

Study of Heavy Metal Overloading of Soils in a Model Experiment

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In agricultural areas one source of heavy metal contamination in soils is the deposition of sewage sludges containing these potentially toxic elements (BERGLUND et al., 1984; CHANG et al., 1984; VERMES, 1987; JUSTE & MENCH, 1992). The mobility and adsorption of an element in the soil is influenced by the following parameters: its chemical properties (tendency to form complexes and precipitates, oxidation conditions, etc.), and the texture, pH, CaCO_3 and organic matter contents, cation exchange capacity and redox conditions of the soil (LINDSAY, 1979; SPOSITO, 1983; ELLIOTT et al., 1986; McBRIDGE, 1989; ALLOWAY, 1990; SAUERBECK, 1991; KABATA-PENDIAS & PENDIAS, 1992). The amount of heavy metals accumulating in the soil can decrease by deflation, water erosion, leaching and plant uptake (KABATA-PENDIAS & PENDIAS, 1992). The above parameters and processes determine to what extent a given soil may be loaded by different heavy metals without environmental hazards.

Heavy metals in the soil may occur at ion exchange sites, may be incorporated into or on the surface of inorganic precipitates or into organic compounds, or may be present in the soil solution (DOWDY & VOLK, 1983). The present investigations were focussed on Zn, Pb, Cr and Cd, which may be present in relatively high amounts in the soil in comparison to their "background" concentrations, as well as in sewage sludges and waste waters, and can be very harmful to man. Cadmium occurs in soil predominately as a divalent cation adsorbed by clay, but it also forms complexes with hydroxyl and chloride. Chromium is very sparingly soluble. Lead is readily adsorbed by organic matter and so is preferentially held on the surface of the soil. Zinc occurs as a divalent cation, but it is in strong competition for exchange sites with calcium and magnesium; some zinc compounds have anionic forms and others can be chelated (BRIDGES, 1989).

Heavy metals are especially hazardous for the environment when entering the liquid phase of the soil because, they are most easily available to plants in

water-soluble forms, and by the movement of the soil solution they can be leached into the groundwater. Data relating to the heavy metal content of the soil solution are limited (MULLINS & SOMMERS, 1986; CAMPBELL & BECKETT, 1988; LINEHAN et al., 1989; cit. in ALLOWAY, 1990). One way to model the real soil solution is to separate it from the wet soil with a force corresponding to the conventional wilting point of plants. Such a method was developed in our institute.

The fate of heavy metals in the soil and their concentrations in the soil solution are influenced by environmental changes (decrease in pH, drying-rewetting, change in redox conditions, etc.). Recently, several studies have been devoted to evaluating the behaviour of heavy metals with changing pH and the effects of soil acidification (caused by wet and dry atmospheric depositions and by the improper application of mineral fertilizers), and to studying the so-called "chemical time bomb"-effect (the mobilization of previously immobile, accumulated soil pollutants due to changing environmental circumstances) (LINDSAY, 1979; SALOMONS & FÖRSTNER, 1984; STIGLIANI, 1988; LODENIUS & AUTIO, 1989; cit. in KABATA-PENDIAS & PENDIAS, 1990; Chemical Time Bombs, 1992).

The objectives of this study were

1. to model the effect of sewage sludge application on heavy metal concentrations in the soil solution, and
2. to follow concentration changes due to acidification.

Studies were made on several factors (loading rate, soil moisture content, adsorption time and acidification) which may influence the concentration of heavy metals in the soil solution and also their mobilization in the soil.

Materials and Methods

Air-dried samples of the A-horizon of an acidic brown forest soil (Ragály), a Ramann brown forest soil (Gödöllő) and of a calcareous chernozem soil (Pusztaszabolcs) were used in the experiments. The main physical and chemical properties of the soils are listed in Table 1. The soil samples were mixed with aqueous multicomponent solutions of nitrate salts of Zn, Pb, Cr and Cd. (Nitrate anion was selected because it ensures all the test salts being in water-soluble forms.) These model solutions were representative of the heavy metal overloading of soils. The moisture contents of the soil samples resulting from the application of the metal salt solutions were in the potential range between 250 and 0.1 kPa. The concentrations of the applied solutions represented 1, 10 and 100 times the permissible limits of waste water or sludge disposal on agricultural lands as specified by the Hungarian Standard (1990). These limits are 3000 mg Zn, 1000 mg Pb and Cr and 15 mg Cd per kg sludge dry matter. Using these values and assuming that sewage sludge contains 5 % dry matter and 500 t/ha sludge is incorporated in a 20 cm surface soil layer, the per-

Table 1
Some chemical and physical properties of the upper horizons of the test soils

Soil	pH (H ₂ O)	CaCO ₃ %	Org. C %	SP	< 0.02 mm, %	CEC
Acidic brown forest soil (Ragály)	4.3	0	1.6	55	40.8	20.7
Ramann brown forest soil (Gödöllő)	6.3	0.1	1.2	28	18.0	8.5
Calcareous chernozem (Pusztaszabolcs)	7.8	6.6	2.8	50	35.8	28.3

Org. C: organic carbon content; SP: saturation percentage; <0.02 mm: clay plus silt fraction; CEC: cation exchange capacity, meq/100 g soil

missible amounts of elements per kg soil were: 25 mg Zn, 8.33 mg Pb and Cr and 0.125 mg Cd.

The soil samples were kept with the metal salt solutions for one week in air-tight vessels and were mixed three times during this period. After one week the liquid phase was separated by centrifugation. The method was a modification of GILLMAN's (1976). The centrifugation was carried out with a rotor speed corresponding to 1500 kPa suction (i.e. the conventional wilting point of plants).

Centrifugation was implemented in special double-bottomed tubes, which were made from the 500 ml tubes of the Beckman J2-21 type centrifuge. (For the scheme of the tubes see NÉMETH et al., 1993.) The centrifugal speed was calculated by applying an equation used by CASSEL and NIELSEN (1986). The relationship between the centrifugation speed (n) and the average moisture potential (h) was expressed as follows:

$$h = (-\omega^2 / 6g)(2r_2 + r_1)(r_2 - r_1) \quad (1)$$

where:

$\omega = 2\pi n/60$: the angular velocity (1/min)

n : the centrifugation speed (rpm)

g : the acceleration due to gravity (m/sec²)

r_1 , and r_2 (m): the shortest and longest distance of the soil sample from the axis of rotation

The centrifugation speed in the Beckman J2-21 centrifuge, with the moisture potential set to 1500 kPa, was 5000-5400 rpm (appr. 3000 g) (depending on the quantity of the soil, i.e. on the value of r_1).

As 1500 kPa is the conventional upper limit of the suction exerted by plant roots, the separated solutions, which are retained in the soil with suctions less than 1500 kPa, model the soil solution fractions available to plants from the physical point of view. From water-saturated soil, for example, a solution is centrifuged at soil moisture potentials between 1500-0.1 kPa, while from the sample kept at field capacity, a solution is obtained at 1500-20 kPa.

To study the effect of adsorption time on the Ragály soil at 10x and 100x loading, a saturation paste and soil suspensions with soil : metal salt solution ratios of 1:1, 1:2, 1:2.5, 1:5, 1:10 were also prepared, shaken and kept for 1 hour, 1 day, 1 week and 1 month, after which the liquid phases were separated with standard centrifugation and filtration methods (BUZÁS, 1988). To study the effect of acidification on the release of heavy metals, samples of the Ragály soil, loaded 10 times the allowed limit at field capacity (20 kPa) moisture content, were air-dried, then rewetted again to 20 kPa with distilled water or 0.001, 0.1 and 1.5 mol/L HNO_3 solutions and centrifuged afterwards.

The Zn, Pb, Cr and Cd concentrations of the initial model solutions and of the soil solutions and extracts separated from the unloaded, loaded and loaded + acidified soil samples were determined by ICP spectrometry. The solutions were prepared for analysis by adding cc HNO_3 to ensure uniform pH in all samples (pH 0 was maintained throughout).

Results and Discussion

Loading rate, moisture content

It was shown previously (NÉMETH et al., 1993) that the Pb, Cr and Cd concentrations in the liquid phase of the original, uncontaminated soil samples were below the detection limit of ICP measurement, while the Zn concentration was negligible. The element concentrations were also negligible in the 0.001 mol/L HCl extracts. When the 1x loading rates corresponding to the permitted limits for agricultural deposition were applied, the concentrations in the soil solution were also low in all three soils (Table 2) as the soils adsorbed 97-100 % of the Zn, Pb, Cr and Cd from the applied solutions.

With an increasing loading rate the concentrations in the soil solution increased to different extents in the studied soils:

- Practically all metals were adsorbed or precipitated in the CaCO_3 -containing chernozem, even when applied in amounts 100x the permitted limit (Table 2). Only Zn was found in an appreciable concentration in the soil solution.

- In the liquid phase of the forest soils the concentrations increased with increasing loading and decreasing soil moisture content (Table 2; see also Figures 3, 4 for the Ragály soil in NÉMETH et al., 1993). At 1x and 10x loading rates the concentrations were similar in both soils (Table 2); the differences may be

Table 2
Heavy metal concentrations (mg/L) in the liquid phase of the studied soils at 0.1 kPa moisture potential (maximum water capacity) [1] and at 20 kPa (field capacity) [2]

Soil L	Zn		Pb		Cr		Cd	
	1	2	1	2	1	2	1	2
<i>Acidic brown forest soil</i>								
1x	1.7	1.3	0	0.1	0.04	0.04	0.01	0.01
10x	130	192	0.6	0.8	1.1	1.4	0.5	0.7
100x	5140	7766	266	405	223	336	26	39
<i>Ramann brown forest soil</i>								
1x	0.2	1.2	0.06	0.05	0.04	0.1	0	0.01
10x	130	189	0.1	0.6	0.2	0.5	0.2	0.5
100x	9310	15420	495	1392	337	937	30	75
<i>Calcareous chernozem</i>								
1x	0.04	0.4	0	0	0	0.1	0	0
10x	0.2	0.9	0	0.2	0.02	0.4	0	0.01
100x	14	17	0.1	0.2	0	0.07	0.2	0.1

L (loading): 1x, 10x, 100x the allowed upper limits determined by the Hungarian Standard (1990) for the deposition of sewage sludges. Adsorption time: 1 week.

attributed to procedural errors (separation, analysis). This agreement can be explained by assuming that the effects of different texture and pH (Table 1) compensate each other at these loadings.

In the liquid phase of these soils at 10x loading the Zn concentration increased to the greatest extent (Table 2). This is in agreement with the data of ELLIS et al. (cit. in DOWDY & VOLK, 1983), which show a great increase in the Zn concentration of the groundwater after loading a light-textured soil with sewage sludge. They also found no appreciable leaching of Pb, Cr or Cd.

- At the 100x loading rate the concentrations in the liquid phase of the Gödöllő soil were approximately twice as high as those of the Ragály soil. The volume of the applied model solution was calculated from the moisture retention curve of the soil. In the case of the light-textured Gödöllő soil, it was necessary to moisten the air-dry soil samples with solutions of smaller (half) volume but of higher (twice) concentrations, compared to Ragály soil, to ensure the same metal loading at similar soil moisture status. Therefore, at this extremely high overloading the soil solution concentrations were also about twice as high in the Gödöllő soil as in the Ragály soil.

The heavy metal concentrations of the liquid phase of the three contaminated soils were found to be comparable to the permitted concentrations in underground (Hungarian Standard, 1984), river (cit. in KABATA-PENDIAS &

PENDIAS, 1990) and drinking waters (see Table 11.6, cit. in BOHN et al., 1985; Hungarian Standard, 1989). Depending also on soil moisture content, in the two forest soils at the 1x loading, and in the chernozem soil at the 10x loading the element concentrations in the soil solutions were lower than or near to the permitted concentrations in waters.

It was also shown previously (NÉMETH et al., 1993) that in the natural soil moisture content range of the Ragály soil the concentrations (c) increase rapidly with decreasing soil moisture content (Θ). (For Zn, for example, see curves 3 and 7 for the 10x and 100x loading, resp., at one week adsorption time in Figure 1). Over a wide moisture content range the c- Θ relationships can be approximated by the following hyperbolic equation:

$$c = a + b \left\{ 1 / \left(\Theta_w - \Theta_{w'} \right) \right\} \quad (2)$$

where:

c = the element concentration (mg/L);

Θ_w = the gravimetric soil moisture content;

$\Theta_{w'}$ = the moisture content at 1500 kPa potential.

From 250 kPa moisture potential to the 1:10 soil : solution ratio, at 10x and 100x loading in the Ragály soil, the "a" and "b" parameters of the linearized equations for the four elements are given in Table 3, cases 2 and 5. Parameter "b", the slope of the line, characterizes the change in element concentrations with moisture content. This is several orders of magnitudes higher at 100x loading than at 10x loading. The difference between the "b" values for the different elements reflects their concentrations in the soil solution. (Zn has the highest and Cd the lowest "b" value at both loadings.)

Heavy metal adsorption (%) was also studied as a function of loading and moisture content. It was expressed as a percentage of the amounts of the added elements as follows:

$$\% = 100 \cdot (c_m - c_s) / c_m \quad (3)$$

where:

c_m and c_s = the concentrations in the applied model solution and in the soil solution, respectively.

In both soils at 10x and 100x loadings it was found that - in accordance with literary data (KABATA-PENDIAS & PENDIAS, 1990; DUDKA et al., 1990 cit. in KABATA-PENDIAS, 1993) - the adsorption of the more mobile Zn and Cd was smaller than that of Pb and Cr. (The curves of Zn and Pb are represented in

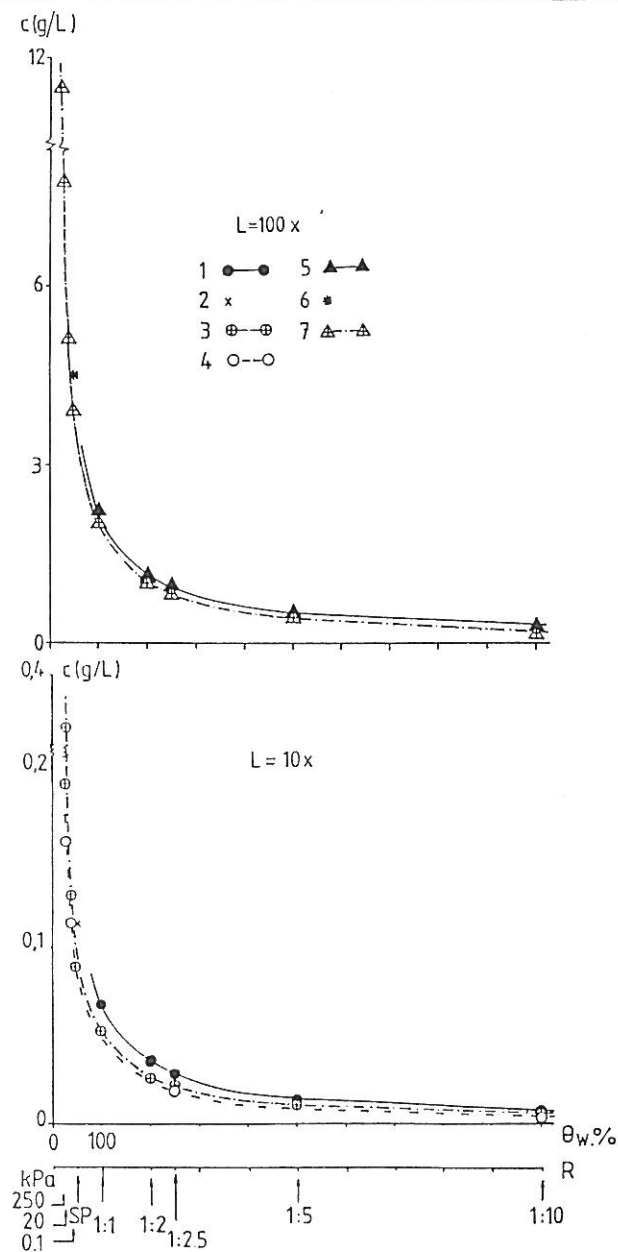


Figure 1

Dependence of the Zn concentration in the liquid phase of an acidic brown forest soil (Ragály) on the gravimetric soil moisture content (Θ_w) and on the adsorption time 1 and 5: 1 hour; 2 and 6: 1 day; 3 and 7: 1 week; 4: 1 month; L (loading): 10 (1,2,3,4) and 100 (5,6,7) times the allowed upper limit (Hungarian Standard, 1990); R: soil:model solution ratio; SP: saturation percentage; kPa: moisture potential

Figure 2. The behaviour of Cd is similar to that of Zn and the behaviour of Cr to that of Pb.) As expected, adsorption decreased with increasing loading, especially for Zn and Cd.

The amounts of heavy metals adsorbed decreased at higher soil moisture contents (Θ) over the whole Θ -range (from 250 kPa to the 1:10 soil : solution ratio). Figure 2 shows that this effect was more pronounced at the higher metal application levels (100x). As can be seen using the Ragály soil as an example (Figure 1 and 2), both the solution concentrations and the amounts of metals adsorbed increased at lower soil moisture contents. This result may be explained by the fact that the metal ion concentrations in the model solutions were different at the different soil moisture contents; it was necessary to apply solutions having higher metal ion concentrations to samples with smaller final moisture contents to ensure that the same total metal loadings would be reached

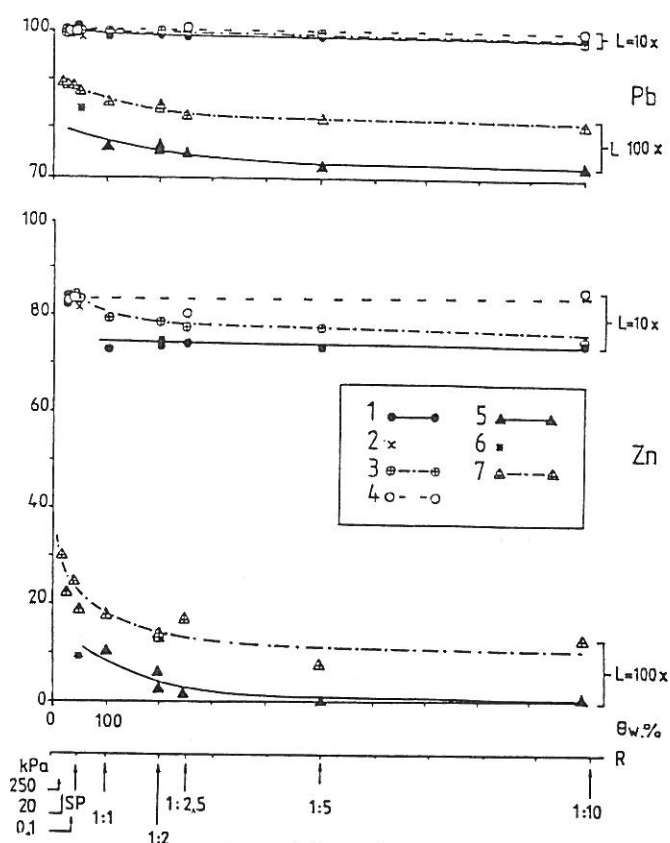


Figure 2

Effect of adsorption time, loading (L) and gravimetric moisture content (Θ_w) on the adsorption (%) of heavy metals in an acidic brown forest soil (Ragály). (%: see equation (3); L, R, SP, kPa: see Fig. 1; adsorption time: 1 and 5: 1 hour; 2 and 6: 1 day; 3 and 7: 1 week; 4: 1 month)

at each value of Θ . The increased adsorption in the drier soil was not enough to decrease the amounts of elements entering the liquid phase of the soil from the applied model solution.

The three studied soils showed the following differences in heavy metal adsorption:

- In the CaCO_3 -containing chernozem soil (Pusztaszabolcs) adsorption was 99-100% in the whole moisture range at the 10x and 100x metal loading rates.

- Comparing the adsorption % - Θ relationships obtained for the Ragály soil (Figure 2) and the Gödöllő soil, curves of similar shape were found. At 10x loading the Pb and Cr curves recorded in Gödöllő coincided with those in Ragály. The Zn and Cd curves from Gödöllő ran about 15% above those from Ragály, because these elements were adsorbed in higher amounts in the Gödöllő soil than in the Ragály soil. At 100x loading in the Gödöllő soil the curves of Zn, Pb and Cd ran 10%, 15% and 10%, resp., above those from Ragály, while the curves for Cr coincided. It seems likely that the effect of texture on the adsorption may be less significant than that of the pH. The degree of adsorption is higher in the light-textured Gödöllő soil because in the Ragály soil the elements were more mobile - as a consequence of its acidic character (pH ~ 4) - than in the Gödöllő soil (pH ~ 6).

Adsorption time

The concentrations of heavy metals in the soil solution and in the aqueous soil extracts at both loading rates were found to decrease somewhat when the adsorption time increased from 1 hour to 1 week, and subsequently to 1 month. This is shown as a function of Θ in the Ragály soil using Zn as the example (Figure 1). Similar curves were obtained for each element.

The parameters of the hyperbolic equations at different adsorption times and loadings are presented in Table 3. These can serve as rough estimations for the prediction of the composition of the soil solution from the data of routine analyses of soil extracts at given loading rates and adsorption times. The concentrations of the elements in the liquid phase of the soil decrease with increasing adsorption time; therefore, the value of the "b" parameter also decreases. From Figure 1 and Table 3 it can be concluded that the soil solution concentration decreases with increasing moisture content and adsorption time and decreasing loading, as expected. On the other hand, longer adsorption periods also increase the amount of adsorbed elements, while - as discussed above - increasing Θ and higher loading rates decrease it, as shown in Figure 2.

Table 3

The parameters of the hyperbolic relationship: $c = a + b \{1/(\Theta_w - \Theta_w')\}$ obtained from the data of centrifuged soil solutions (in the potential range of 250 - 0.1 kPa), as well as of the saturation extract and of aqueous soil extracts (with soil to model solution ratios of 1:1, 1:2, 1:2.5, 1:5 and 1:10)

Statistical index	Zn	Pb	Cr	Cd
1. $L = 10x$; $t = 1$ hour; $n = 6$				
a	2.0	0.05	-0.05	0.005
b	$6.0 \cdot 10^3$	56.9	73.5	26.8
r^2	0.998	0.997	0.993	0.999
2. $L = 10x$; $t = 1$ week; $n = 10$				
a	-4.3	-0.03	0.09	-0.03
b	$4.8 \cdot 10^3$	28.5	38.7	19.9
r^2	0.868	0.660	0.763	0.799
3. $L = 10x$; $t = 1$ month; $n = 4$				
a	5.5	-0.09	0.13	0.01
b	$2.9 \cdot 10^3$	29.9	20.7	11.2
r^2	0.995	0.861	0.867	0.993
4. $L = 100x$; $t = 1$ hour; $n = 6$				
a	125	9.2	-6.3	1.2
b	$1.9 \cdot 10^5$	$1.6 \cdot 10^4$	$2.2 \cdot 10^4$	737
r^2	0.996	0.995	0.999	0.933
5. $L = 100x$; $t = 1$ week; $n = 10$				
a	$1.1 \cdot 10^3$	60.3	31.2	4.5
b	$8.0 \cdot 10^4$	$4.4 \cdot 10^3$	$3.4 \cdot 10^3$	404
r^2	0.916	0.940	0.903	0.921

Acidic brown forest soil; L (loading): 10x and 100x the allowed upper limit (Hungarian Standard, 1990); t: adsorption time; n: number of data; c: ion concentration (mg/L); Θ_w : gravimetric soil moisture content; Θ_w' : soil moisture content at 1500 kPa potential.

Acidification

The effect of soil acidification on the mobilization of the heavy metals was modelled on the Ragály soil samples previously loaded with the multicomponent metal salt solution to field moisture capacity at a rate 10x the permitted limit, then dried for 1 month and rewetted again to field capacity with HNO_3 solutions. The element concentrations in the separated soil solutions were found

to be proportional to the amounts of heavy metal salts applied: the concentration of desorbed Zn was the highest, and that of Cd the smallest. (Cd was applied - in accordance with the Hungarian Standard (1990) - at rates about two

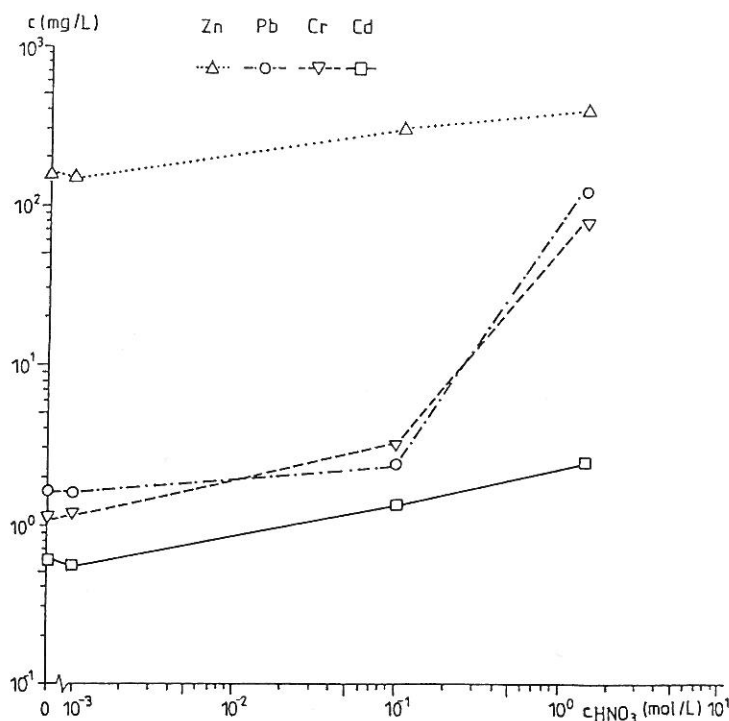


Figure 3

Heavy metal ion concentrations in the liquid phase of a contaminated acidic brown forest soil (Ragály) treated with HNO_3 solutions having different pH values

Loading: 10x the maximum permissible amounts of heavy metals in sewage sludges (Hungarian Standard, 1990); treatment of the soil: wetting it with the heavy metal salt model solution to 20 kPa moisture potential, followed by air-drying and rewetting with distilled water and HNO_3 solutions to 20 kPa; separation of the solutions: centrifugation from the wet soils with a rotor speed corresponding to 1500 kPa

orders of magnitude less than those of Zn.) The concentrations increased with the increasing acidity of the extractant (Figure 3).

The recovery of the heavy metals (%) was expressed as a percentage of the amounts of elements added as follows:

$$\% = 100 \cdot c_s / c_m \quad (4)$$

where:

c_m and c_s = the concentrations in the applied model solution and in the soil solution.

The recovery of the more mobile elements, Zn and Cd, in the liquid phase of the acid-extracted soil samples was higher than the recovery of Pb and Cr (reaching 15% and 10% for Zn and Cd, resp., even when distilled water or 0.001 mol/L HNO_3 solutions were applied). The recovery of Zn and Cd increased with increasing acidity, while Pb and Cr were only able to enter the liquid phase in appreciable amounts after desorption with 1.5 mol/L acid (Figure 4).

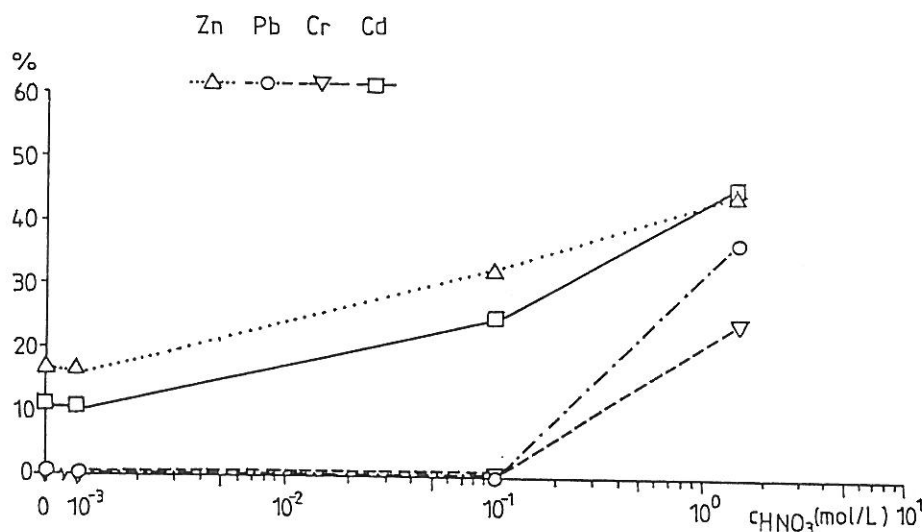


Figure 4

Recovery (%) of heavy metals after acidic treatment of a contaminated acidic brown forest soil (Ragály). (Loading, treatment of the soil, separation of the solutions: see Fig. 3; %: see equation (4))

Consequently, while the desorbed amounts of the metals after the acidic treatment reflected the loading rate applied rather than the mobility of the metals, their recovery in the soil solution, expressed as a percentage of the amount applied, was more closely related to their mobility.

Conclusions

From the model experiment it was concluded that in all three soils only a negligible transfer of Zn, Pb, Cr and Cd to the soil solution occurred when the maximum allowed quantities (1x) of these elements were applied. So sludges, if applied in accordance with the official regulations, may not pose an immedi-

ate environmental hazard. Nevertheless, abrupt overloading or environmental changes (decrease in pH) might increase heavy metal concentrations in the soil solution depending on the prevailing properties of the soil and the chemical characteristics of the element applied.

The adsorption and release of metals, their concentration in the liquid phase, and the extent to which these phenomena are influenced by such factors as soil moisture status, adsorption time and acidification, are different for the four heavy metals selected. The differences observed reflect their different mobility in the soil.

These experiments also indicate that heavy metals contained in sludges may act as "chemical time bombs" under changing environmental conditions, even in soils presently judged to be suitable for sludge deposition.

Summary

A model experiment was carried out to measure the concentration of heavy metals in the liquid phase of the upper horizon of three Hungarian soils, previously contaminated with aqueous multicomponent solutions of Zn, Pb, Cr and Cd nitrates. The concentrations applied were chosen according to the Hungarian Standard for the deposition of sewage sludges on agricultural fields. 10 and 100 times the permitted limits were also applied to study the increase in element concentrations in the soil solution as a consequence of overloading. The effects of different factors (loading rate, moisture content, adsorption time, decrease in pH) on the concentrations of the elements in the soil solution were also determined.

The liquid phase of the soils was separated with a new method: it was centrifuged at a speed corresponding to the conventional wilting point of plants (1500 kPa). The separated soil solution is considered to represent the liquid phase available to plants from a physical point of view.

From a comparison of the concentrations of the soil solution and the applied model solution conclusions were drawn on the adsorption and mobilization of the elements studied. It was shown that the forest soils had a lower relative rate of adsorption (as a percentage of the amount applied). On the other hand, the calcareous chernozem adsorbed practically all the metals applied. The adsorption of the more mobile elements Zn and Cd was shown to be less than that of Pb and Cr. Both the adsorbed amounts and solution concentrations of the metals increased at lower soil moisture contents. Metal ion concentrations in the liquid phase decreased with increasing adsorption time. Acidic desorption was proportional to the loading rates previously applied, while the recoveries reflected the order of mobilities of the heavy metals.

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