

MOBILITY OF SOME HEAVY METALS IN SOIL-PLANT SYSTEMS STUDIED ON SOIL MONOLITHS

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ABSTRACT

The soil can act as a natural buffer by retaining toxic materials present in municipal and industrial wastes and sewage sludges. Countries of Eastern Europe currently have a limited industrial infrastructure for recycling wastes. One of the most rational and economic ways for these countries to dispose of their waste waters and sludges is to apply them to agricultural fields, thereby utilizing also their nutrient content. A U.S.-Hungarian research project was recently started with the aim of studying the fate and transport of selected heavy metals in the soil profile of cropped undisturbed soil monoliths. Preliminary experiments were carried out to study the adsorption-desorption processes of these chemicals on disturbed soil samples, and to investigate the plant-availability of different metal forms. Concentrations of Zn, Pb, Cr and Cd in the soil solution were found to decrease with increasing soil moisture content and length of the adsorption period, both showing hyperbolic relationships. Lower soil moisture contents increased both the solution concentrations and the adsorbed concentrations of the elements. Release of adsorbed Zn and Cd was higher than that of Pb and Cr. Higher plant-availability of inorganic forms of Ni correlated with a higher phytotoxicity as compared to Ni applied in sewage sludge.

KEYWORDS

Heavy metals; undisturbed soil monoliths; solute transport; plant-availability; phytotoxicity; time-domain reflectometry (TDR); quadrupole mass spectrometry.

INTRODUCTION

Large amounts of heavy metals such as Cd, Cr, Ni, Pb and Zn are often present in sewage sludges and waste waters. These metals pose a potential threat to the environment when applied to agricultural lands. Their release to the soil liquid phase may cause leaching through the soil profile to the groundwater table, and also facilitate plant uptake of the heavy metals. The increased availability of Ni and Zn for plant uptake may lead to phytotoxicity, whereas less phytotoxic elements may accumulate in higher amounts in plants. This latter process enhances their transfer into the food-chain, thus posing serious environmental hazards to the population.

Once applied to agricultural fields, the availability and uptake of heavy metals by plant roots is determined by what happens at or near the soil-plant root interface. Hence, reliable information is needed about the most important transport processes and associated soil and plant properties affecting the behavior and transport of toxic elements in the soil, their uptake by agricultural crops, and their potential movement through the vadose zone to underlying groundwater systems.

A joint U.S.-Hungarian research project involving the U.S. Salinity Laboratory (Riverside, CA) and the Research Institute for Soil Science and Agricultural Chemistry (RISSAC, Budapest) was initiated in 1991, with as main objectives:

1. To characterize the plant-availability of selected toxic metals by quantifying their release into the soil solution of undisturbed soils from element loadings similar to or exceeding their permissible levels in wastes applied to agricultural lands, and to follow their redistribution in the solid and liquid phases under different soil moisture conditions,
2. To quantify the transport of these elements to, and their distribution in, different parts of plants as a function of element loadings,
3. To identify stress situations in plants as indicated by changes in the composition and/or quantity of different gases (O_2 , CO_2 , N_2 , water vapor) generated in plant tissues and the soil as a result of toxic trace elements loadings; the gases will be measured using a quadrupole mass spectrometer equipped with microprobes suitable also for *in vivo* measurements, and
4. Using the experimental data, to develop a theoretical model which predicts the transport and fate of the heavy elements in undisturbed soil profiles, and their uptake by plant roots.

This paper provides information about the experimental set-up. Preliminary results are presented of adsorption-desorption experiments involving Zn, Pb, Cr and Cd (applied in inorganic form to two soils), as well as the response of plants to different forms of Ni.

MATERIALS AND METHODS

Experimental set-up for measurements in large undisturbed soil monoliths

Undisturbed 40-cm diameter, 100-cm long soil monoliths were prepared according to the method of Homeyer et al. (1973) and modified by Nemeth et al. (1991) for application to a large number of soils having different textures. The monoliths were excavated and coated with fiber glass cloth impregnated with a synthetic resin. After the coatings solidified, the monoliths were lifted from the field site and transported to the laboratory. The coatings made extremely close contact with the soil surface by imbibing the outer micropores, thus eliminating possible "wall effects" during the transport experiments. The excellent insulating properties of the coating also eliminated leakage from the monoliths.

Figure 1 shows a block diagram of the experimental set-up. Each soil monolith contained three temperature sensors, six soil moisture probes attached to a TDR multiplexer, and ten special microprobes for measurement of the gas composition. The gas microprobes were coupled to a quadrupole mass spectrometer (QMS). In addition, five pairs of measuring points for a soil moisture capacitance meter were attached to the coatings. Automatic collection and analysis of TDR data from two columns and QMS data from four columns, all operated simultaneously during the experiments, were facilitated by a computer unit. This unit also controlled the QMS and the ion source and vacuum systems of the mass spectrometer. Column weights were recorded using a movable scale.

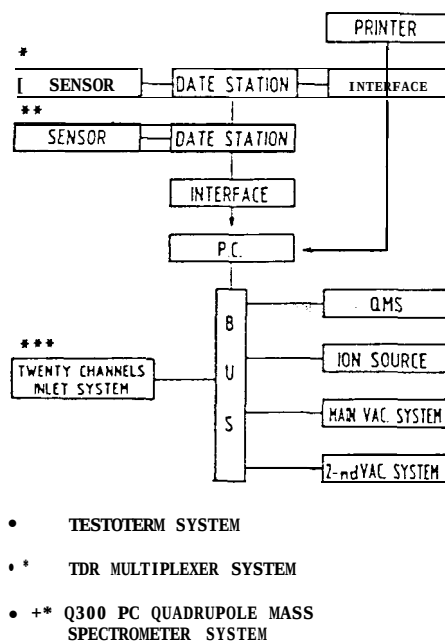


Figure 1. Block diagram of the experimental set-up.

Soil moisture contents in the monoliths were regulated by saturating the columns from the bottom through a special valve, or by sprinkler irrigation at the soil surface. Water was added on the basis of TDR measurements and/or weighting.

Measurement of adsorption-desorption of Zn, Pb, Cr and Cd in the soil

Adsorption and desorption experiments were carried out to quantify the heavy metal adsorption capacity of soils after applying different loadings of Zn, Pb, Cr and Cd. Aqueous solutions of nitrate salts of these elements were mixed with air-dried samples of the upper horizons of an acidic brown forest soil (Ragaly) and a calcareous chemozem (Pusztaszabolcs). The main physical and chemical properties of the soils are listed in Table 1. The metals were applied at rates of 1, 10 and 100 times the allowed upper limits as specified by the Hungarian Standard for deposition of sewage sludges to agricultural lands. These limits are 3000 mg Zn, 1000 mg Pb, 1000 mg Cr and 15 mg Cd per kg sludge dry matter (Hungarian Standard, 1990). Using these values and assuming that sewage sludge contains 5% dry matter and that 500 t/ha sludge was incorporated in a 20-cm surface soil layer, the permissible amounts of elements per kg soil were calculated. The amounts obtained in this manner were 25 mg Zn, 8.33 mg Pb, 8.33 mg Cr and 0.125 mg Cd per kg soil. These values correspond to 75, 25, 25 and 0.375 kg/ha, respectively, for the specified sludge application. U. S. Environmental Protection Agency standards are 172, 125, 530, and 18, respectively, under the most restrictive conditions of land use (USEPA, 1989; see also Chang et al., 1992). However, in Hungary, if sludge application is prolonged over several years, the application rate depends on the duration of this practice, and the cumulative amount of heavy metals originating from sludge application or any other sources must not exceed the total permitted amount of heavy metals in the soil. This total amount is equal to 250 mg Zn, 100 mg Pb, 100 mg Cr and 2 mg Cd per kg soil (for soils with adsorption capacity of 15-25 me/100 g soil), corresponding to 800 kg Zn, 320 kg Pb, 320 kg Cr and 6.4 kg Cd per ha.

Table 1. Some Relevant Properties of the Two Test Soils.

Soil	pH(H ₂ O)	CaCO ₃ %	org-C %	SP	0.02 mm % me/100	CEC g soil
Ragaly	4.3	0	1.6	55	40.8	20.7
Pusztaszabolcs	7.8	6.6	2.8	50	35.8	28.3

org-C: organic carbon content; SP: saturation percentage; CEC: cation exchange capacity

After incubating the soil samples with the metal solutions for one week in air-tight vessels and mixing them three times during this period, soil solutions were separated by centrifugation using a rotor speed corresponding to 1500 kPa pressure, i.e. the wilting point of plants (Csillag et al., 1991). Saturation extracts and aqueous extracts of different soil:solution ratios were prepared by standard methods in order to study the effect of soil moisture content changes on heavy metal concentration of the liquid phase over a wide range of moisture contents. Concentrations of Zn, Pb, Cr and Cd in the solutions were determined using a Jarrel Ash ICP spectrometer.

Adsorbed concentrations of the elements in the soil were calculated from the soil solution and added model solution concentrations. The time dependence of heavy metal sorption was studied on suspensions of the acidic brown forest soil. The suspensions were shaken for 1 h with heavy metal solutions ensuring 10 and 100 times loading rates (see Fig. 6.). Similar experiments were carried out on wet soil samples having similar loading rates and incubated in air-tight vessels for 1 week, as well as on 10 times loadings involving air-dried (for appr. one month) and subsequently rewetted soil samples. The effect of extract pH on the release of the heavy metals was studied using the acidic brown forest soil, loaded 10-fold, air-dried for about one month, and then rewetted to field and maximum water capacity using both distilled water and solutions having different concentrations of nitric acid.

Plant uptake and phytotoxicity of different Ni forms

Phytotoxicity is described as an intoxication of living plants by substances present in the growth medium, when these substances are taken up and accumulated in plant tissues (Chang et al. 1992). In order to assess phytotoxicity of different forms of Ni, growth response of plants to NiSO₄ and Ni applied in the form of Ni-enriched sewage sludge were studied on bush bean plants (*Phaseolus vulgaris* L.) grown for one month on inorganic nutrient solutions containing different amounts of Ni in the above forms. Plant response was evaluated on the basis of fresh and dry weights of the leaves, stems and roots. Plant uptake of Ni and its accumulation in the plant parts were estimated by measuring Ni concentrations by ICP after wet digestion (H₂SO₄+H₂O₂) of the air-dried samples of roots, stems, and successive leaves.

RESULTS AND DISCUSSION

Experimental setup-up for measurements in large undisturbed soil monoliths

Four undisturbed soil monoliths were used simultaneously in the experiments. Values of soil temperature, soil moisture content, soil gas composition at several depths, and the reference gas composition of the air, were recorded to obtain data about the initial status of the undisturbed monoliths. The gas composition (water vapor, O₂, N₂, and CO₂) in the top and bottom parts of one of the monoliths are shown in Figures 2 and 3, respectively. Similar reference data for the outside air are presented in Figure 4. Previous results on the gas composition of soil are given by Partay et al. (1992). Thus far, the monoliths have been allowed to dry very slowly. No water has yet been added to the columns, nor has drainage taken place. A relatively high initial moisture content measured at approximately 60 cm depth was attributed

to the presence of a fine-textured soil layer at this depth as observed in the field during excavation of the monoliths.

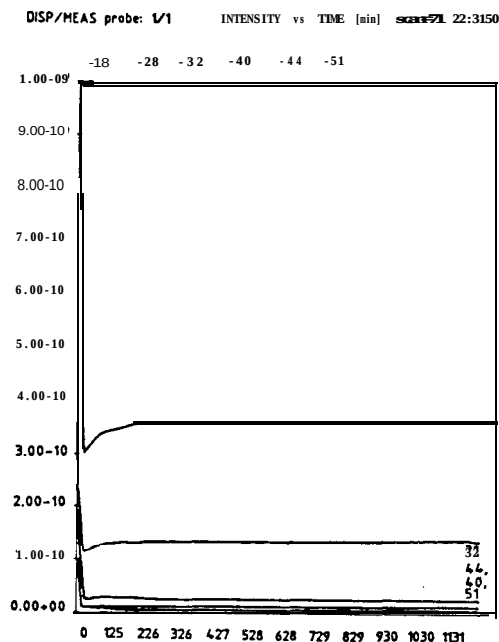


Figure 2. Gas Content of a soil monolith at 10cm depth.

(18: water vapor, 28: N_2 , 32: O_2 , 40: Ar, 44: CO_2 , 5 1: molecule fragment of coating).

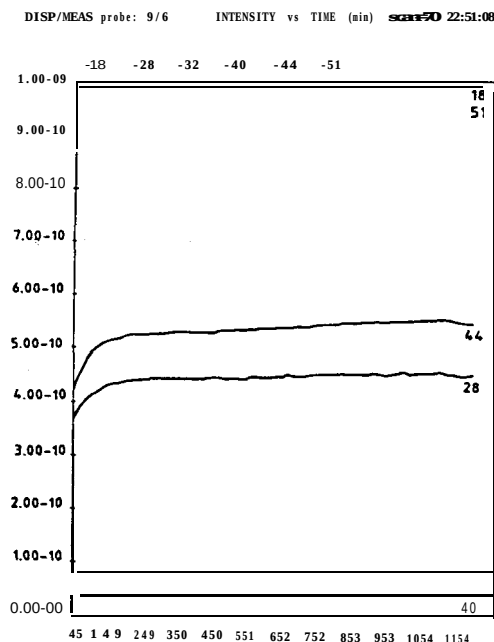


Figure 3. Gas Content of a soil monolith at 90cm depth.

Figs. 2 and 3 show that the gas **composition** in the soil monoliths remains relatively constant with time. This reflects the undisturbed state of the columns. Stress situations caused by the presence of toxic amounts of heavy metals in the root zone are reflected by changes in composition of gases originating from air-filled pores and from the soil liquid phase, as well as in the inner gas composition of plants depending on several interacting metabolic processes. We previously demonstrated such features (Buzas et al., 1987; Partay et al. 1987) for several other stress factors such as having extreme dry or wet soil, temperature changes, salt effects, and pesticide applications using methods based on quadrupole mass spectrometry for qualitative and quantitative in vivo measurement of the gas composition (Hungarian Patent No. 183.810).

Measurement of adsorption-release of Zn, Pb, Cr and Cd in the soil

Initial concentrations of Pb, Cr and Cd in the liquid phase of uncontaminated soil samples were found to be below the detection limit, while those for Zn were negligible. Of the maximum permissible waste loading applied (the 1-time loading), 97-100 % of the heavy metals were adsorbed by both soils at the field soil moisture content range. The very small amount entering the liquid phase of the soil may not pose an immediate environmental hazard. For the forest soil, at the 10-times loading, only the Zn concentration was not negligible in the liquid phase of the soil, even at the lower soil moisture contents. The strong adsorption of Zn is likely related to the relatively high clay content (14.7%) of this soil.

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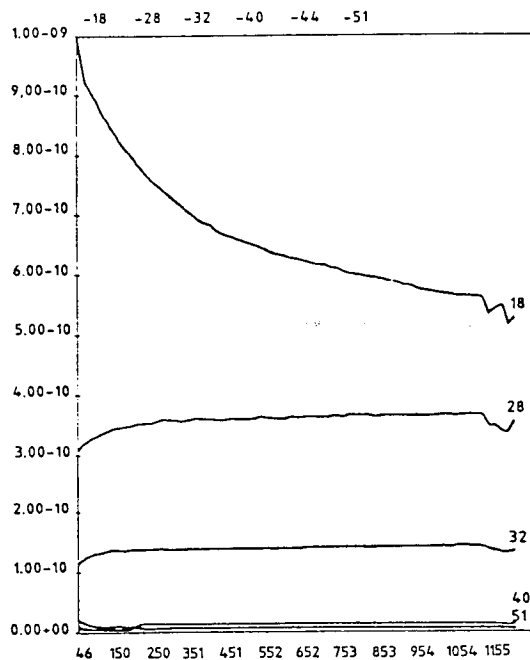


Figure 4. Gases measured in the atmosphere surrounding the monoliths.

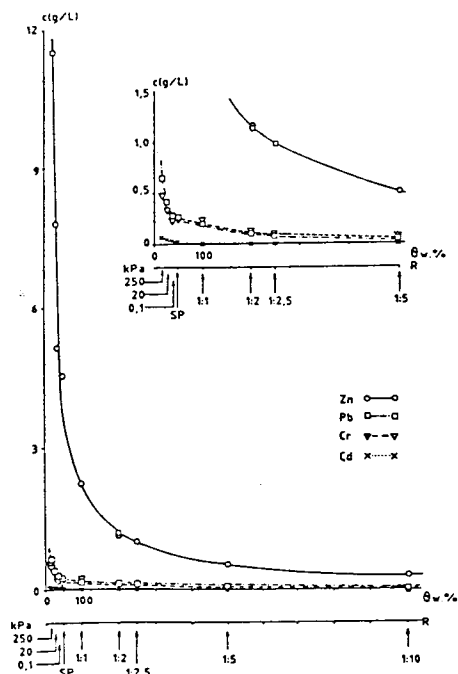
Figure 5. The dependence of heavy metal ion concentrations in the liquid phase of an acidic brown forest soil moisture content ($\theta_w\%$). Loading 100 times the allowed upper limit; R: Soil/water ratio; SP: saturation percentage; kPa: moisture potential.

Figure 5 shows that the concentrations, c , for the 100-times loading rate increase rapidly with decreasing soil moisture content (θ) in the field soil moisture content range. The c - θ relationships over the complete θ range were approximated by hyperbolic equations. Table 2 lists the parameters of the linearized equations. The slopes, b , of the lines characterize the change of the element concentration in the soil solution with changing soil moisture content. Except for Cr, the goodness of fit increased significantly if a quadratic member were included in the regression equations. Similar c - θ hyperbolic relationships were established for different adsorption periods (1 hour, 1 week and 1 month) at the 10-times and 100-times loading rates. Soil solution concentrations were found to decrease with increasing adsorption time and increasing θ values.

Table 2. Parameters of the Hyperbolic Relationships.

stat. index	E l e m e n t s							
	Zn		Pb		Cr		Cd	
	1	2	1	2	1	2	1	2
a	1.2×10^3	282	89	48	104	106	5.0	0.7
b	7.9×10^4	1.7×10^5	4.1×10^3	8.0×10^3	2.9×10^3	2.7×10^3	400	805
d	0	-6.2×10^5	0	-2.7×10^4	0	1.1×10^3	0	-2.8×10^3
r ²	0.909	0.997	0.920	0.980	0.804	0.801	0.992	0.995

(1) $c = a + b\{1/(\theta - \theta_w')\}$ and (2) $c = a + b\{1/(\theta - \theta_w')\} + d\{1/(\theta - \theta_w')\}^2$ obtained from data of centrifuged soil solutions in the potential range of 250-0.1 kPa, as well as of saturation extracts and of aqueous soil extracts having soil to model solution ratios of 1:1, 1:2, 1:2.5, 1:5 and 1:10, (Ragaly, acidic brown forest soil; loading 100 times the allowed upper limit; c = ion concentration (mg/L); θ_w = soil moisture content expressed in weight percentage; θ_w' = soil moisture content at 1500 kPa potential.

The calcareous chemozem soil adsorbed practically all toxic metals, even at the 100-times loading. Only Zn was detectable in the soil solution, but only at the lower moisture contents. For metal adsorption on the acidic brown forest soil we found that smaller amounts of Zn and Cd were adsorbed as compared to Pb and Cr. This is in accordance with literature data (Kabata-Pendias and Pendias, 1992). Lower soil moisture contents increased both the adsorbed and solution concentrations of the heavy metals. This feature may be explained by the fact that it was necessary to apply solutions with higher metal concentrations at the lower moisture contents to ensure the same total metal loading at each value of θ . The relative adsorption capacity increased with decreasing soil moisture content for Zn, Pb and Cd, but not for Cr. This increase was more pronounced at the higher loadings. The adsorption % of all four metals decreased substantially when the loading increased. Longer adsorption periods also increased the amount adsorbed as shown in Fig. 6 for Zn.

Release of heavy metals from soil samples loaded previously at field capacity with metal solutions at a rate 10 times the allowed limit, then dried for 1 month and rewetted again, was about 30-50% of the heavy metal release from soil samples incubated for 1 week under relatively moist conditions (Table 3). If 0.001N, 0.1N and 1.5N HNO₃ solutions were applied for rewetting the metal-loaded soil, the element concentrations in the extract increased with increasing acidity and, with the exception of Cr, were higher at field capacity than at the maximum water content. Recovery of the more mobile Zn and Cd elements (expressed as percentage of the added amounts) was higher than the recovery of Pb and Cr. These last two elements desorbed only with strong acid as shown by the data in Table 4. We note that the effects of wetting and drying are important to release of the heavy metals as previously shown by Bartlett and James (1980). Chromium mobility in particular is dependent on the soil aeration status since Cr(VI) is more toxic and mobile than Cr(III) (Bartlett and Kimble, 1976). Fresh field soils may readily oxidize Cr(III) to Cr(VI) (Bartlett and James, 1979).

Table 3. Concentrations (mg/l) in the Liquid Phase of a Contaminated Brown Forest Soil After Rewetting to Field Capacity.

Treatment	Zn	Pb	Cr	cd
1	371.3	2.68	3.43	1.65
2	158.5	1.56	1.13	0.59

1: soil wetted with heavy metal salt solution for 1 week
 2: soil wetted with heavy metal salt solution, air-dried for 1 month, rewetted with distilled water for 1 week

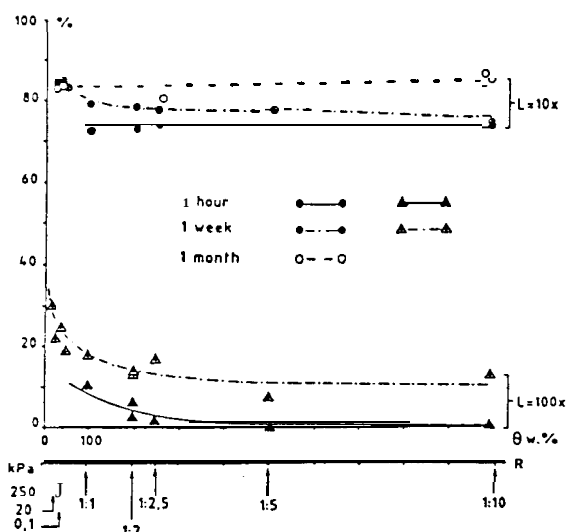


Figure 6. Effect of adsorption time, loading (L) and gravimetric soil moisture content (θ_w) on the adsorption of heavy metals in an acidic brown forest soil (Ragaly). Adsorption is expressed as % of the added elements: $\% = (c_s - c_m)100/c_m$, where c_s and c_m are element concentrations (mg/L) in the soil solution and in the model solution, respectively; R is soil:water ratio; kPa is moisture potential.

From the above adsorption-desorption experiments we conclude that the amounts of Zn, Pb, Cr and Cd entering the liquid phase of the two soils used in this study was relatively small upon application of only one (maximum) loading. However, repeated applications can quickly raise the concentrations of these metals in the soil solution. This, in turn, will increase their availability for plant uptake, as well as promote their downward leaching to the groundwater table. The soil moisture content was found to affect the amount of metal entering the soil solution. At constant loading more metal adsorption occurred at the lower soil moisture contents: however, as expected, the increase was not enough to decrease metal concentrations in the liquid phase.

TABLE 4. Heavy Metal Ion Concentration in the Liquid Phase of a Contaminated Brown Forest Soil, Treated with Nitric Acid Solutions, and Recovery of the Elements.

Extrac- tant	θ_w , %	kPa	concentrations (mg/L)				Recovery (%)			
			Zn	Pb	Cr	cd	Zn	Pb	Cr	cd
dist. water	37.0	1.0	112.4	0.43	1.15	0.42	16.2	0.17	0.49	10.9
	26.3	28.2	158.5	1.56	1.13	0.59	17.0	0.45	0.24	11.1
0.001n HNO ₃	38.9	0.25	106.2	0.27	1.10	0.38	15.3	0.11	0.46	9.9
	26.1	20.2	147.1	1.56	1.11	0.55	15.8	0.45	0.33	10.2
0.1n HNO ₃	37.4	0.0	203.0	3.39	4.87	1.29	40.8	1.39	2.05	33.9
	26.9	22.4	309.2	2.41	3.27	1.35	33.2	0.69	0.98	25.2
1.5n HNO ₃	40.4	0.1	339.0	124.8	94.4	2.15	48.8	51.2	39.9	56.4
	27.8	17.8	421.3	130.8	81.9	2.45	45.3	37.4	24.5	45.8

θ_w % gravimetric moisture content

kPa: moisture potential

Recovery expressed as a percentage of added elements: $\% = c_s \times 100 / c_m$, where c_s and c_m are element concentrations (mg/L) in the soil solution and in the solution added to the soil, respectively.

Treatments: wetting the soil with heavy metal salt solutions to moisture content at 20 kPa suction, then air-drying and rewetting it with the extractants shown.

Separation of soil solution: by centrifugation of the wet soils with a rotor speed corresponding to 1500 kPa.

Plant uptake and phytotoxicity of different Ni forms (see Table 5)

We have shown earlier for Ni that different phytotoxic actions are possible depending upon the chemical form of the heavy metal. We used bush bean as an indicator plant because of its sensitivity to Ni. Plant growth as measured by fresh and dry weight of shoots and roots decreased much more when Ni was applied in the form of sulfate salt than as Ni-spiked sewage sludge at the same total Ni concentration. At the same time, Ni accumulation in the shoots of the plants was 5 to 10-fold higher from the inorganic salt form as compared to sludge, i.e. the plant-availability of Ni from inorganic Ni-salt was much higher than of Ni derived from the sludge. The higher Ni-content correlated with a higher phytotoxicity of the inorganic Ni. These results seem to be in contrast to findings by Chang et al. (1992) which indicate that even higher loadings of Ni (100–425 mg/kg) from sludge may not increase Ni levels in plant tissues of corn. Also, Hinesly et al. (1979) demonstrated that Zn and Cd levels in corn decreased upon the addition of digested sewage sludge containing 112 mg Zn and 71 mg Cd per kg. We conclude by emphasizing that our uptake and phytotoxicity experiments were not carried out in soil but in nutrient solutions in order to obtain more direct information on the susceptibility of plants to different Ni forms. Adsorption processes in the natural soils will likely alter the activity, and hence phytotoxicity, of the different forms of heavy metals in the soil solution. Actual metal uptake under field conditions will probably be lower than that obtained in nutrient or greenhouse pot experiments (Chang et al., 1992).

TABLE 5. Growth Response and Ni Content of Bean Shoots Supplied with Different Forms of Ni.

Ni ppm	Chemical Form	Fresh Weight [mg]	Weight Ni [ppm]	Dry Weight [mg]	Weight Ni [ppm]
0		1930	0.1	145	2.8
8	Sludge	1718	1.2	135	15.8
	NiSO ₄	335	100.8	55	992.4
	Sludge	1023	10.4	90	123.2
16	NiSO ₄	398	141.9	49	1212.1
	Sludge	937	34.2	108	297.4

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