chlopecka (1990) observed leaching of Cd, Cr, Ni, Pb, and Zn in a lysimeter experiment on a sandy loam contaminated with sewage sludge containing large amounts of these elements. In contrast, Dowdy and Volk (1983), Chang et al. (1984), and Alloway (1990) reported retention of these elements within the zone of sludge incorporation during both column and field experiments.

Metals originating from anthropogenic sources usually occur in the soil in forms different from the original, native metal content of the soil, thus their mobility and availability is also different. This may change when the freshly added metals enter the dynamic equilibria among the various forms of the elements in the soil chemical processes. When evaluating the biological and ecological impacts of soil contamination, it is necessary to estimate the total amounts of the toxic elements which may become available even after longer periods. Treatment of soil samples with 2 mol/L HNO_3 at 100°C as proposed by Andersson (1976) was shown to be a suitable method to determine the *total potentially available fraction* of the metals in the soil.

Extractions and Bioavailability

The plant-available concentrations of heavy metals occurring in the soil are typically estimated by different chemical extraction methods. Several extractants and extraction procedures have been proposed to determine the availability of essential elements, as well as of some elements potentially toxic to plants. Much research has been carried out to develop a universal extractant characterizing plant availability, and applicable to several elements in soils having widely different properties. One of the most generally useful extractants of this type is acid ammonium acetate+EDTA (AAAc-EDTA). This extractant has been found suitable for the simultaneous extraction of both macro- and micronutrients (Lakanen and Erviö, 1971), and is now included in the procedures adopted by the Soil Advisory Service in Hungary. Extensive FAO studies involving 30 countries proved that this extraction methodology is appropriate for the micronutrients Zn, Fe, Cu, and Mn (Sillanpää, 1982), and also for some toxic elements such as Cd, Pb, Co, and Se (Sillanpää and Jansson, 1992).

Theoretically, the best measure of the availability of elements in a specific soil-plant system should be their actual amounts taken up by the plants. These amounts are often poorly correlated with extractable amounts of the elements in the soil (Marschner, 1991; Chang et al., 1992; McBride, 1995), since they depend not only on soil factors but also on several plant properties and are governed by physiological and biochemical processes. In contrast, soil extraction methods depend on the laws of soil chemistry. Thus, the fractions of the element content utilized by the plants and assessed by plant analyses are not the same as those measured by the soil chemist. However, plant analyses have many practical limitations, and plant uptake processes are susceptible also to environmental factors (Sillanpää and Jansson, 1992). Hence, chemical extraction methods remain useful tools to assess phytoavailability of the elements in the soil.

Recent evidence suggests that elemental concentrations in the soil solution itself may serve as a useful diagnostic tool for plant uptake of the various elements. It is reasonable to expect that plant uptake will be a function of the soil solution concentrations since

water-soluble forms of an element are generally most easily and immediately available for plant uptake (Petruzzelli, 1989). However, there is only a limited amount of data in the literature to support this idea for the toxic elements (Alloway, 1990).

Several laboratory methods have been developed for obtaining the liquid phase from undisturbed bulk soils or from air-dried, ground and rewetted soil samples. Many investigators attempted to characterize the energy status of the liquid phase to be separated from soils. Some of these studies focused mainly on macro-elements (Zabowski and Ugolini, 1990; Jones and Edwards, 1993; Csillag et al., 1995). Others have determined the heavy metal content of the soil solution (e.g., Mullins and Sommers, 1986; cit. in Campbell and Beckett, 1988; cit. in Kabata-Pendias and Pendias, 1992).

CASE STUDY

The initial hypothesis of this case study presented here is as follows. Following the application of heavy metals to the soils, quasi-equilibrium concentration in the soil solution fraction which is held in the soil by forces corresponding to less than $-1500\,kPa$ (pF 4.2 = the conventional wilting point of plants), i.e., which are directly accessible to the roots, may be regarded as the most important variable characterizing plant availability of the elements. To test this hypothesis, sewage sludge spiked with Cd, Cr, Ni, Pb, and Zn nitrates was applied to the top layer of large undisturbed soil monoliths. The distributions of the total potentially available and the plant-available fractions (characterized by the AAAc-EDTA extractable amounts and also by the directly plant-accessible soil solution concentrations) of the applied metals in the soil profile of the monoliths are discussed here. Other aspects of the study were presented elsewhere (Németh et al., 1994; Bujtás et al., 1995).

A brown forest soil (Ochrept, from Gödöllö) and a slightly acidic sandy soil (Psamment, from Somogysárd) were included in the experiments, each one with four monoliths. The major physical and chemical properties of these soil types are shown in Table 12.1. The undisturbed, 40-cm diameter, 100-cm long soil monoliths were prepared following the methods proposed by Homeyer et al. (1973) and modified by Németh et al. (1991). The monoliths were excavated at the selected field sites and their cylindrical surfaces were coated with fiberglass cloth impregnated with a synthetic resin. After the coatings solidified, the monoliths were lifted, and the bottoms were similarly coated. The monoliths were subsequently transported by truck to the laboratory. The coatings made extremely close contact with the soil surface by imbibing the outer micropores, thus eliminating possible "wall effects" during the experiments. The excellent insulating properties of the coating also eliminated leakage from the monoliths.

Weights of the columns at the beginning and at the end of the experimental procedure were recorded on a movable scale. Changes in temperature, soil moisture content, and gas composition along the soil profile were followed by sensors inserted into the monoliths at various depths through holes drilled in the coatings. Temperature was recorded daily. Ambient temperature during the experiments was about 25°C, with 4.1°C difference between the two extreme values. Variation in temperatures of the monoliths was less than 2.0°C. Soil water content was followed by time-domain reflectometry (TDR), and was regulated along the soil profile by saturating the columns from the bottom through a special built-in valve connected to a hanging water-column or by sprinkler irrigation at the

Table 12.1. Some Chemical and Physical Properties of the Soils Used in This Study

Depth (cm)	Horizon	pH H_2O	pH KCl	Organic Matter (g/kg)	CEC (cmol$_c$/kg soil)	SP	<0.02 mm (%)
Brown forest soil, Ochrept (Gödöllő)							
0–8	A$_p$	5.90	5.02	10	9.0	25	19.5
8–16	A$_1$	6.26	5.29	12	8.5	28	18.9
16–43	B	5.85	5.01	11	8.5	28	20.5
43–66	BC	6.51	5.24	[a]	10.1	28	23.3
>66	C	7.15	5.75	[a]	58.0	74	54.4
Slightly acidic sandy soil, Psamment (Somogysárd)							
5–15	A$_p$	5.63	4.48	13	6.7	27	20.2
40–50	B	6.07	4.84	3	4.7	30	12.2
80–90	C	6.38	5.56	[a]	2.3	24	5.0

[a] No measurements.

soil surface. Irrigation water was added on the basis of TDR measurements and/or weighting. Soil gas phase was sampled by special capillary microsensors, and concentrations of water vapor, N_2, O_2, and CO_2 were measured by quadrupole mass spectrometry (QMS) (Pártay et al., 1994). Supplemental light was provided in 12 hours day/night cycles.

The monoliths were air-dried to constant weight, then via a bottom-valve gradually filled up to the surface with deionized water. This step was followed immediately by gravitational drainage through the bottom-valve. The aim of these procedures was to bring the soils to a fairly uniform physical status with a moisture content of maximum water capacity (pF = 0). Also, the procedure compensated the temporary shrinkage of monoliths caused by the long initial air-drying period of the field moist soils.

When gas composition and soil moisture data remained constant for several days after completion of drainage, communal sewage sludge spiked with Cd-, Cr-, Ni-, Pb-, and Zn-nitrates was mixed into the upper 10 cm of the soil. Dry matter content of the compressed sludge was 20.6%, and the inorganic matter content 48.2%. Original concentrations of the selected metals in the sludge were: 12.3 mg Cd, 217 mg Cr, 109 mg Ni, 210 mg Pb, and 3026 mg Zn per kg d.m. These values are comparable to or less than the limits specified in the Hung. Techn. Dir. (1990). The metal nitrates were added to the sludge so that the final metal loading rates in the soil were equivalent to 10, 30, and 100 times the permitted loading limits (L-values) specified in the Hungarian Technical Directive assuming average sludge application practices in Hungary (i.e., 500 t/ha sewage sludge containing 5% dry matter incorporated into a 20-cm surface soil layer). Loadings corresponding to 1L are 0.125 mg Cd, 8.33 mg Cr, 1.67 mg Ni, 8.33 mg Pb, and 25 mg Zn per kg soil. Original, unspiked sludge was used as control treatment at rates of 400 g sludge dry matter per column, resulting in loadings of 0.25 mg Cd, 4.48 mg Cr, 2.25 mg Ni, 4.34 mg Pb, and 62.5 mg Zn per kg soil. Identical amounts of the same sludge were used for each treatment in order to obtain as uniform conditions as possible in terms of such additional factors in the sludge as organic matter content, nutrient levels, and concentrations of other elements.

One week after sludge application, nine corn (*Zea mays* L.) seeds were sown per monolith. When the plants reached a suitable developmental stage, microsensors of the QMS

system were implanted into the stems (one per monolith) to study the gas metabolism in vivo inside the plants. By the end of the experiment the plants had already finished their vegetation period. After harvesting the mature corn plants, the upper parts of the monoliths were cut into four consecutive soil layers at the 0–10, 10–15, 15–20, and 20–30 cm depth intervals. Water potentials of the soil samples were determined, as were relative root distributions.

Soil pH and total potentially available metal concentrations in the soil (after 2 mol/L HNO$_3$ extraction as described by Andersson, 1976) were measured in air-dried soil samples, and plant-availability of the metals was estimated by: (a) metal concentrations in acid ammonium acetate-EDTA soil extracts (Lakanen and Erviö, 1971) of air-dried soil samples, and by (b) directly plant-available concentrations in the soil solution obtained by centrifugation of the moist soil samples immediately after the cutting procedure, from each layer of the monoliths in triplicates (Csillag et al., 1995).

Elemental concentrations in the 2 mol/L HNO$_3$ and AAAc-EDTA soil extracts, and in the soil solution, were measured by inductively coupled plasma atomic emission spectrometry (ICP-AES). Concentration values in the soil solution were related to the mass of the dry soil instead of the volume of the liquid phase, in order to eliminate the differences caused by the slightly different moisture content of the soil samples (water potential $\cong$ pF 0). Recovery of the elements in the potentially available forms was related to *added* metal amounts. Metal budgets, based on the total potentially available amounts were calculated for each depth increments and for the whole columns. The so-called "soil available factor," SA, expressing the "percentage of the total content of an element in the soil which is available for uptake to plants" (Coughtrey et al., 1985), is often used when describing the distribution and transport of radionuclides in terrestrial ecosystems, but it can be applied similarly to the stable forms of the elements. A similar approach was adopted to evaluate the availability of the applied metals in our experiments. Metal concentrations measured either in the plant-available soil solution fractions (c_S) or in the AAAc-EDTA extracts (c_{AE}) were related to the total potentially available metal concentrations measured in the 2 mol/L HNO$_3$ soil extract (c_m):

$$SA_S = 100\ c_S/c_m, \quad \text{and} \quad SA_{AE} = 100\ c_{AE}/c_m$$

The calculated percentages (SA_S and SA_{AE}) characterize the proportion of the directly plant-available and of the supposedly plant-available metal forms, respectively, in the total potentially available metal pool of the soil. Also, the total amounts of the metals found in the liquid phase of the soil layers were calculated from the metal concentrations of the soil solution samples, for each depth increments and for the whole columns. These values were compared to the total potentially available metal contents of the columns.

NITRIC ACID EXTRACTION

The 2 mol/L nitric acid-extractable concentrations of all the five metals increased proportionally to the initial loading rates in the upper 10 cm layer, i.e., in the initially contaminated zone containing the metal-spiked sludge. Figure 12.1 shows linear relationships between the extracted total metal concentrations and the metal loadings (L) for the top layer in the acidic sandy soil. Similar linear relationships were obtained also for the
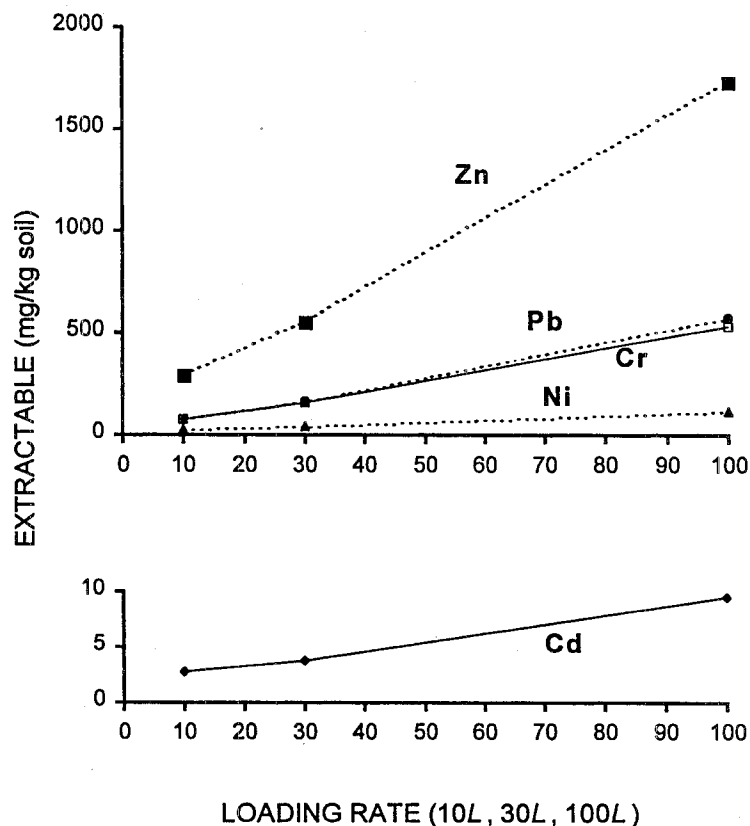
Figure 12.1. Correlations between 2 mol/L HNO$_3$-extractable soil concentrations and loading rates of the metals in the 0–10 cm layer of the slightly acidic sandy soil.

brown forest soil. The measured total metal concentrations in the top 10 cm soil layer accurately reflected at each loading level the differences among the application rates of the five metals, being the highest for Zn and the lowest for Cd, and very similar for Cr and Pb which were applied in identical amounts (Figures 12.1, 12.2a.). The differences are shown by the values of the slopes of the linear regression equations, calculated for the relationship shown in Figure 12.1, where Y is the total extracted metal concentration and X the applied metal loading (L):

$$
\begin{aligned}
\text{Cd:} \quad & Y = 0.076\,X + 1.807 \quad && R^2 = 0.9945 \\
\text{Cr:} \quad & Y = 5.17\,X + 13.87 \quad && R^2 = 0.9984 \\
\text{Ni:} \quad & Y = 1.03\,X + 11.75 \quad && R^2 = 0.9977 \\
\text{Pb:} \quad & Y = 5.63\,X + 8.75 \quad && R^2 = 0.9984 \\
\text{Zn:} \quad & Y = 16.3\,X + 102.5 \quad && R^2 = 0.9983
\end{aligned}
$$

The slopes correspond closely to the ratios among the loading rates of the metals, i.e., Cd : Cr : Ni : Pb : Zn = 0.075 : 5 : 1 : 5 : 15. The brown forest soil showed no substantial increases in metal concentrations in the deeper layers, even at the higher metal application rates, with the exception of Ni and Zn which had slightly elevated concentrations in
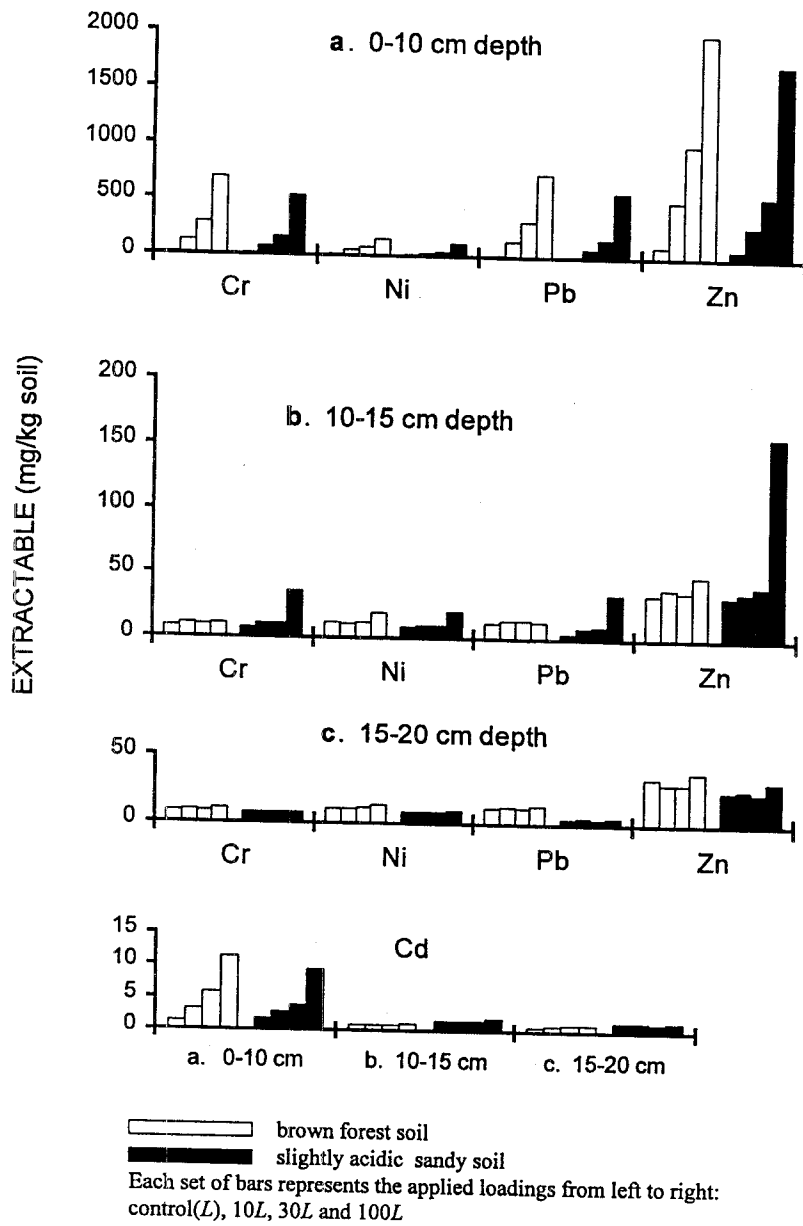
Figure 12.2. Metals extracted with 2 mol/L HNO$_3$.

the 10–15 cm and 15–20 cm depth interval at the highest contamination level. For the more acidic sandy soil we observed a somewhat more pronounced downward movement of the elements below 10 cm at the 100L loading rate (Figure 12.2b).

Distribution of the total metal contents among the sampled layers of the upper 20 cm also shows this feature (Table 12.2). Although most of the metals (generally more than 95% of the total potentially available contents of the upper 20 cm) were found between 0 and 10 cm, small but significant amounts of the applied metals from the metal nitrate enrichments of the sludge were recovered in the layers between 10 and 15 cm, especially

Table 12.2. Recovery of the 2 mol/L-Extractable Metal Forms in the Top 20 cm from the Metal Nitrates Added as Enrichment of the Sewage Sludge, in the Slightly Acidic Sandy Soil

Loadings		Recovered Amount of the Metals					Added Metals
		0–10 cm	10–15 cm	15–20 cm	Total		
		mg/column			mg/column	%	mg/column
10 L	Cd	18.8	0.1	−0.1	18.8	77	24.4
	Cr	1190	25.7	0	1220	75	1630
	Ni	252	7.2	2.4	261	80	326
	Pb	1240	35.0	2.8	1280	79	1630
	Zn	4080	36.6	4.5	4120	126	3260
30 L	Cd	38.2	−1.0	−1.6	35.6	49	73.3
	Cr	2770	31.6	−4.5	2800	57	4890
	Ni	548	5.9	−4.7	549	56	978
	Pb	2980	48.6	0.2	3020	62	4890
	Zn	9030	76.6	−14.9	9090	93	9780
100 L	Cd	145	3.5	−0.4	148	60	244
	Cr	9850	266	4.2	10100	62	16300
	Ni	1960	105	6.2	2070	64	3260
	Pb	10600	291	3.8	10900	67	16300
	Zn	31300	1160	65.2	32500	100	32600

at the highest loading rate. Metal budgets for the brown forest soil showed similar features, with somewhat higher total recovery but less downward movement of the metals.

Metals originating from the sludge might not have reached the deeper layers as it is indicated by the distribution of the total potentially available metal contents in the control treatments of both soils. Although in these treatments the total amounts of the metals, reflecting both the native metal content of the soils and the metal amounts added in the original sewage sludge, were different in the two soils; metal contents in percentage of the total content of the upper 20 cm were nearly identical, with about 60–70% of the metals found in the sludge-containing zone, and about 15–20% in each of the two deeper 5-cm-layers (Table 12.3). The similarity of the metal contents in the two deeper layers indicates that no metal may have moved downward from the sludge.

Andersson (1976) showed that the 2 mol/L HNO_3 extraction procedure gave a good estimate of the total pollution potential of the soil from heavy metals: the method released 57% (Cr)–86% (Cd) of the total content of various heavy metals from normal, unpolluted soils, and between 65 and 92% of the total content from sewage sludge-treated soils. The differences between the extracted amounts accounted for 82–96% of the total amounts of Cd, Cr, Cu, Ni, Pb, and Zn accumulated during several years of sewage sludge application. Similar results were obtained in our laboratory (A. Lukács, personal communication), where after 2 mol/L HNO_3 extraction the recoveries of Cr, Cu, Ni, Pb, and Zn were between 69 and 99% of the amounts measured in aqua regia extracts in a sewage sludge amended soil (BCR No. 143, 1983), but only between 21 and 77% when compared to the total metal content in an unpolluted reference soil sample (CCRMP, 1979) that contained the metals mostly in various minerals. The results suggest that nearly the total elemental content, with the exception of the most strongly fixed, residual forms are extracted from the soil by this method, which thus may be regarded as a good estimation of the total potentially available amount of the elements in the soil.

Table 12.3. Distribution of the 2 mol/L Nitric Acid-Extractable Metal Contents in the Upper 20 cm of the Control Columns

	0–10 cm		10–15 cm		15–20 cm		Total
	mg/column	%	mg/column	%	mg/column	%	mg/column
Brown forest soil							
Cd	25	63.4	8	19.5	7	17.1	39
Cr	256	62.2	80	19.5	75	18.3	412
Ni	292	57.6	113	22.3	102	20.1	507
Pb	300	58.1	111	21.6	105	20.3	516
Zn	1880	74.3	327	12.9	326	12.8	2540
Slightly acidic sandy soil							
Cd	34	54.2	15	23.7	14	22.1	63
Cr	200	58.6	73	21.4	68	20.0	341
Ni	203	54.9	86	23.3	80	21.8	369
Pb	148	63.6	42	18.2	42	18.2	233
Zn	1440	72.2	316	15.8	240	12.0	2000

In our experiments where the soil was contaminated by a low-metal sewage sludge spiked with metal nitrates and the extraction procedure took place about 3 months after the metal contamination, relatively less of the metals was extracted by this method at the extremely high contamination levels, but recovery of the metals was remarkably uniform for Cd, Cr, Ni, and Pb. When calculating the metal budgets, it was found that at $10L$ loading rate in the slightly acidic sandy soil, about 80% of the applied metal-nitrate enrichment of the sludge was recovered from these four metals by the 2 mol/L nitric acid-extraction in the upper 20 cm of the monoliths (Table 12.2). Total recovery was somewhat smaller, about 50–60% at the two higher loading rates. The added Zn was practically totally recovered in the upper 20 cm soil layer at all application rates.

AAAc-EDTA EXTRACTION

This extraction provided similar results to the nitric acid extraction. In the slightly acidic sandy soil the concentrations of the metals increased in the layer between 0–10 cm when the initial loading rates were higher (Figure 12.3). Very small increases (detectable only at the highest load) were found also in the layer below the application zone (Figure 12.4), that is between 10–15 cm for the more mobile Cd, Ni, and Zn, and for Pb as well. Similar results were obtained for the brown forest soil (Figure 12.3), but the AAAc-EDTA extractable amounts did not increase in the deeper layer even at the highest application rate as it is shown on the example of Zn (Figure 12.4).

The ratios among the metal concentrations in the AAAc-EDTA extracts were somewhat different from the application ratios. The AAAc-EDTA extractable concentrations of Cd, Ni, and Zn reflected fairly well the original application rates. In contrast, relatively more Pb was extracted than Cr (Figure 12.3) although the initial application rates of these elements were identical. The concentration of Pb in the extracts followed well the loading rates, while the concentration of Cr was relatively smaller and decreased with increasing loading rates as compared to the applied amounts. The difference between these two elements at the lower application rates was about twofold, while at the
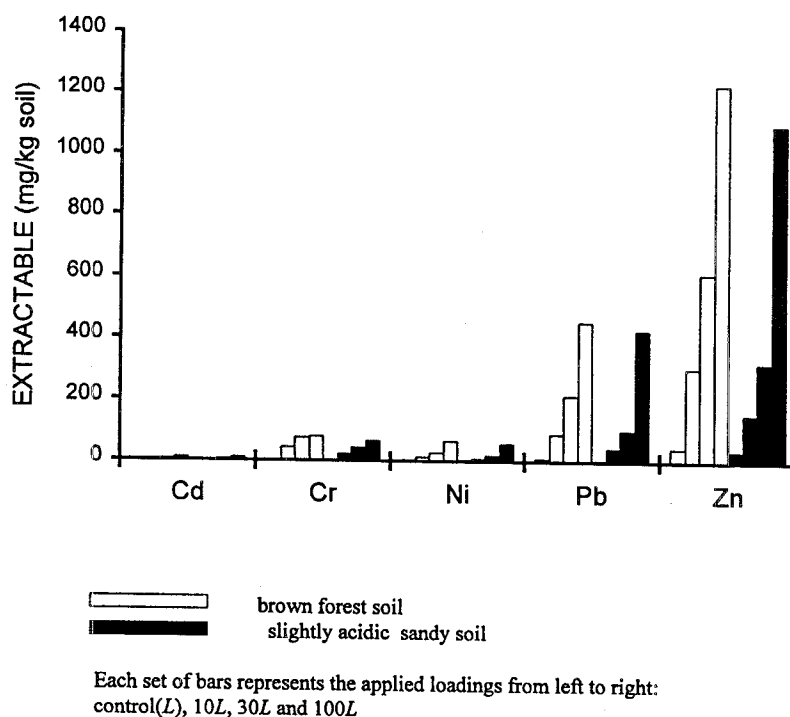
brown forest soil
slightly acidic sandy soil

Each set of bars represents the applied loadings from left to right:
control(L), 10L, 30L and 100L

Figure 12.3. Metals extracted with AAAc-EDTA at 0–10 cm depth.

highest application rate the extractability of Cr was only 1/6 that of Pb in both soils. In contrast, 2 mol/L HNO_3-extracted amounts of Cr and Pb were similar, in agreement with the application rates as was shown on Figures 12.1 and 12.2a.

The similar behavior of Cd, Ni, Pb, and Zn with respect to extractability by the acid ammonium acetate + EDTA is in agreement with the stability constants of the reactions of these metals with EDTA (Me + L $\leftrightarrow$ MeL), given in Lindsay (1979) as 16.36 for Cd, 18.52 for Ni, 17.88 for Pb, and 16.44 for Zn. Chromium forms more stable complexes with EDTA; value of the stability constant for Cr(III) EDTA is 24.0. However, complexes of Cr(III) are described as "inert" since they attain the equilibrium very slowly (Dwyer and Mellor, 1964). Such behavior might have resulted in a smaller extractability of Cr during the limited period of the extraction procedure, despite its stronger affinity to EDTA.

Among the components of the AAAc-EDTA extractant, the acid and neutral ammonium acetate extract the readily soluble and exchangeable fractions of the trace elements. The addition of EDTA as a suitable chelating agent makes possible the extraction of trace elements bound by soil organic matter (Lakanen and Erviö, 1971). However, only about 5% of the total Cr in soil was shown to be available to common extracting solutions such as acetic acid or EDTA, and the majority of Cr entering the soil is rapidly immobilized (Coughtrey and Thorne, 1983). Neutral and acidic ammonium acetate were shown to dissolve only very small fractions of Cr (Andersson, 1976). In sludge-treated soils, a great proportion of Cr was bound to Fe-Mn-oxides (Dudka and Chlopecka,
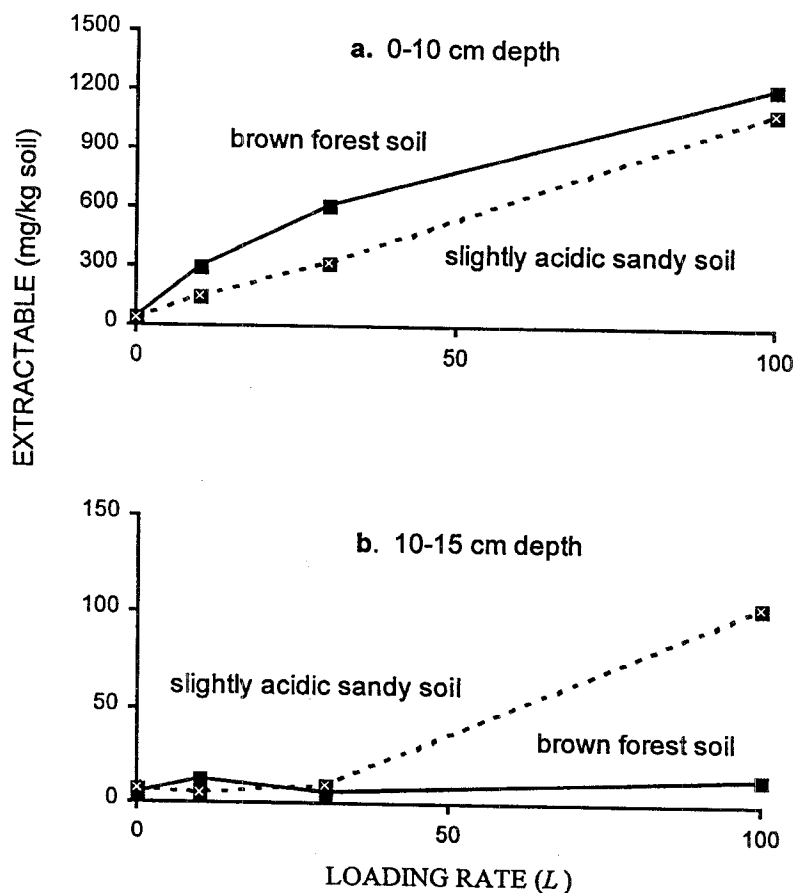
Figure 12.4. AAAc-EDTA extractable amounts of Zn in the contaminated zone and in the layer below it at different loading rates.

1990) and/or was found in residual forms (Legret et al., 1988). Thus, the AAAc-EDTA mixture may not be expected to extract most of the Cr.

CONCENTRATIONS IN SOIL SOLUTION

Metal concentrations in the soil's liquid phase were determined using a centrifugation sampling technique to obtain soil solution fractions available for plant uptake. The centrifugal speed was calculated by applying an equation used by Cassel and Nielsen (1986), to correspond to −1500 kPa water potential, which is the conventional value of the wilting point of plants. Plants generally cannot take up those fractions of soil water which are held in the soil more strongly than −1500 kPa; thus the soil solution fractions separated with −1500 kPa are considered to represent the liquid phase available for the plants at natural soil water contents because they are retained in the soil with suctions less than the suction corresponding to the wilting point. From water–saturated soil, for example, solutions at soil water potentials between −1500 and −0.1 kPa are separated with this technique, while from samples at field capacity, solutions between −1500 and − 20 kPa can be obtained. By analyzing these solution fractions, the quantity and chemical

composition of the soil solution utilizable for the plant (in the sense of energy conditions) is modeled.

Other methods applied widely for the separation of the soil solution do not represent soil moisture available to plants. In the case of suction methods, for example, the maximum suction that can be exerted is -100 kPa, whereas plants can exert much higher values. Displacement methods also do not give information about the quantity and energy status of the solution remaining in the soil after the extraction. It is also probable that the extreme high pressures applied to the moist soil samples in a hydraulic pressure apparatus during the extraction of the soil solution, disturb the prevailing equilibrium between the soil phases.

Metal concentrations in the soil solution were generally several orders of magnitude lower than the 2 mol/L HNO_3 extractable total concentrations, with the exceptions of Cd, Ni, and Zn in the sandy soil and of Ni and Zn in the brown forest soil at the highest loading rate (Table 12.4). Notice that in Table 12.4 we used the more convenient unit of μg/kg for the soil solution concentration, rather than mg/kg for the total concentrations in Figures 12.1 and 12.2.

Chromium entered the liquid phase of the soils in negligible amounts, even at the highest metal loading. Lead showed similar low soil solution concentrations as did Cr in the brown forest soil, but in the sandy soil Pb concentrations were significantly higher than Cr concentrations, for all loading rates. Compared to loading rates, release of Cd, Ni, and Zn into the soil solution was much higher than of Cr and Pb, and increased substantially at the higher metal application rates in the top 10 cm. Similar increases also occurred in the originally uncontaminated soil layers directly below the application zone. Concentrations of Cd, Ni and Zn in the soil solution were several orders of magnitude higher at the 30 L and 100 L loading rates than in the control treatment, in the top 10 cm. Of these three metals, Cd was found in much lower concentrations in the soil solution. The observed low Cd concentrations are consistent with the relatively low application rate of this metal as compared to those for the other elements. Release of the metals into the soil solution at all metal application rates was significantly higher in the slightly acidic sandy soil than in the brown forest soil (Table 12.4).

It is difficult to compare our data, which hold for soil solution concentrations in heavily contaminated soils, with the highly variable literature data obtained under different experimental conditions and using a wide array of methods. Still, our results show similar tendencies to those cited by Kabata-Pendias and Pendias (1992) or by Kabata-Pendias and Adriano (1995); i.e., the relatively mobile metals, Cd, Ni, and Zn occur in a relatively larger proportion in the solution phase than the less mobile Cr and Pb. These findings cited were obtained for natural soil solutions separated by centrifugation from different soils.

Soil solution concentrations expressed as percentage of the total potentially available concentrations (SA_S) indicated very low availability of Pb and especially of Cr in those fractions of the soil's liquid phase which are directly accessible for plant uptake, since only negligible amounts of these elements were released into the soil solution (Table 12.5). In contrast, Cd, Ni, and Zn were more readily available for uptake in both soils, and the proportion of the directly plant-available amounts of these metals increased sharply at the highest application rate (Figure 12.6); they were more than one order of magnitude higher than in the control treatment. Such increases were observed not only for the

Table 12.4a. Concentrations of the Metals in the Soil Solution in Brown Forest Soil[a]

Element	Depth (cm)	(μg/kg dry soil) Control	Loading 10 L	30 L	100 L
Cd	0–10	b	0.4	1.2	90.2
	10–15	b	b	b	11.6
	15–20	b	b	b	b
Cr	0–10	1.9	1.4	0.7	7.0
	10–15	0.6	3.0	b	2.3
	15–20	b	2.4	3.7	b
Ni	0–10	4.3	12.9	39.2	2600
	10–15	2.1	4.9	6.8	225
	15–20	5.6	3.5	11.3	13.7
Pb	0–10	b	5.9	b	7.8
	10–15	b	3.3	6.1	11.5
	15–20	b	6.5	2.8	b
Zn	0–10	50.8	120	219	28600
	10–15	81.0	82.6	127	761
	15–20	130	140	125	232

[a] Detection limits in mg/L: Cd – 0.005, Cr – 0.005, Pb – 0.05.
[b] Concentrations below detection limit.

Table 12.4b. Concentrations of the Metals in the Soil Solution in Slightly Acidic Sandy Soil

Element	Depth (cm)	(μg/kg dry soil) Control	Loading 10 L	30 L	100 L
Cd	0–10	2.1	2.0	16.5	357
	10–15	1.7	1.4	2.2	13.2
	15–20	0.7	1.0	1.1	1.2
Cr	0–10	0.4	2.9	7.2	10.7
	10–15	3.0	17.4	4.8	10.8
	15–20	3.2	2.9	1.7	6.0
Ni	0–10	24.5	49.3	375	9197
	10–15	27.0	23.6	39.0	623
	15–20	17.0	12.8	22.5	29.4
Pb	0–10	18.2	10.4	14.1	154
	10–15	20.1	30.1	16.9	33.6
	15–20	34.3	14.0	9.7	28.1
Zn	0–10	283	500	3492	106200
	10–15	395	273	342	6249
	15–20	184	78	168	266

application zone of the metal-enriched sludge, but also for the originally uncontaminated 10–15 cm depth interval (Figure 12.6). The breakthrough-like increases in the relative amounts of the directly phytoavailable metal forms indicate a decrease in the metal-buffering capacity of the soil at this extreme metal application rate. The calcula-

Table 12.5. Recovery of the Metals in the Liquid Phase of the Slightly Acidic Sandy Soil per Thousand of the Total Potentially Available Amounts

Loadings		Amount of the Metals Recovered in the Liquid Phase					Total Potentially Available Amounts
		0–10 cm	10–15 cm	15–20 cm	Total		
		mg/column			mg/column	‰	mg/column
			Brown forest soil				
	Cd	a	a	a	a	0	40
	Cr	0.04	0.01	a	0.05	0.1	411
Control	Ni	0.08	0.02	0.05	0.15	0.3	507
	Pb	a	a	a	a	0	516
	Zn	0.96	0.76	1.23	2.95	1.2	2530
	Cd	1.70	0.11	a	1.81	8.1	224
	Cr	0.13	0.02	a	0.15	0.01	13100
100 L	Ni	49.0	2.12	0.13	51.3	16.3	3140
	Pb	0.15	0.11	a	0.26	0.02	14100
	Zn	539	7.17	2.19	548	13.6	40200
			Slightly acidic sandy soil				
	Cd	0.04	0.02	0.01	0.07	1.1	63
	Cr	0.01	0.03	0.03	0.07	0.2	341
Control	Ni	0.46	0.25	0.16	0.87	2.4	369
	Pb	0.34	0.19	0.32	0.85	3.7	232
	Zn	5.33	3.73	1.73	10.8	5.4	2000
	Cd	6.74	0.12	0.01	6.87	33	211
	Cr	a	0.10	0.06	0.16	0.02	10400
100 L	Ni	173	5.88	0.28	179	73	2440
	Pb	2.90	0.32	0.26	3.48	0.3	11200
	Zn	2000	58.9	2.51	2060	60	34500

[a] Values below detection limit (see Table 12.4a).

tions revealed a higher availability and mobility of the elements in the liquid phase of the slightly acidic sandy soil as compared to the brown forest soil (Table 12.4, Figure 12.6).

Such differences are shown not only by the metal concentrations but also by the distribution of the total amounts of the metals in the soil's liquid phase. Data for the control treatment and for the highest contamination level are shown in Table 12.5. While distribution of the metals among the liquid phases of the three sampled soil layers was fairly uniform in the control treatments, at the highest contamination level most of the metals were found in the top 10 cm, with slight increases of the Ni and Zn amounts between 10 and 15 cm.

The soil pH in our experiments decreased somewhat as the metal loading rate increased (Figure 12.5). This decrease is likely caused by the acidity of the nitrate salts being used in our study. The lower pH may have contributed to the increased mobility and availability of the metals at the higher loadings. Also, the somewhat more acidic character of the sandy soil may have been responsible for the higher availability of the metals in this soil. This explanation is in agreement with literature data about the effect of acidification on the availability and mobility of heavy metals (Løbersli et al., 1991; Marschner, 1991). The influence of soil pH on the mobility of trace metals depends also
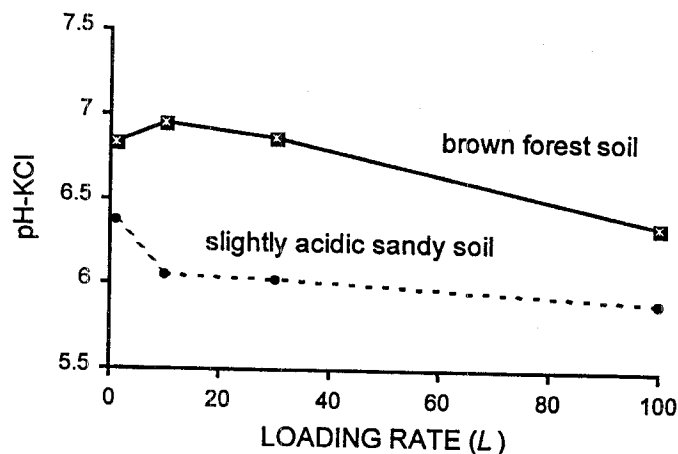
Figure 12.5. Soil pH in the 0–10 cm layer at the end of the experiment.

upon the geochemical properties of the metal: for example, mobility of Cd has been classified as medium up to pH 6, and that of Ni and Zn up to pH 5, while Cr and Pb have only weak mobility above pH 4.5 and 4, respectively (Kabata-Pendias and Pendias, 1992). Thus, the differences among mobilities of various metals may have been influenced also by the pH of the soil liquid phase.

Amounts of the elements entering the soil solution seemed to be rather low in comparison to literature data. For instance, the highest value of Zn in our experiments was only 5.8% of the total potentially available amounts, while values up to 50% have been reported in the literature (Coughtrey et al., 1985). One likely reason for this disparity is that literature data are generally based on extraction procedures that use chemical desorption and wide soil:extractant ratios. Such methods should give much higher elemental concentrations than those which occur in the soil liquid phase at natural field soil water contents.

The proportion of the phytoavailable metal fractions was by about one order of magnitude higher when the calculations were based on the AAAc-EDTA extractable metal concentrations (SA_{AE}) as compared to the phytoavailabilities calculated from the soil solution concentrations (SA_S). In an extensive study comparing the availabilities of the elements in the Hungarian soils (1013 samples), using different extractants, the AAAc+EDTA-available amounts of the metals included in our study were between 39 and 91% of their 0.5 M HNO_3-extractable amounts (Marth, 1990).

MOVEMENT

While SA_S of Cd, Ni, and Zn showed a breakthrough-like phenomenon at the highest loading rate (Figure 12.6), especially in the slightly acidic sandy soil, values of SA_{AE} increased linearly or to a smaller extent when the metal loading rates increased. A further difference between the results of the two methods used to estimate the phytoavailability of the metals was that while the directly available amounts of Cr and Pb in the soil solution were similar to each other (in agreement with the similar application rates), the AAAc-EDTA-extractable amounts of these elements were much differ-
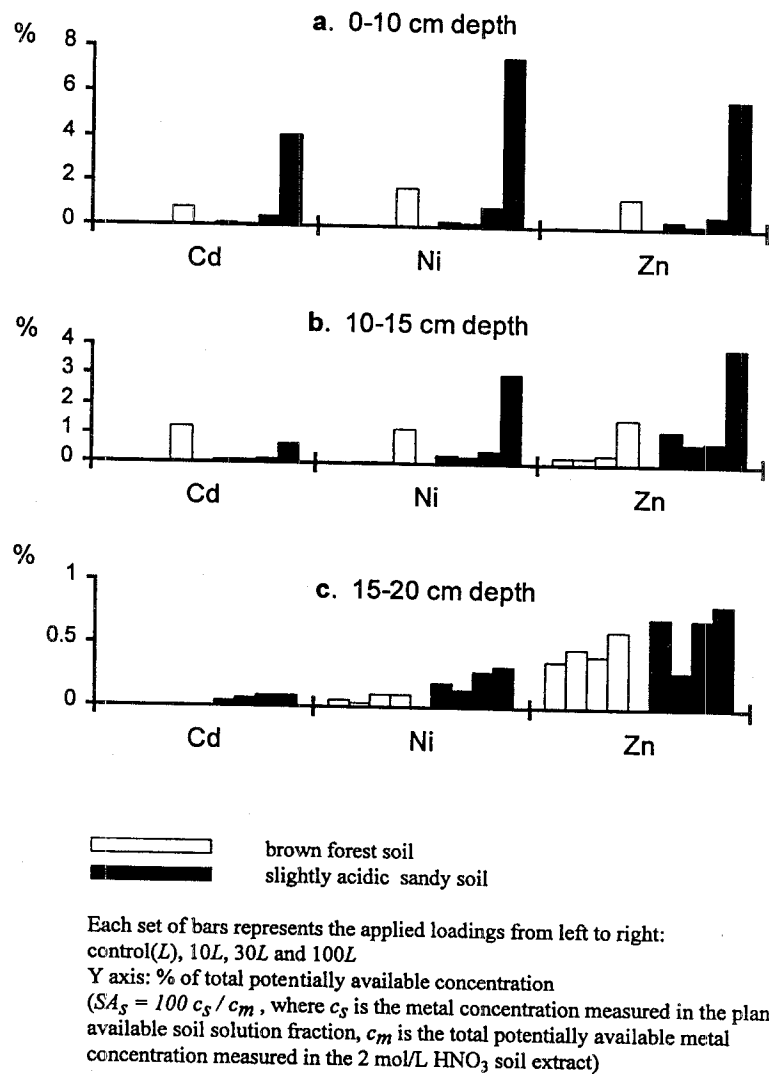
Figure 12.6. Soil availability factors (SAs) of the metals.

a. 0-10 cm depth

b. 10-15 cm depth

c. 15-20 cm depth

☐ brown forest soil
■ slightly acidic sandy soil

Each set of bars represents the applied loadings from left to right:
control(L), $10L$, $30L$ and $100L$
Y axis: % of total potentially available concentration
($SA_S = 100\ c_S / c_m$, where c_S is the metal concentration measured in the plant-available soil solution fraction, c_m is the total potentially available metal concentration measured in the 2 mol/L HNO_3 soil extract)

ent. The availability of added Pb, as estimated by the acidic ammonium acetate-EDTA extraction, was comparable to the availability of Zn and Cd, and somewhat exceeded that of Ni in both soils (Figure 12.7). In the brown forest soil it increased only slightly at the higher loading rates, while in the slightly acidic sandy soil it followed more closely the increasing metal pollution levels. Again, in this respect its behavior was similar to those of Cd, Ni, and Zn.

Metal budgets calculated for the liquid phase of the upper 20 cm also show an increased proportion of the directly plant-available forms of Cd, Ni, and Zn in per thousand of their total potentially available amounts in these layers, at highly elevated metal application rates (Table 12.5). Literature data on the possible leaching of the elements show only small downward movement of the heavy metals, and mostly in coarse-textured, sandy, or gravelly soils. However, in many cases the applied metal concentrations
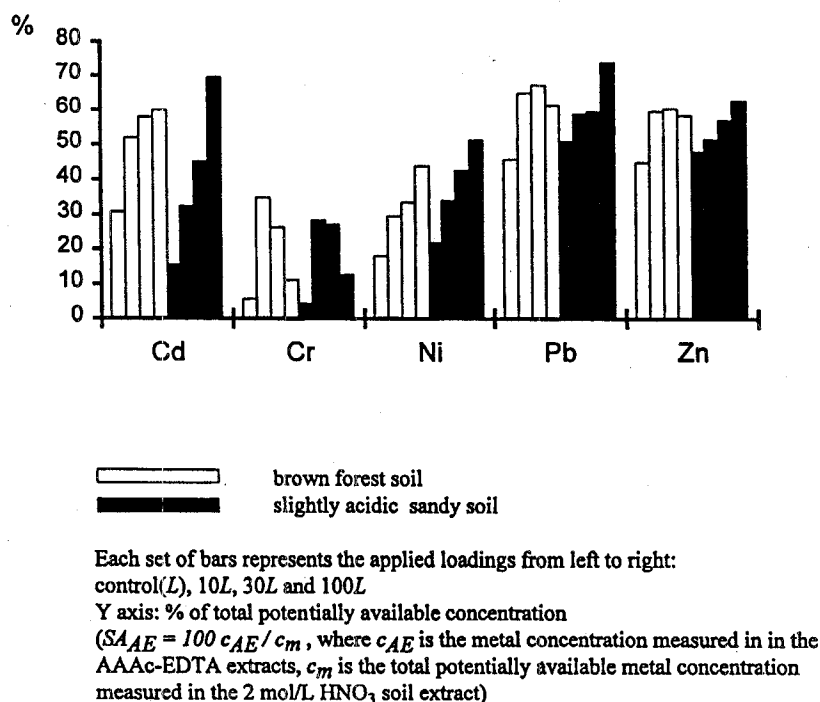
brown forest soil
slightly acidic sandy soil

Each set of bars represents the applied loadings from left to right:
control(L), 10L, 30L and 100L
Y axis: % of total potentially available concentration
(SA_{AE} = 100 c_{AE}/c_m, where c_{AE} is the metal concentration measured in in the
AAAc-EDTA extracts, c_m is the total potentially available metal concentration
measured in the 2 mol/L HNO_3 soil extract)

Figure 12.7. Soil availability factors for the AAAc-EDTA extractions (SA_{AE}) at 0–10 cm depth.

were much smaller than the provocative overloading of 100 L in our experiments. Careful evaluation of some data interpreted as being proof of no metal movement reveals such a slight movement of the metals, which is in the range expectable from the relatively low metal application rates, and which are sometimes interpreted as resulting from inadvertent mixing of the soil layers (e.g., in the papers summarized in Dowdy and Volk, 1983).

Downward movement of the metals involves the leaching of the water-soluble forms. The movement of toxic metals was studied most often in the percolate water of lysimeter experiments. Our experiments, conducted under natural soil moisture conditions, with no addition of extra water that might have caused leaching (as shown by the TDR measurements along the soil profile), showed that only a very small percentage of the polluting metals may enter the soil solution at field soil moisture contents, even at provocative overloadings. Thus, the expectable concentrations of the metals in the liquid phase of the deeper layers are small. Such small values are regarded often as proofs of no substantial movement.

Although in many experiments no metal movement was found in the deeper layers below 60 cm, in some instances significant increases were reported. In a sludge-amended clay loam soil under a forest vegetation and with a surface pH of 5, about 3% of the applied Zn and 4–7% of the applied Cd was leached beyond 120 cm (cit. in Dowdy and Volk, 1983). In a lysimeter experiment on a sandy loam contaminated with sewage sludge containing large amounts of Cd, Cr, Ni, Pb, and Zn, the mobility of these elements, measured as their concentration in the percolate water, increased two times in sludge-amended soil (Dudka and Chlopecka, 1990). Since in this chapter various metal inputs

and outputs (g/ha) are also presented, the amount of the leached, water-soluble forms in percentage of the total input can be calculated. These values are 5.4% for Cd, 0.003% for Cr, and 0.17% for Ni and Zn. The Cd and Cr data are comparable to the relative availabilities of these metals in the soil solution in our experiments (Figure 12.6).

SUMMARY

The biological and ecological effects of heavy metal pollution of soils depend not only on the total amount of the contaminating metals, but to a great extent on their biologically and ecologically active, easily soluble and mobile fractions. The approach discussed in this chapter focused on determining those fractions of the soil's metal content which are directly and easily available for plant uptake (using two different methods to characterize the phytoavailability), or which are potentially becoming available for the plants during longer periods. Ratios of the directly available and potentially available metal concentrations were used to estimate the bioavailability of the elements in soil columns contaminated with sewage sludge spiked with (Cd + Cr + Ni + Pb + Zn)-nitrates.

The total potentially available amounts of the metals reflected well the application rates, and did not increase or only slightly increased in the soil layers lying directly below the application zone. Proportion of the directly plant-available amounts of Cd, Ni, and Zn (measured in the soil solution considered as directly available for the plants) increased sharply at the highest application rate, and such increases were observed not only in the contaminated layer but also in the originally uncontaminated 10–15 cm depth interval. We want to stress the ecological significance of the movement of these water-soluble forms. Since the solubility of the heavy metals in soils has great significance in their bioavailability and their migration (Kabata-Pendias and Pendias, 1992), relatively small increases in solution metal concentrations may have an impact on the environment. The breakthrough-like increases in the relative amounts of the directly phytoavailable metal forms might also indicate a decrease in the metal-buffering capacity of the soil at this extreme metal application rate. In contrast, Cr and Pb entered the liquid phase (i.e., were directly available for the plants) in negligible amounts, even at the provocative overloadings. This is in agreement with the majority of the literature data about the transport of these elements into the plants.

The AAAc + EDTA extraction which is a method used to estimate the plant-availabilities of both macro- and micronutrients simultaneously, after a single extraction procedure, and which was shown to be appropriate also for several toxic elements, indicated much greater availability of the metals than was estimated from the metal concentrations measured in the soil's liquid phase. Estimated availability (i.e., extractability) of Cr was less and that of Pb was higher than expected on the basis of the application rates. In the AAAc + EDTA extraction procedure Pb behaved similarly to Cd, Ni, and Zn, which are regarded as mobile elements in the soil.

Thus, the two methods used to assess the plant availability of the selected metals gave different estimations of the phytoavailable proportions. Comparison of the estimated phytoavailabilities with the actual metal uptake by plants should give support in favor of one of these methods. However, further studies have to consider that plant concentrations measured at a specific point during the vegetation period reflect the cumulative uptake of the elements until that time, while soil solution concentrations pertain only to

a specific situation (soil water content, temperature, etc.) at a specific moment and soil extraction techniques cannot take into account the plant physiological processes.

ACKNOWLEDGMENTS

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