

## Relations among Differently Available Forms of Heavy Metals in Contaminated Soils

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### Introduction

The environmental risks of heavy metal pollution of soils depend not only on the total amount of the contaminating metals, but rather on the amounts of their biologically and ecologically active, easily soluble, mobile fractions. Generally, the main sources of heavy metal contamination in agricultural soils are sewage sludge disposal and fertilizer application in addition to wet and dry aerial deposition (LUKÁCS et al., 1984; CSATHÓ, 1994; TAMÁS & FILEP, 1995; RAVEN & LOEPPERT, 1997). Metals originating from anthropogenic sources usually occur in soil in forms differing from the original, native metal content of the soil, thus their mobility and availability are also different.

When evaluating the biological and ecological impacts of soil contamination, it is necessary to estimate, before all, the total amounts of the toxic elements which may become available even after longer periods. Extraction of soil samples with 2 mol/L HNO<sub>3</sub> at 100 °C as proposed by ANDERSSON (1976) was shown to be a suitable method for determining the *total potentially available fraction* of the metals in the soil.

*The plant-available concentrations* of elements occurring in soil are typically estimated by different chemical extraction methods. Several extractants and extraction procedures have been applied 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 with widely different properties. One of the most generally useful extractants of this type is acidic ammonium acetate+EDTA (AAAc-EDTA). This extractant has been found suitable for the simultaneous extraction of both macro- and micro-nutrients (LAKANEN & ERVIÖ, 1971), and is included in the procedures adopted by the Soil Advisory Service in Hungary (Hungarian Agricultural Standards,

1989). Extensive FAO studies involving 30 countries proved that this extraction methodology is appropriate not only for the micronutrients Zn, Fe, Cu, and Mn (SILLANPÄÄ, 1982), but also for some toxic elements such as Cd, Pb, Co, and Se (SILLANPÄÄ & JANSSON, 1992).

Recent evidence suggests that elemental concentrations in the soil solution itself may serve as a useful diagnostic tool for plant uptake of various elements. „Soil solution composition proves to be the most directly correlated soil index of absolute bioavailability” (WOLT, 1994). Concentrations in the soil solution are regarded as indicators of the mobile pool of metals in soils, as water soluble forms of an element are easily available for leaching and for plant uptake (KABATA-PENDIAS & PENDIAS, 1992; KABATA-PENDIAS & ADRIANO, 1995). 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 the most easily and immediately available for plant uptake (PETRUZZELLI, 1989). However, there is only a limited amount of data in literature to support this idea for toxic elements (ALLOWAY, 1990).

Data on heavy metal concentrations in the soil liquid phase are available in literature (CAMPBELL & BECKETT, 1988; LORENZ et al., 1994; KABATA-PENDIAS & PENDIAS, 1992; BIERMAN et al., 1995), but there are only few data on the heavy metal content of the soil solution at defined energy status (KELLER, 1995; CSILLAG et al., 1998).

The purpose of this study was to determine the distribution of five selected metals (Cd, Cr, Ni, Pb, and Zn) in the solid and liquid phases of a sludge-treated soil, and to follow their downward movement in undisturbed soil monoliths. Distribution 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. Data on plant studies were presented elsewhere (BUJTÁS et al., 1995; AID Res. Rep., 1996).

### Materials and Methods

A brown forest soil (Gödöllő) and a humous sandy soil (Somogyárd), having a relatively low buffering capacity, were included in laboratory experiments, each one with four monoliths. The major physical and chemical soil properties are shown in Table 1. Communal sewage sludge enriched with Cd, Cr, Ni, Pb, and Zn nitrates was applied to the top 10 cm of the undisturbed, 40 cm diameter, 100 cm long soil monoliths. The experimental set-up is described in detail in NÉMETH et al. (1994).

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 dry matter. These values are comparable to or less than the limits speci-

Table 1

Some chemical and physical properties of the upper horizons of the studied soils

Depth cm	pH		Organic matter, g/kg	CEC cmol <sub>e</sub> /kg soil	<0.02 mm %	< 0.002 mm %
	H <sub>2</sub> O	KCl				
<i>Brown forest soil (Gödöllő)</i>						
0-8	5.90	5.02	10	9.0	19.5	12.6
8-16	6.26	5.29	12	8.5	18.9	12.4
<i>Humous sand, non calcareous (Somogyárd)</i>						
5-15	5.63	4.48	13	6.7	20.2	12.7

fied in the Hung. Techn. Dir. (1990). 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). 1L was calculated by approximating sludge application practices in Hungary (25 t/ha sludge dry matter load (Techn. Guidelines, 1984) was assumed to be incorporated into a 20 cm surface soil layer). So loadings corresponding to 1L were 0.125 mg Cd, 8.33 mg Cr, 1.67 mg Ni, 8.33 mg Pb, and 25 mg Zn per kg soil. The original, unspiked sludge was used as the control treatment. Corn was grown as a test plant on the sludge-treated monoliths under controlled conditions until maturity.

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.

Soil pH and total potentially available metal concentrations in the soil (after 2 mol/L HNO<sub>3</sub> extraction as described by ANDERSSON (1976)) were measured in air-dried soil samples.

Plant-availability of the metals was estimated by: a) metal concentrations in acidic ammonium acetate-EDTA soil extracts (LAKANEN & ERVIÖ, 1971) of air-dried soil samples, and b) directly plant-available concentrations in the soil solution obtained by centrifugation of the moist soil samples (CSILLAG et al., 1995) immediately after the cutting procedure, from each layer of the monoliths in triplicates. All data shown later represent averages of these triplicates.

Elemental concentrations in the 2 mol/L HNO<sub>3</sub> 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, to eliminate the differences caused by the slightly different moisture content of the soil samples (water potential  $\cong$  pF 0).

Availability of the metals was characterized in terms of the soil availability factor, *SA*. *SA* is the „percentage of the total content of an element in the soil which is available for uptake to plants” (COUGHTREY et al., 1985). Metal concentrations measured either in the plant-available soil solution fractions (*c<sub>S</sub>*) 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 ( $c_M$ ):

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

The calculated percentages ( $SA_S$  and  $SA_{AE}$ ) characterize the proportion of the directly plant-available and of the supposedly plant-available metal forms, resp., in the total potentially available metal pool of the soil.

## Results and Discussion

The 2 mol/L  $HNO_3$ -extractable concentrations of all 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. At each loading level the differences among the application rates of the five metals were accurately reflected, being the highest for Zn and the lowest for Cd, and very similar for Cr and Pb which were applied in identical amounts (Fig. 1A). These differences are also shown by the values of the slopes of linear relationships, where  $Y$  is the total extracted metal concentration and  $X$  the applied metal loading ( $L$ ). The linear regression equations for the top layer in the sandy soil are as follows:

Cd:	$Y = 0.076 X + 1.81$	$R^2 = 0.994$
Cr:	$Y = 5.17 X + 13.87$	$R^2 = 0.998$
Ni:	$Y = 1.03 X + 11.75$	$R^2 = 0.998$
Pb:	$Y = 5.63 X + 8.75$	$R^2 = 0.998$
Zn:	$Y = 16.3 X + 102.5$	$R^2 = 0.998$

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. Similar linear relationships were also obtained for the brown forest soil.

In the deeper layers, the brown forest soil showed no substantial increases in metal concentrations even at the higher metal application rates, with the exception of Ni and Zn which, compared to the control sample, had slightly elevated concentrations in the 10-15 cm and 15-20 cm depth interval at the highest contamination level. For the more acidic sandy soil a slight downward movement of the elements was observed below 10 cm at the 100L loading rate (Fig. 1B). Literature data on the possible leaching of the elements generally also show only a slight downward movement of heavy metals, and mostly in coarse-textured, sandy, or gravelly soils. 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 & CHLOPECKA (1990) observed leaching of Cd, Cr, Ni, and Zn in a lysimeter experiment on a sandy loam contaminated with sewage sludge containing large amounts of these elements. In contrast, DOWDY & VOLK (1983), CHANG et al.

(1984) and ALLOWAY (1990) reported the retention of these elements within the zone of sludge incorporation during both column and field experiments.

ANDERSSON (1976) showed that the 2 mol/L HNO<sub>3</sub> 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

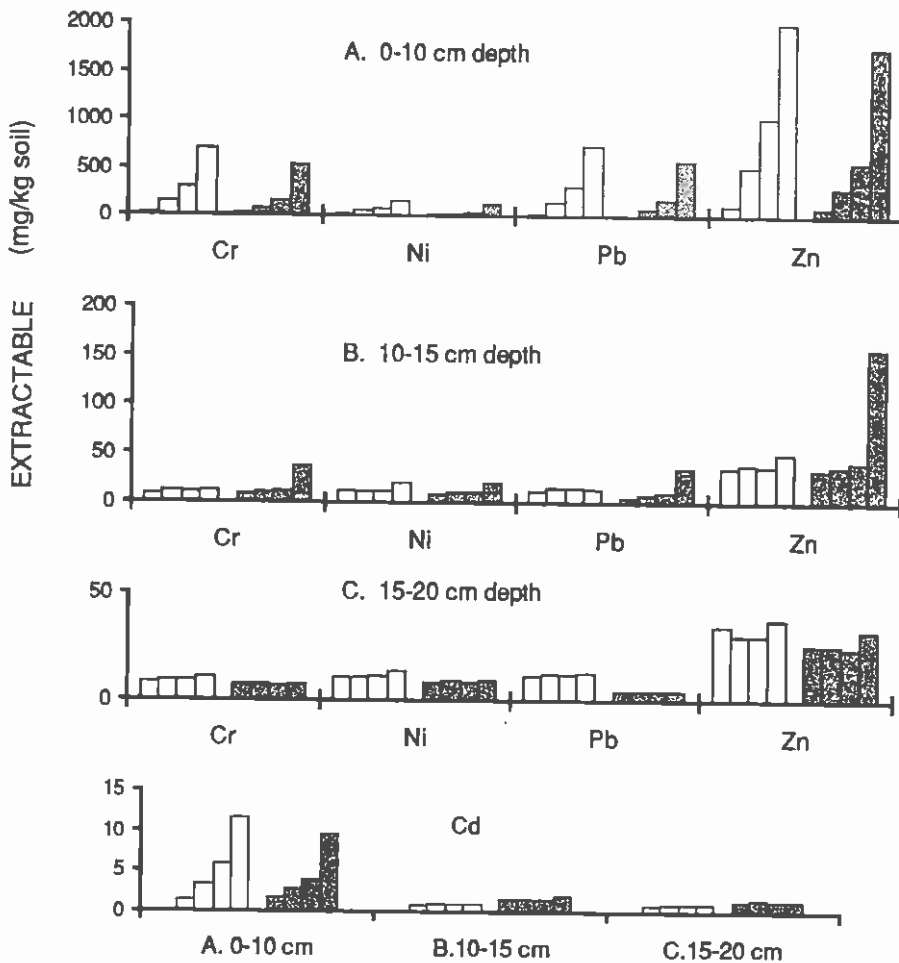


Figure 1

Metals extracted with 2 mol/L HNO<sub>3</sub> from the 0-10, 10-15 and 15-20 cm layer of the brown forest soil (clear, unshaded bars) and the sandy soil (shaded bars). Each set of bars represents the applied loadings from left to right: control (L), 10L, 30L and 100L

amounts extracted from the polluted and unpolluted soils 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 (LUKÁCS, 1996) where – after 2 mol/L HNO<sub>3</sub> 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.

The AAAC-EDTA extraction gave similar results as the nitric acid extraction. In both soils the concentrations of the metals increased in the 0-10 cm layer following the initial loading rates. In the sandy soil small increases were also found in the layer below the application zone (10-15 cm) for the more mobile Cd, Ni, and Zn, and for Pb as well but only at the highest load. In the brown forest soil the AAAC-EDTA extractable amounts did not increase in the deeper

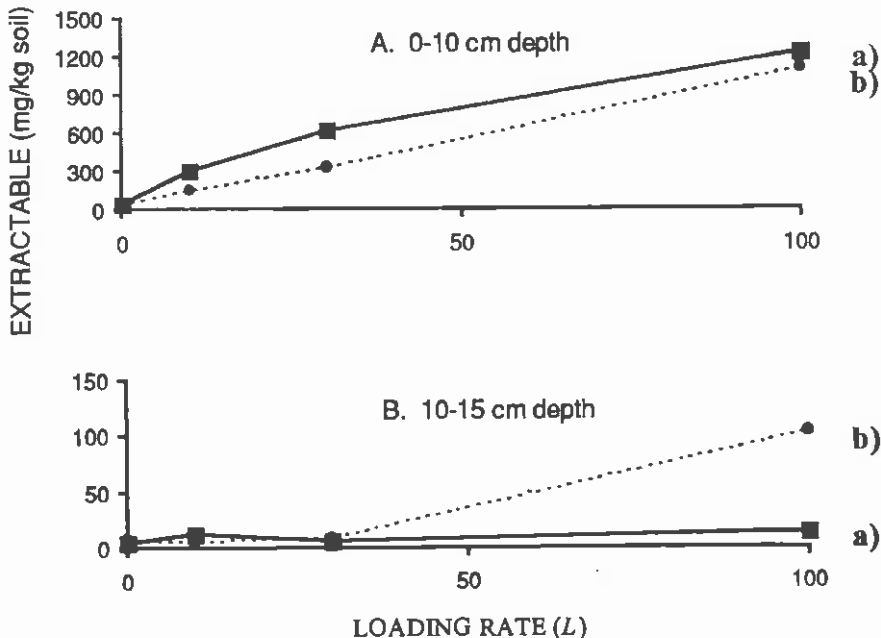


Figure 2

AAAC-EDTA extractable amounts of Zn in the contaminated zone (0-10 cm depth) and in the 10-15 cm layer of the brown forest soil (a) and sandy soil (b) at different loading rates

layer even at the highest application rate, as it is shown on the example of Zn (Fig. 2).

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, 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 did not increase 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 highest application rate the extractability of Cr was only one-sixth of that of Pb in both soils. In contrast, 2 mol/L HNO<sub>3</sub>-extracted amounts of Cr and Pb were similar, reflecting their same application rates, as it was shown in Fig. 1A. The smaller extractability of Cr by the AAAC-EDTA extractant is in agreement with literature data. 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 & CHLOPECKA, 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.

*Metal concentrations in the soil's liquid phase* were determined using a centrifugation sampling technique to obtain soil solution available for plant uptake. The centrifugal speed was calculated to correspond to -1500 kPa water potential, 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 separated soil solution is considered to represent the liquid phase utilizable for plants at natural soil water contents (in the sense of energy conditions).

Metal concentrations in the soil solution were generally several orders of magnitude lower than the 2 mol/L HNO<sub>3</sub> 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 2). Notice that in Table 2 we used the more convenient unit of µg/kg for the soil solution concentration, rather than mg/kg for the total concentrations as in Fig. 1.

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 Cr did 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, the release of Cd, Ni, and Zn into the soil solution was much higher than that 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 much higher at the 30L

Table 2  
Concentrations of the metals in the soil solution ( $\mu\text{g}/\text{kg}$  dry soil)

Element	Depth cm	Brown forest soil				Sandy soil			
		Control	10L	30L	100L	Control	10L	30L	100L
Cd	0-10	*	0.4	1.2	90.2	2.1	2.0	16.5	357
	10-15	*	*	*	11.6	1.7	1.4	2.2	13.2
	15-20	*	*	*	*	0.7	1.0	1.1	1.2
Cr	0-10	1.9	1.4	0.7	7.0	0.4	2.9	7.2	10.7
	10-15	0.6	3.0	*	2.3	3.0	17.4	4.8	10.8
	15-20	*	2.4	3.7	*	3.2	2.9	1.7	6.0
Ni	0-10	4.3	12.9	39.2	2600	24.5	49.3	375	9197
	10-15	2.1	4.9	6.8	225	27.0	23.6	39.0	623
	15-20	5.6	3.5	11.3	13.7	17.0	12.8	22.5	29.4
Pb	0-10	*	5.9	*	7.8	18.2	10.4	14.1	154
	10-15	*	3.3	6.1	11.5	20.1	30.1	16.9	33.6
	15-20	*	6.5	2.8	*	34.3	14.0	9.7	28.1
Zn	0-10	50.8	120	219	28600	283	500	3492	106200
	10-15	81.0	82.6	127	761	395	273	342	6249
	15-20	130	140	125	232	184	78	168	266

\* concentrations below detection limit  
(detection limits in  $\text{mg}/\text{L}$ : Cd - 0.005, Cr - 0.005, Pb - 0.05)

and 100L 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 of the other elements. Release of the metals into the soil solution at all metal application rates was significantly higher in the sandy soil than in the brown forest soil (Table 2).

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 as those cited by KABATA-PENDIAS & PENDIAS (1992) or by KABATA-PENDIAS & 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.

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, as only negligible amounts of these elements were released into the soil solution (Table 3). 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; they were more than one order of magnitude higher than in the control treatment. Such increases were observed not only for the application zone of the metal-enriched sludge, but also for the originally uncontaminated 10-15 cm depth interval. The calculations revealed a higher availability and mobility of the elements in the liquid phase of the sandy soil than in the brown forest soil.

Table 3

Relative availabilities of the metals in the soil solution ( $SA_S$ ) and in the AAAC-EDTA extracts ( $SA_{AE}$ ) expressed in percentage of the potentially available concentrations in the 0-10 cm layer of the brown forest soil (a) and sandy soil (b)

	Control				100L loading			
	$SA_S$		$SA_{AE}$		$SA_S$		$SA_{AE}$	
	a	b	a	b	a	b	a	b
Cd	*	0.114	30.8	15.4	0.791	4.07	60.1	69.5
Cr	0.014	0.004	5.46	4.36	0.001	0.002	11.3	12.8
Ni	0.028	0.228	18.0	21.9	1.73	7.61	44.0	51.8
Pb	*	0.232	46.0	51.3	0.001	0.026	61.7	74.3
Zn	0.051	0.369	45.4	48.6	1.37	5.83	58.9	63.3

\* values below the detection limit (see Table 2)

The soil pH in our experiments decreased somewhat as the metal loading rates increased (Fig. 3). This decrease is likely caused by the acidity of the nitrate salts 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. The influence of soil pH on the mobility of trace metals also depends upon the geochemical properties of the metal: for example, the 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 & PENDIAS, 1992).

Amounts of the elements entering the soil solution seemed to be rather low in comparison to literature data. For instance, the highest Zn content in the soil solution was only 5.8% of the total potentially available amounts in our experiments, while values up to 50% have been reported in 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.

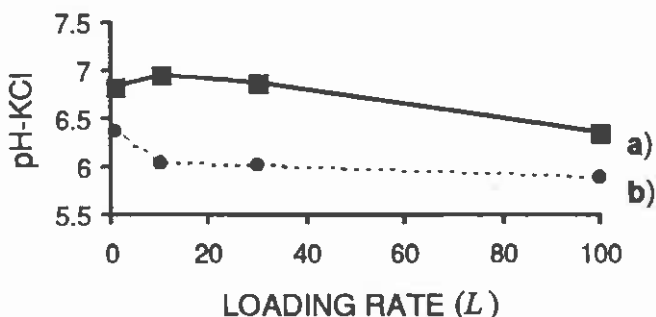


Figure 3

Soil pH in the 0-10 cm layer of the brown forest soil (a) and the sandy soil (b) at the end of the experiment

The proportion of the phytoavailable metal fractions was much 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 ( $SA_S$ ) (Table 3). In an extensive study comparing the availabilities of elements in Hungarian soils (1013 samples), using different extractants, the AAAC-EDTA-extractable amounts of the metals included in our study were between 39 and 91% of their 0.5 M  $HNO_3$ -extractable amounts (MARTH, 1990).

While the directly available amounts of Cr and Pb in the soil solution were very low and similar to each other (in agreement with the similar application rates), the AAAC-EDTA-extractable amounts of these elements greatly differed. The availability of added Pb, as estimated by the acidic ammonium acetate-EDTA extraction, was comparable to the availability of Zn and Cd, and exceeded that of Ni in both soils (Table 3).

### Conclusions

To assess plant availability of heavy metals in contaminated soils, those fractions of the soil's metal content were determined which are directly and easily available for plant uptake (using two different methods to characterize the phytoavailability), or which may potentially become available for plants during longer periods.

The 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 signifi-

cance of the movement of these water-soluble forms. As the solubility of heavy metals in soils has great significance in their bioavailability and their migration (KABATA-PENDIAS & PENDIAS, 1992), relatively small increases in solution metal concentrations may have an impact on the environment. 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 literature data about the transport of these elements into 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 favour 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.

### Summary

Heavy metals released from sewage sludge to agricultural fields and entering the soil liquid phase may be readily available for plant uptake. Ratios of the directly available and potentially available metal concentrations were used to estimate the bioavailability of the elements in soil columns of a brown forest soil and a sandy soil contaminated with sewage sludge spiked at various levels with (Cd + Cr + Ni + Pb + Zn) - nitrates.

Total potentially available metal concentrations were estimated by using 2 mol/L HNO<sub>3</sub> acid extraction (ANDERSSON, 1976). Plant-availability of the metals was estimated on the basis of a) metal concentration in AAAC-EDTA soil extracts (LAKANEN & ERVIÖ, 1971) and of b) directly plant-available concentrations assessed in soil solution samples that were obtained by centrifugation of the initially moist soil samples (CSILLAG et al., 1995).

The total potentially available amounts of the metals reflected well the application rates, and did not or only slightly increased in the soil layers lying

directly below the application zone. Metal concentrations in the soil solution were generally several orders of magnitude lower than the potentially available ones. The „soil available factor”,  $SA_S$ , directly characterizing plant-available metal forms, indicates low availability of Pb and especially of Cr, while that of the mobile Cd, Ni, and Zn increased considerably at the higher application rates: it was more than one order of magnitude higher than in the control treatment. Much higher availabilities of these elements were obtained in the sandy soil as compared to the brown forest soil.

The AAAC-EDTA extraction procedure gave much higher element concentrations, consequently higher availabilities ( $SA_{AE}$ ) than those estimated on the base of concentrations in the soil solution at natural field soil water contents ( $SA_S$ ).  $SA_{AE}$  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.

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