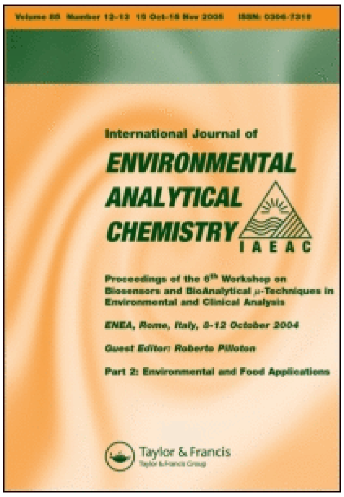

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EXTRACTION OF SOIL SOLUTION FOR ENVIRONMENTAL ANALYSIS

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A centrifugation technique was applied to extract the soil solution regarded to be available for plants and to estimate in it the most mobile part of the soil's metal content. Three soils having different pH, texture and water-retention characteristics were contaminated with multicomponent solutions of Cd, Cr, Ni, Pb and Zn nitrates and one of them was contaminated+acidified to different extents. The impact of the presence of sewage sludge on element concentrations in the soil solution was also assessed. The release of metals into the liquid phase was high only at excessive metal contamination and extreme acid pollution.

Keywords: Soil solution extraction; heavy metal contamination; sewage sludge; acid pollution

INTRODUCTION

Soil solution, the mobile aqueous liquid phase of soils, containing many kinds of dissolved substances, is a medium in which a large part of soil chemical reactions takes place[1,2]. It is also mentioned as "blood circulation of the soil body"[3]. Its chemical composition is a dynamic index of the soil status, an important parameter for indicating the chemical degradation of the soil. Main types of degradation are contamination, acidification, alkalization and salinization[4–8].

Heavy metals, which are among the most harmful environmental pollutants, represent especially serious risks when they accumulate in the soil solution, since they might be leached towards the groundwater and are the most easily available for plant-uptake in water soluble forms. Generally, in agricultural lands the main sources of heavy metal contamination of soils are sewage sludge disposal and fertilizer application[6,9–11]. The concentration of heavy metals in the soil li- quid phase is considered as an indicator of their mobile pool[12].

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TABLE I Methods for the extraction of the soil liquid phase

	references	*advantages*	*limitations*
In situ extraction techniques			
Free-drainage soil solution sampling	2, 3, 18–21, 31	extraction of the liquid phase at natural state from undisturbed soil	solution can be obtained only from a fairly wet soil
Vacuum suction sampling method			maximum suction cannot be greater than the atmospheric pressure (–100 kPa), while plants can exert much higher suctions (conventional wilting point: –1500 kPa)
Laboratory methods			
Displacement in column with organic solvents	2, 22, 31	extraction of strongly retained liquid phase of relatively dry soils is also possible	the energy status of the solution remaining in the soil after extraction is not defined
Centrifugation with immiscible liquid	2, 6, 23, 24		the immiscible liquids may be volatile and toxic
Hydraulic pressing	22, 25	extraction of the soil solution is possible even at very low soil water content	the extreme high pressures disturb the equilibria between the soil phases
Pressure membrane filtration	2, 22, 31	characterization of the energy status of the solution to be extracted from the soil is possible	the cellophane membrane in the pressure filtration apparatus adsorbs part of the dissolved heavy metals, protons and aluminium
Centrifugation	2, 19, 20, 22, 23, 26–30	RISSAC[29] method: for the extraction the conventional upper limit of the suction exerted by plant roots is modelled → plant available soil solution can be extracted	

Concentrations of the metals in the soil solution are influenced not only by the extent of contamination, but also by environmental changes such as soil acidification[13–15]. The decrease of the acid neutralizing capacity of the soil may lead to the so called chemical time bomb (CTB) effect[16,17].

To determine the chemical composition of the soil solution, several in situ or laboratory methods exist to gain the liquid phase from wet undisturbed or bulk soils or from air-dried, ground and rewetted soil samples. The advantages and limitations of the most important soil solution extraction methods are summarized in Table I. Though the term "extraction" usually is reserved for a separation procedure which is based on distribution equilibrium between immiscible phases and material transport between them (e.g. displacement of the soil solution with organic solvents), it is also used in the literature related to soil solution chemistry to describe the removal of the liquid phase by such methods as centrifugation[20,23,26,27,30] and vacuum or free drainage filtering[18,20], when extracting agents are not applied in the separation procedure.

Since the chemical composition of the soil solution is greatly influenced by the sampling technique, in studies on soil solution chemistry an exact detailed description of the extraction method is generally given for the interpretation of data on element concentrations. Despite the limitations and drawbacks of the various techniques (Table I), under standardized conditions they provide solutions which approximate better the "true" soil solution than the easily prepared aqueous soil extracts of wide soil:water ratios. These extracts, which are often applied in the routine soil chemical laboratory practice, cannot give adequate informations on soil chemical reactions, phase interactions in the soil or element uptake by plants. Survey[2, 22, 31] or comparison[19, 20, 22, 23, 30, 32, 33] of different soil solution sampling techniques are the objects of several studies.

Compared to the huge number of publications dealing with soil solution chemistry, there are relatively few studies which characterize the energy status of the soil solution to be separated. The plant-available quantity of soil moisture is influenced by the energy of water; plant water uptake is determined by the water-retention of the soil and the suction exerted by the plant.

The potential of the soil liquid phase, which is the sum of different component potentials, is related to that of pure, free water[34, 35]. The relationship between this potential and the soil water content expressed in volume percentage is by definition the soil water-retention curve[35] (Table II, Figure 1). For a given soil, the lower is soil water content, the higher is the level of its potential. The soil water-retention curve is influenced by several soil properties, such as particle size distribution, organic matter content, bulk density, cation exchange capacity and clay mineralogy[36]. By convention, −1500 kPa (pF 4.2) is the potential considered as the upper limit of the potential of water accessible for plants (Table II). The water content at this potential is called the wilting percentage or wilting point. Its value is low in sandy soils (<5 volume %) and relatively high in clays (>25 volume %). In real situations the upper limit of the potential of plant available water covers a wide interval: e.g. it was shown to be around –2000 kPa for tomato or –3800 kPa for cotton[37], while xerophyta and especially halophyta plants can exert far higher suctions than the conventional wilting point (in extreme cases it may reach –20000 kPa[38]).

TABLE II Special points of soil water-retention characteristics

kPa	*water (cm)*	*pF*	*soil water characteristics*
-0.1	1	0	maximum water capacity (water saturated soil)
- 1	10	1.0	
-10	100	2.0	
-20	200	2.3	field capacity
-50	500	2.7	
-250	2500	3.4	
-1500	15000	4.2	conventional wilting point
<-1500	>15000		unavailable water

pF: logarithm of suction expressed in water column cm.

Data on heavy metal concentrations in the soil liquid phase are available in the literature[6, 11, 12, 15, 39, 40] but there are only few data on heavy metal content of the soil solution at defined energy status[30].

The aim of this study was to assess the impact of *soil contamination* and *acidification* on Cd, Cr, Ni, Pb and Zn concentrations in the liquid phase extracted at identical energy status from various soils having different soil water-retention characteristics. The force applied during extraction of the soil solution in our experiment corresponded to –1500 kPa, the value equal to the conventional wilting point of plants, in order to study the composition of the *plant-available* liquid phase of heavy metal contaminated soils.

In studies on salt-affected soils this value was used to extract soil solution by pressure membrane filtering method in the forties (cit. in the detailed surveys of Komarova[22] and Wolt[2]). After using this method in soil solution chemistry studies, we modified former centrifugation techniques[22, 23, 26, 27] to extract the plant available liquid phase of alkali soils by applying a centrifugal force equal to –1500 kPa[29]. In the study presented here, this centrifugation technique was applied to model the plant-available soil solution from polluted soils. The pressure membrane filtering method was not suitable for this purpose, since the cel-

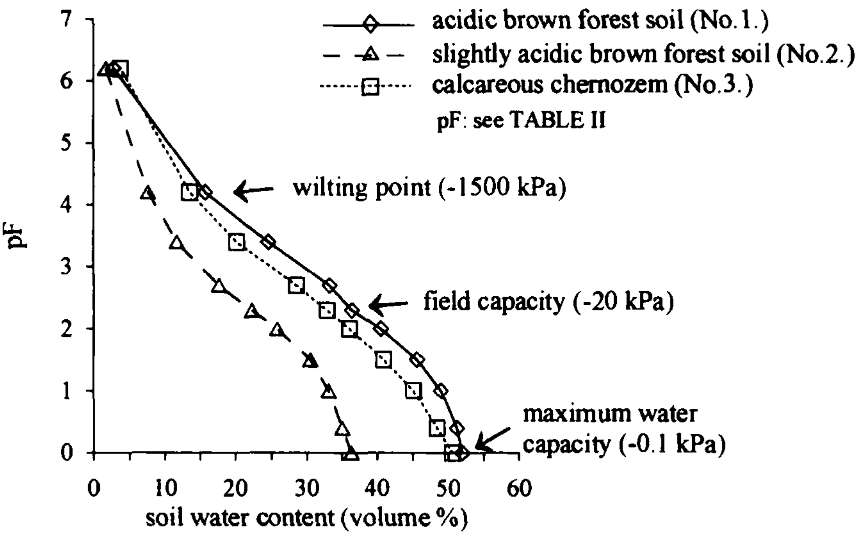

FIGURE 1 Soil water-retention curves

lophane membrane of the pressure filtering apparatus adsorbed a great part of protons and heavy metals from test solutions (unpublished data).

EXPERIMENTAL

Preparation of soil samples

Soil solution was extracted from samples of the upper horizon of an acidic and a slightly acidic brown forest soil and of a calcareous chernozem soil (Table III, Figure 1). The air-dried soil samples (1–1 kg) were contaminated with aqueous multicomponent solutions of Cd, Cr, Ni, Pb and Zn nitrates (soil+Me system). The solutions were added in such quantities that the resulting water potentials of the wet soil samples corresponded to field and maximum water capacities (FC = –20 kPa and MC = –0.1 kPa, resp.). The contaminated wet soil samples were equilibrated at room temperature for one week (as proposed in the literature[15, 30]), during which they were kept in air-tight plastic vessels and were mixed three times. Prior to centrifugation the exact water content of the homogenous wet soil samples was measured by oven-dry method at 105 °C. Expressing soil water content in volume percentage by multiplying measured gravimetric water content and bulk density data (Table III), the exact water potential in the soil samples was determined from the water–retention curves (Figure 1).

TABLE III Some chemical and physical properties of the studied soils

soils No.	*depth [cm]*	*pH*		*$CaCO_3$ [%]*	*organic matter[%]*	*CEC [cmol/kg soil]*	*<0.02mm*	*<0.002mm*	*bulk density*
		H_2O	*KCl*				*[weight %]*		*[g/cm^3]*
1.	5–15	4.3	3.2	0	1.6	20.7	40.8	27.8	1.34
2.	8–16	6.3	5.3	0	1.2	8.5	18.9	12.8	1.66
3.	0–20	7.7	7.0	6.6	2.8	28.3	35.8	22.1	1.32

No. 1. acidic brown forest soil (Ragály).
No. 2. slightly acidic brown forest soil (Gödöllö).
No. 3. calcareous chernozem (Pusztaszabolcs).

CEC: cation exchange capacity.
<0.02 mm: clay + silt fraction.
<0.002 mm: clay fraction.
bulk density: the ratio of the mass of dry solids (determined after drying the soil to constant weight at 105 °C) to the bulk volume of the soil (as taken in the field)[41].

Extraction of the soil solution of defined energy status – modelling plant available soil solution

The equation of Cassel and Nielsen[42], expressing a relationship between the centrifugation speed and the average water potential, was applied to calculate the centrifugal speed corresponding to –1500 kPa water potential.

By this soil solution-extraction method the "true" soil solution, i.e. the quantity of soil moisture directly available to plants is modelled: solutions held in the soil with suctions less than that corresponding to the conventional wilting point can be obtained. Thus, the physical origin of the extracted solution is known: from water-saturated soil, solutions at water potentials between –1500 and –0.1 kPa are extracted with this technique, while from samples at field capacity, solutions between –1500 and –20 kPa can be obtained.

Description of the centrifugation procedure

The soil solution was extracted with a technique similar to that of Keller[30]. Special double bottomed tubes were constructed by modifying the 500 mL polypropylene tubes of the Beckman J2–21 type centrifuge[29]. The wet soil was put in a polyamide gauze bag which was placed into the tube on a perforated teflon plate covered with a filter paper. This teflon console makes possible to separate the soil's liquid phase from the solid one. During the centrifugation procedure the soil solution is collected at the bottom of the tube, and is not allowed to get into contact with the solid phase. (Without this isolation of the liquid phase from the solid particles, the liquid phase would shift toward the surface of the wet soil but would remain inside since the soil is unsaturated with water.) When the water potential was set to –1500 kPa, the centrifugation speed in the Beckman centrifuge was between 5000 and 5400 rpm, depending on the quantity of the soil.

A one hour centrifugation procedure was applied since it was shown previously (unpublished data) that, – in agreement with literature suggestions[23, 27, 30], – the volume and consequently the chemical composition of the extracted solution practically did not change after this period.

As the teflon consoles adsorbed a part of the studied metals from single nitrate salt test solutions (Cd: 30%, Cr: 4%, Pb: 16%, Zn: 11%), their standard acidic pretreatment was necessary before every centrifugation. The consoles were soaked in 1 mol/L HNO_3 solution overnight, then washed free from acid with distilled water. As a result of this cleaning procedure, the adsorption of the elements by the teflon from test salt solutions became negligible.

To test the reproducibility of our soil solution extraction method, the procedure was applied to 5 parallel samples of soil No. 1. (these samples originated from a different sampling than those used in the contamination experiments). Soil samples were moistened to FC and MC at 100Me (see later) contamination level. The combined error of the sample preparation, extraction procedures and chemical analyses was calculated.

Soil contamination and acidification experiments

In order to determine quantitatively the retention and mobilization of Cd, Cr, Ni, Pb and Zn in the three studied soils, different contamination levels and acid loadings were applied. The loading rates were based on the upper limits of permitted heavy metal contents of sludges to be deposited onto agricultural lands, as specified by the Hung. Techn. Dir.[10], i.e. 15 mg Cd, 1000 mg Cr and Pb, 200 mg Ni and 3000 mg Zn per kg sludge dry matter. Assuming an average sludge application practice (i.e. incorporation of 500 t/ha sewage sludge containing 5% dry matter into a 20-cm surface soil layer), calculated soil loadings in the soil+Me system were: 0.125 mg Cd, 8.33 mg Cr and Pb, 1.67 mg Ni and 25 mg Zn per kg soil (1Me). In order to model extreme overloadings, 10 and 100 times more concentrated contaminating solutions were also applied (10Me and 100Me, resp.).

To assess the impact of *sludge application* on soil solution concentrations, the slightly acidic forest soil (No. 2.) was treated with compressed municipal sewage sludge enriched with the metal nitrates at 100 times overloading (soil+[Me+sludge] system; 100Me+Ss). Original concentrations of the selected metals in the sludge, as determined after 2 mol/L HNO_3 extraction at 100 °C following the method of Andersson[43], were: 12.3 mg Cd, 217 mg Cr, 109 mg Ni, 210 mg Pb and 3026 mg Zn per kg dry material. These values are comparable to or less than the limits specified in the Hung. Techn. Dir.[10] (Dry and inorganic matter contents in the sludge were 20.6% and 48.2%, resp.). The volume of the contaminating sludge and concentrations of the added metals were chosen so that the water potential (gravimetric water content) and metal content in the soil+[Me+sludge] mixture would be FC and 100 times overloading, resp., similarly as in the soil+Me system. The same amounts of metal nitrates were added also to the sludge itself (sludge+Me system) to assess the sorption of the added metals on sludge constituents. The liquid phases were extracted as described above, but in the case of the sludge+Me mixture, having relatively higher water content, the original centrifuge tubes (without the separating teflon console) were used.

Impact of *soil acidification* on the desorption of the elements and their recovery in the soil solution was studied on the slightly acidic forest soil (No. 2.). 0 – 10 cm layers of undisturbed large (diameter: 40 cm) columns of this soil were contaminated with the same metal-spiked sludge as in the previous experiment. Four treatments were carried out: by applying the original sludge (0Me+Ss) and 10Me+Ss, 30Me+Ss and 100Me+Ss metal enrichment levels. The sludge was added on the soil columns in the same amount in all treatments. The columns were kept in the laboratory during three months at a fairly constant water content, then samples from the contaminated layers were left to air-dry. Detailed description of the experiment is given in Bujtás et al.[44]

When measuring the impact of soil acidification on the mobilization of heavy metals in the [Me+sludge] treated soil, the air-dried soil samples were rewetted with distilled water, or 0.001, 0.1 and 1.5 mol/L HNO_3 solutions to MC and equilibrated for one week, similarly as previously the non-acidified samples. The soil solution was obtained as described above.

Cd, Cr, Ni, Pb and Zn concentrations in the contaminating metal salt solutions and in the liquid phase extracted from the wet uncontaminated, contaminated and contaminated+dried+acidified soil samples were measured by inductively coupled plasma atomic emission spectrometry (ICP-AES). The measurements were carried out with a JARREL ASH apparatus supplied with a polychromator, which enabled simultaneous analysis of the elements. This was needed because the volume of the liquid phase extracted from soils of natural moisture status was small.

RESULTS AND DISCUSSION

Test of the reproducibility of the soil solution extraction method

The numerical values of the combined error of sample preparation, extraction and chemical analysis of the soil solution are given in Table IV. From the data of 5 parallel measurements at 100Me contamination level it can be concluded that our method is suitable to extract soil solution with good reproducibility. The coefficients of variation (CV) practically did not differ at water potentials corresponding to FC and MC. At such high heavy metal concentrations similar or better reproducibility was obtained than in the case of two salt affected soils, at similar water potentials, for ions present in high concentrations in the soil solution[45]. (In the case of a carbonate-hydrocarbonate containing meadow solonetz soil, for example, at –0.5 kPa water potential, CV values for Na^+, CO_3^{2-}+HCO_3^-, SO_4^{2-} and Cl^- were below 7.8%. For a sulphatic solonchakized solonetz soil, at –0. 1 kPa and in the range between –13 kPa and –22 kPa, CV values were less than 11.5% and 6.9%, resp., for Ca^{2+}, Mg^{2+}, Na^+, SO_4^{2-} and Cl^-.)

TABLE IV Error of the soil solution extraction method: soil solution concentrations (mg/L) at field capacity (FC) and at maximum water capacity (MC) (soil No. 1., 100Me; n=5)

statistical index	*Cd*	*Cr*	*Ni*	*Pb*	*Zn*
FC					
x	35.5	244	491	352	7660
s	1.2	9	11	14	160
CV (%)	3.3	3.6	2.2	4.0	2.1
h(±)	1.1	9	11	14	155
MC					
x	26.4	189	359	259	5570
s	1.1	7	5	9	50
CV (%)	4.3	3.5	1.3	3.5	1.0
h(±)	1.1	6	4	9	50

n: number of data.
x: mean value.
s: standard deviation.
CV: coefficient of variation.
h: confidence limit at $t_{5\%}$ level.

Impact of contamination level

To model the impact of contamination level on the concentrations of Cd, Cr, Ni, Pb and Zn in the soil solution, at first aqueous multicomponent solutions of the metal nitrates were applied to moisten the soils.

In the uncontaminated samples of all three soils Cd, Cr, Ni, Pb and Zn concentrations in the soil solution were small or below the detection limit (Cd: 5, Cr: 5, Ni: 5, Pb: 50 and Zn: 5 μg/L in single salt solutions). Zn concentrations were the highest: 0.7, 0.4 and 0.3 mg/L at FC in soils No. 1., 2. and 3., resp. When the maximum permitted quantities (1Me) were applied, only a negligible transfer to the soil solution occurred; nearly 100% of the metals present in the applied contaminating solutions were adsorbed by the soils. Again Zn concentrations were the highest, 1.3 mg/L in the liquid phase of the forest soils and 0.4 mg/L in the chernozem at FC. The element concentrations in the soil solutions were shown to be lower or near to the allowed concentrations in drinking waters and ground-, surface and river waters (Table V).

When provocative heavy metal overloadings were modelled (10Me and 100Me), the concentrations in the soil solution increased in all three soils, but to a different extent. The soils′ reaction, texture and cation exchange capacity

(Table III) represented a wide variety of soil properties which have a significant role in buffering toxic materials. While the medium textured, calcareous chernozem (soil No. 3.) containing also relatively much organic matter, supposedly buffers well heavy metals, soils No. 1. or No. 2., having acidic character or light texture and low cation exchange capacity, resp., were theoretically expected to poorly retain heavy metals.

TABLE V Limit values of heavy metal concentrations (mg/L) in waters

source	*Cd*	*Cr*	*Ni*	*Pb*	*Zn*
1	0.005	0.05	-	0.05	1.0
2	0.005	0.05	-	0.05	-
3	0.005	0.05	0.05	0.05	5.0
4	0.006	0.030	0.075	0.075	0.8
5	0.01	0.05	-	0.05	5.0
6	0.0055	0.033	0.020	0.057	0.33
7	0.01	0.10	0.20	5.0	0.50

1. drinking water[46].
2. WHO-Guidelines for drinking water quality[47] (p. 726).
3. Directive of the Council of the European Communities on the quality of water for human consumption; maximum admissible concentration (MAC)[47], (pp. 740–742).
4. provisional Dutch soil sanitation standards for groundwater[48].
5. surface water quality criteria of US Dept. of Interior, Fed. Water Pollut. Control Admin.[9] (p. 34).
6. river water, Rhine, Germany[49].
7. irrigation water (guidelines in[50], pp. 232–234).

In the calcareous chernozem nearly all metals were adsorbed even at 100Me, only Zn was found in appreciable concentration in the soil solution (17 mg/L at FC and 15 mg/L at MC). Concentrations of Cd, Cr and Pb (Ni was not applied) were below 0.2 mg/L.

In the forest soils concentrations of Cd, Cr and Pb somewhat increased in the liquid phase at 10Me contamination level but still remained below 1.5 mg/L. Concentration of Ni in the slightly acidic forest soil (No. 2.) was 13 and 5 mg/L at FC and MC, resp., while that of Zn, which was added in high amount to the soils, approximated 200 mg/L at FC and 130 mg/L at MC in both soils.

At 100Me contamination level concentrations of all elements increased substantially in the forest soils (Figure 2). At both overloadings (10Me and 100Me) much higher soil solution concentrations were measured at field capacity than at maximum water capacity. This is explained partly by the dilution effect in the

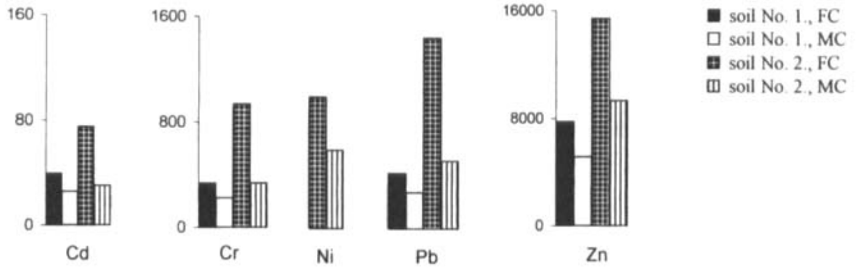

FIGURE 2 Heavy metal concentrations (mg/L) in the liquid phase of the forest soils at 100Me contamination level (soil No. 1. not treated with Ni; FC and MC: field and maximum water capacities, resp.)

less dry soil, and by the differences in the metal concentrations of the added contaminating solutions. In order to ensure the same loadings at both water potentials, addition of more concentrated multicomponent metal nitrate solutions was necessary at FC where smaller volume of water was needed to give the required water potential than at MC (Figure 1).

Similarly, at 100Me, the much higher element concentrations in the liquid phase of soil No. 2. than in soil No. 1. (Figure 2) partly originated from the concentration difference of the contaminating solutions. Soil No. 1. and No. 2. had very different water-retention characteristics (Figure 1): smaller volume of water was necessary to reach the same water potential in soil No. 2. than in soil No. 1. Approximately twice as high concentrations were necessary in the contaminating metal salt solution for soil No. 2. to provide equal loadings in the two soils. While the concentrations in the liquid phase of the acidic, medium textured soil (No. 1.) and of the slightly acidic, light textured soil (No. 2.) were similar at 1Me and 10Me, they were about twice as high in soil No. 2. than in soil No. 1. at 100Me. At this extremely high overloading the impact of the different volume, consequently different concentration of the polluting solutions probably prevailed over the combined effects of pH, texture and cation exchange properties of the two soils. At 1Me and 10Me these factors supposedly compensated each other.

The order of element concentrations in the liquid phase (Figure 2) generally matched the order of the contamination ratios (Cd<Ni<Cr=Pb<Zn). Concentrations of Cd, Ni and Zn reflected well the loading rates, but the release of the less mobile Cr and Pb was smaller. Thus, in soil No. 2. concentrations of Ni somewhat exceeded those of the strongly adsorbed Cr (Figure 2).

The relative adsorption of the elements in the two forest soils at 10Me and 100Me contamination levels was expressed as percentage of the amounts added.

(Data for the calcareous chernozem are not presented since they were nearly 100 % in all treatments.) In the forest soils the relative adsorption decreased considerably with increasing contamination levels, especially for Cd, Ni and Zn (Table VI). In agreement with literature data[51, 52] their adsorption was much lower than that of the less mobile Cr and Pb in both forest soils, at both contamination levels.

TABLE VI Adsorption (%) of heavy metals in the forest soils at field capacity, depending on the contamination level

soils No.	*10Me*					*100Me*				
	Cd	*Cr*	*Ni*	*Pb*	*Zn*	*Cd*	*Cr*	*Ni*	*Pb*	*Zn*
1.	86.5	99.6	-	99.8	83.5	26.8	90.1	-	88.1	22.2
2.	95.7	99.9	92.8	99.5	91.4	32.5	91.9	32.7	88.7	25.8

% = 100 $(c_m - c_s)/c_m$, where c_m and c_s are concentrations (mg/L) measured in the applied metal salt solutions and the soil solutions, resp.

This is in accordance with the concept of metal ion hydrolysis: specific adsorption of metallic cations onto mineral surfaces is stronger for those metals that hydrolyse in water at relatively low pH. The ability of the studied metals to undergo hydrolysis reaction in water is expressed with the pK value of the reaction: $Me^{2+} + H_2O = MeOH^+ + H^+$, and are in the order: Cr (4.0)<Pb (7.7)<Zn (9.0)<Ni (9.9)<Cd (10.1)[14, 53]. With decreasing pK values, heavy metal adsorption increases. The correlation between the order of pK values and metal adsorption, which was established for standard systems (as goethite), may be influenced and modified by several factors in real systems. The very similar adsorption behaviour of Cd, Ni and Zn, and the stronger adsorption of Pb and particularly of Cr in the studied soils are in accordance with this concept. The relatively lower adsorption of Zn, which does not correspond to the order of pK values, can be explained with its dominance in the contaminating solutions.

The somewhat less adsorption of Cd and Zn in soil No. 1. may be explained with its more acidic character (Table III) which effect probably dominates over the impacts of the texture and cation exchange capacity on element adsorption. The fact that both adsorption and the element concentrations in the soil solutions are higher in soil No. 2. than in soil No. 1. means that the somewhat higher adsorption in soil No. 2. was not enough to decrease sufficiently the amount of heavy metals entering the soil solution from the approximately twice as concentrated contaminating solutions.

Impact of sludge application

Adsorption of the elements was much more higher in the presence of communal sewage sludge which contained substantial amounts of adsorptive inorganic and organic materials. When soil No. 2. was contaminated to 100Me with the metal-spiked sludge, the metal concentrations in the soil solution were many times, for Cr and Pb by 2–3 orders of magnitude smaller (Figure 3) than when only the multicomponent metal salt solution itself was applied onto the soil (Figure 2, soil No. 2., at FC). The concentrations of Cd, Ni and Zn in the liquid phase of soil+(100Me+Ss) system (Figure 3) were 5, 43 and 30 % of their respective concentrations measured in the liquid phase of the soil+100Me system (Figure 2). Such comparison gave only 0.08% for Cr and 0.4% for Pb.

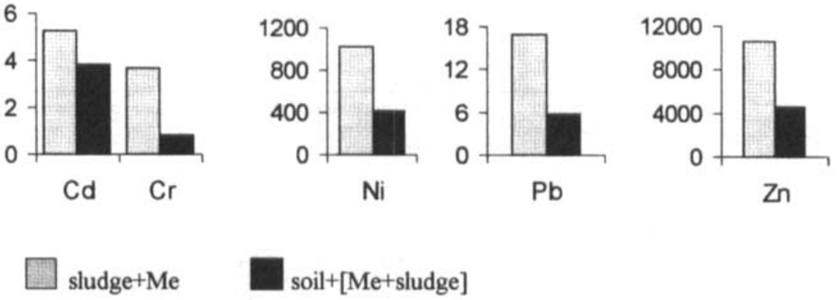

FIGURE 3 Heavy metal concentrations (mg/L) in the liquid phases of the metal-contaminated sludge and soil+sludge (sludge+Me and soil+[Me+sludge] systems, resp.; contamination level: 100Me; for soil+Me see soil No. 2. at FC in FIGURE 2)

Generally much lower metal concentrations were found in the liquid phase of the contaminated sludge (Figure 3, sludge+Me) than in the soil solution separated from sludge-free contaminated soil (Figure 2), with the exception of Ni. For Cr and Pb the difference was about two order of magnitude or higher.

In our experiments the metal concentrations in the soil solution were much higher than many literature data. In two sandy soils (pH-H_2O 4.1 and 3.8), considered to be fairly free of pollution (original Cd contents 0.07 and 0.46 mg/kg), approximately 10 µg/L Cd was found in the soil solution extracted by centrifugation method[30]. In a peaty soil (pH-H_2O 4.3, organic matter content 1.1 %) resembling somewhat our soil No. 1, 0.184 mg/L Zn and 0.026 mg/L Cd were found, not in soil solution but in 1:5 soil:water extracts[54]. However, since the total concentrations in the soil were only 26 mg/kg Zn and 3.7 mg/kg Cd (origin and residence time unknown), the recoveries for both elements were about

3.5 %. In a nonacid soil, total soluble Zn concentration, measured by anodic stripping voltammetry[55], was $3 \cdot 10^{-5}$ mol/L, i.e. about 2 mg/L. This soil was treated with sludge almost 20 years earlier. Zinc loading was 974 kg/ha, which corresponds to about 325 mg Zn/kg soil, (calculated from 1.5 g/cm^3 soil density and supposing that Zn remained in the upper 20 cm).

However, at high soil contamination levels, much higher soil solution concentrations can be found. For instance, pollution of a sandy soil in the vicinity of a metallurgy plant reached 60 mg Cd, 1400 mg Pb and 6800 mg Zn per kg soil[15]. (These values are even higher than the 100Me level used in our experiments.) Ranges in concentration of these metals in the soil solution, centrifuged at pF from 0 to 2.5, were: Cd 22 – 265, Pb 1.4–7.6, and Zn 1000–21900 mg/L, depending on the pH of the solution which varied from 4 to 6. Our results for Cd and Zn concentrations at the 100Me loading rate are in the reported range, but Pb values are much higher (Figure 2). These high Pb values may be attributed to the application of Pb as nitrate salt, in contrast with the natural systems where other anions e.g. sulphates may be present in high amounts, causing precipitation of soluble Pb-compounds.

Impact of acidic loads

As a consequence of the decrease of pH, release of heavy metals into the soil solution increased. However, extreme high acid load (1.5 mol/L HNO_3) was necessary to increase considerably the concentrations of the elements in the liquid phase. By less strong acidic treatments only Zn was released in appreciable amounts and only at 100Me+Ss loading level (Table VII and VIII). At the highest acid load the order of metal concentrations after the acidic desorption matched the contamination ratios (Cd<Ni<Cr=Pb<Zn) with the exception of the strongly adsorbed Cr (Table VII.: Cd<Cr<Ni<Pb<Zn). The increase of element concentrations with increasing metal contamination is shown on the example of Zn in Table VIII. (The relatively high Zn concentration at 0Me+Ss originated from the native Zn content of the soil plus that of the sludge, which enters the liquid phase due to the extreme high acid load.)

The relatively smaller release of Cr and Pb is shown also by the recovery values expressed as percentage of the total amounts: recoveries of the mobile Cd, Ni and Zn were much higher than those of Pb and mainly of Cr (Table VII). This is in accordance with literature data related to the mobility of heavy metals in soils and/or effect of pH on their mobilization[12, 14, 16, 40, 49, 53].

TABLE VII Heavy metal concentrations and pH values in the liquid phase, and recovery values after acidic treatment of the previously contaminated soil (soil No. 2.; 100Me+Ss; maximum water capacity)

	extractant							
	distilled water		*0. 001 mol/L HNO_3*		*0.1 mol/L HNO_3*		*1.5 mol/L HNO_3*	
pH	6.6		6.7		4.5		1.3	
	concentrations (mg/L and mg/kg soil)							
	mg/L	*mg/kg*	*mg/L*	*mg/kg*	*mg/L*	*mg/kg*	*mg/L*	*mg/kg*
Cd	0.55	0.12	0.78	0.19	1.46	0.30	46.5	10.2
Cr	0.024	0.01	0.041	0.01	0.25	0.05	469	103
Ni	4.65	1.04	5.46	1.36	17.2	3.58	559	123
Pb	0.098	0.02	0.14	0.04	0.28	0.06	1140	250
Zn	61.0	13.7	76.8	19.2	411	85.6	8900	1950
	recoveries (%)							
Cd		1.08		1.69		2.66		89.1
Cr		0		0.001		0.008		15.0
Ni		0.69		0.91		2.38		81.7
Pb		0		0.01		0.01		33.9
Zn		0.65		0.92		4.09		93.5

% = 100 c_s/c_m, where c_s and c_m are concentrations (mg/kg soil) in the soil solution and in contaminated bulk soil, resp.

c_m: determined after 2 mol/L HNO_3 extraction at 1:20 soil:extractant ratio[43].

mg/kg soil: concentrations related to the mass of the dry soil instead of the volume of the liquid phase were necessary to get equal dimensions for c_s and c_m to calculate recovery values: mg/kg = (mg/L × gravimetric water content)/100.

TABLE VIII Zn concentrations (mg/L) in the liquid phase of the variously contaminated soil samples treated with HNO_3 solutions (soil No. 2.; presence of sludge; maximum water capacity)

	extractant			
contamination level	*distilled water*	*0.001 mol/L*	*0.1 mol/L*	*1.5 mol/L*
			HNO_3	
0Me+ Ss	1.79	-	0.67	242
10Me+Ss	0.70	-	1.57	1290
30Me+Ss	3.29	2.09	4.41	2160
100Me+Ss	61.0	76.8	411	8900

-: not measured.

Evaluation of the results in comparison with other approaches

When comparing our results with literature data, we must emphasize that in our experiments metal treatments represented not only metal loadings usually applied under field conditions, but also very high, provocative overloadings. Such overloadings are rare but sometimes might occur, since beside industrial activities, the possibility of improper or illegal waste depositions or accidental contaminations cannot be excluded despite the strict environmental regulations. These local accumulations ("hot spots") are extremely hazardous for the environment, since the soil may not be able to retain the huge amount of toxic metals so these appear in high amounts in the mobile liquid phase.

Also, in our experiments, metals were either freshly added to the soil in metal salt solutions and in the form of metal-enriched sludge with a one-week-equilibration time, or as metal-enriched sludge about 3 months prior to extraction of the soil solution when effects of acidification were studied. In contrast, in literature data on the availability of metals, soil samples are often taken from such sites where metal-containing sludges were applied a long time prior to the experiments. Long contact periods between soil and sludge, with repeated drying-rewetting cycles, may alter the solubility/availability of the metals[55]. Data obtained for such circumstances may not be fully comparable with our experimental situations.

Moreover, our results are in many cases hardly comparable with literature data because of the differences in the extraction methodology. The physical origin of the solutions obtained by the majority of the methods is uncertain. In our method the soil moisture directly available to plants is modelled: those fractions of the soil's liquid phase are separated which were retained in the soil below the conventional wilting point of plants.

We must note that several authors postulated/showed correlations between element concentrations in the soil solution and the element uptake by the plants[2, 40, 54–56]. Such correlations were often based on various soil extracts instead of separating the plant-available soil solution. Metal concentrations extracted by water or dilute salt solutions with a soil:solution ratio of 1:5 and considered to approximate the soil solution concentrations, showed better correlation with plant uptake than total metal concentrations in the soil[54]. Del Castilho and Chardon[56] found that both the estimated Cd distribution factor (model-calculated concentration in the soil solution / concentration in the soil) and the Cd transfer factor (concentration in plant / concentration in soil) for three plant species depended similarly on pH. This finding supported the hypothesis that the metal ion concentration in the soil solution governs metal content in crops. Concentrations of Cd and Zn in the soil solution, obtained by the centrifugation method presented in this paper, showed better correlation with Cd and Zn concentrations in corn shoots, than metal concentrations in 1:20 acidic ammonium acetate+EDTA soil extracts[44]. However, it should be considered that plant concentrations measured at a specific point during the vegetation period reflect the cumulative uptake of elements, while soil solution concentrations pertain only to a specific situation (soil water content, temperature, etc.) at a specific moment.

CONCLUSIONS

The soil solution extraction method presented here allows an approximation of the actual chemical composition of the "true" soil solution. This technique is probably also suitable for the determination of the concentrations of other environmentally hazardous materials like water soluble organic pollutants in the plant-available soil solution fractions.

The easily soluble part of the total amount of the contaminating metals, which is of highest ecological importance playing significant role in their migration and bioavailability, was negligible in all three soils in a one-time maximum load model experiment. The risk of the release of toxic elements into the soil solution may increase as a consequence of environmental changes, such as soil acidification. But our results indicate that significant acidic desorption is improbable even in soils of low buffering capacity unless extreme conditions exist, that is excessive metal contamination and/or strong acid pollution take place.

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