RELEASE OF HEAVY METALS FROM METAL-ENRICHED SEWAGE SLUDGE AND THEIR STRESS EFFECTS IN CROPPED SOIL MONOLITHS

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Abstract

Deposition of waste waters and sludges on agricultural fields is one of the most rational and economic ways to dispose of the liquid wastes. However, heavy metals are characteristic contaminants in these materials, limiting their applicability. To have a better understanding of the fate and effects of metal contamination, several aspects of a soil-plant experimental system were studied in laboratory experiments on large, undisturbed soil monoliths. Communal sewage sludge or aliquots enriched with Cd, Cr, Ni, Pb, and Zn nitrates were applied into the top 10 cm to give final metal loading rates in the soil equivalent to the limits specified in the Hungarian Technical Directive (Anon, 1990), or 10-, 30-, and 100-fold this amount. Maize and tomato were grown as test plants till maturity. The gas phases in the soil and in the plants' stem were sampled by capillary microsensors directly attached to the inlet system of a quadrupole mass spectrometer (QMS), measuring the amounts of N_2, O_2 and CO_2 during the whole experiment. Directly plant-available concentrations of the metals were assessed at the end of the experiment in soil solution samples obtained by centrifugation at a speed corresponding to the conventional wilting point of plants. Lead, and especially Cr entered the soil's liquid phase in negligible amounts. Release of Cd, Ni, and Zn into the soil solution as compared to their applied amounts was much higher than of Cr and Pb, and increased substantially at the higher metal application rates in the top 10 cm and somewhat also below the original application zone. The QMS technique was shown to be suitable to follow changes in the soil gas phase under the influence of physical (soil water content) and chemical factors (sludge). Increasing amounts of metals had no significant effect on the soil gas phase in the contaminated soil layer, but presented a stress situation for the plants. The onset and dynamics of plant stress were established on the basis of CO_2/O_2 ratios in the plants during their life-cycle.

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Introduction

Recent data show that approximately 22 million tons of municipal wastes per year are now being produced in Hungary (Molnár et al., 1995). These wastes are collected mostly non-selectively, and industrial infrastructure for recycling is limited. While about 52 % of the industrial wastes is reused or recycled, only 10 % of solid municipal waste is subjected to such procedures.

Waste waters and sludges may be applied to agricultural fields, thereby exploiting their water and nutrient content. Currently, this practice is becoming increasingly important in many countries, as one of the most rational and economic ways to dispose of the liquid wastes. Unfortunately, heavy metals are characteristic contaminants not only of industrial but also of communal waste waters and sludges, and may occur in these materials in appreciable quantities, limiting their applicability in agriculture (Chang et al., 1984; Lukács et al., 1984; Juste and Mench, 1992). It is well known that potentially toxic heavy metals are especially hazardous to the environment when they enter the liquid phase of the soil; they may then move through the vadose zone (Kabata-Pendias and Pendias, 1992), and they may also enter the food chain via plant roots, since water-soluble forms of an element are generally the most easily and immediately available for plant uptake (Petruzzelli, 1989). Thus, the potential risks for heavy metal contamination in agricultural fields depend on the relative amounts of metals being adsorbed versus amounts entering the liquid phase of the soil. The concentration of heavy metals in the soil solution is regarded as an indicator of the mobile pool of metals in soils (Kabata-Pendias and Adriano, 1995).

Simultaneous occurrence of excess, although subtoxic, amounts of several metals in the soil-plant system presents a stress situation and may cause unexpected toxic effects. Changes in the gas phase inside the plants were previously shown to respond characteristically to various stressors such as water and temperature stress, increased concentrations of mineral salts, pesticides, etc. (Hung. Pat., 1982; Pártay et al., 1987). Also, qualitative and quantitative changes in the composition of the soil gas phase, with special emphasis on the biologically important gases (O_2, CO_2), and water vapor, may reflect the extent of stress caused by heavy metal pollution (Pártay et al., 1992, 1994).

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The aims of the studies presented were

- to determine the release of 5 selected metals (Cd, Cr, Ni, Pb, and Zn) into the soil solution from metal-enriched sewage sludge at various contamination levels;

- to indicate and follow development of metal-stress situations in the soil and inside the plants, by *in situ* and *in vivo* mass spectrometric assessment of the relative amounts of O_2, CO_2, and N_2 in the gas phase,

- in undisturbed soil monoliths.

Material and Methods

A strongly leached typical brown forest soil (USDA '90 classification: Eutrochrept) from Gödöllö, representing a Hungarian soil type typical in agricultural production, was used in the experiment. Large undisturbed monoliths were excavated at the selected field site, covered by a special water-proof coating which imbibed the outer soil macropores (Németh et al., 1991), and transported to the laboratory. The main soil properties of the soil profile are shown in Table 1.

Table 1: Chemical and physical properties of the soil profile at the field site

depth (cm)	hori-zon	pH H_2O	pH KCl	CaC O_3 (%)	organic matter (%)	CEC (meq/100g soil)	SP	<0.02 mm (%)
0-8	A_p	5.90	5.02	*	1.0	9.0	25	19.5
8-16	A_1	6.26	5.29	*	1.2	8.5	28	18.9
16-43	B	5.85	5.01	*	1.1	8.5	28	20.5
43-66	BC	6.51	5.24	*	*	10.1	28	23.3
66-	C	7.15	5.75	0.1	*	58.0	74	54.4

note: * not determined

Four monoliths were used simultaneously in each experiment. Soil water contents were regulated by saturating the columns from the bottom through a special built-in valve connected to a hanging water-column; or by sprinkler irrigation at the soil surface. Temperature, soil water content and gas composition along the soil profile were followed by using various sensors inserted into the monoliths through holes drilled in the coatings. The soil gas phase was sampled by capillary microsensors directly attached to the inlet system of a quadrupole mass spectrometer (QMS). The QMS system enabled 20 simultaneous, independent measurements in the 1-300 atomic range without time limitations. In the present experiments the range 17-56 was used to determine N_2 (28), O_2 (32) and CO_2 (44) during the whole experiment. QMS

microsensors were inserted also into the stem of the experimental plants growing on the monoliths.

The metals were applied as communal sewage sludge enriched with Cd, Cr, Ni, Pb, and Zn nitrates. Dry matter content of the compressed sludge was 20.6 %, and the inorganic matter content 48.2 %. Original low-metal sludge was used as the control treatment. Concentrations of the selected metals in the dry matter of this sludge were 12.3 mg/kg Cd, 217 mg/kg Cr, 109 mg/kg Ni, 210 mg/kg Pb, and 3026 mg/kg Zn. These values are comparable to or somewhat less than the limits specified in the Hungarian Technical Directive (Anon, 1990). The permitted loading levels (1L-values) corresponded to 0.125 mg/kg Cd, 8.33 mg/kg Cr, 1.67 mg/kg Ni, 8.33 mg/kg Pb, and 25 mg/kg Zn in the soil, assuming average sludge application practice in Hungary (i.e., 500 t/ha sewage sludge containing 5 % dry matter incorporated into a 20 cm surface soil layer). Metal nitrates were added to the sludge so that the final metal loading rates in the soil were equivalent to 10L, 30L, and 100L, with the same amount of sludge materials. One week after sludge addition maize (*Zea mays* L.) was sown, or tomato (*Lycopersicon esculentum* Mill.) was planted on the monoliths and grown to full maturity.

At the end of the experiment soil samples were taken from the 0-10, 10-15, 15- 20 and 20-30 cm depth intervals. Total potentially available metal concentrations (after 2 mol/L HNO_3 extraction at 100 C° as described by Andersson, 1976) were measured in air-dried soil samples; directly plant-available concentrations of the metals were assessed in soil solution samples obtained by centrifugation of the initially moist soil samples. The centrifugation speed corresponded to -1500 kPa water potential (pF 4.2, the conventional wilting point of plants). Thus, considering energy conditions, the separated solutions represented the liquid phase utilized by the plants (Csillag et al., 1995). Metal concentrations in the various plant parts were determined after wet digestion by $HNO_3+H_2O_2$. Elemental concentrations of all solid and solution samples, from both plants and soil, were measured by inductively coupled plasma atomic emission spectrometry.

Results and Discussion

The measured *total metal concentrations* in the top 10 cm soil layer, i.e. in the initially contaminated zone containing the metal-spiked sludge, accurately reflected at each loading level the differences among the application rates of the five metals, being the highest for Zn and the lowest for Cd, and very similar for Cr and Pb which were applied in identical amounts. This phenomenon is visible in Figure 1. for the experiment with tomato, where the units for the total

concentrations of the metals (X-axis) had to be set differently so as to match their application rates. The 2 mol/L HNO_3-extractable concentrations of all the five metals increased proportionally to the initial loading rates of $1L$, $10L$, $30L$ and $100L$.

Metal concentrations in the soil solution were generally several orders of magnitude lower than the 2 mol/L HNO_3 extractable total concentrations (note the 1000-fold difference between the units for soil solution and total metal concentrations in Figure 1.). Lead, and especially Cr entered the liquid phase of the soils in negligible amounts, even at the highest metal loading. Release of Cd, Ni and Zn into the soil solution as compared to the applied amounts was much higher than of Cr and Pb, and increased substantially at the higher metal application rates in the top 10 cm. Generally a larger proportion of the soil's total Cd, Ni and Zn content occurs in the liquid phase than of the less mobile Cr and Pb (Kabata-Pendias and Pendias, 1992). In the top layer, the concentrations of Cd, Ni and Zn in the soil solution were several orders of magnitude higher at the $100L$ loading rate than in the control treatment (Figure 1.). The observed low Cd concentrations are consistent with the relatively low application rate of this metal as compared to those for the other elements.

In another experiment, where maize was used as test plant instead of tomato, the metal concentrations measured in the soil and in the soil solution followed similar tendencies, as described above; but the total potentially available metal concentrations were slightly higher and soil solution concentrations of the more mobile Cd, Ni, and Zn were substantially (by about one order of magnitude) higher than in the experiment with tomato as test plant (Table 2.). Also, these elements were found in appreciable quantities in the originally uncontaminated soil layers directly below the metal+sludge application zone, indicating some downward movement of the plant-available part of the metals. Differences between the metal uptake in the two plant species could not be responsible for this discrepancy, since the amounts taken up during the vegetation period were negligible as compared to the amounts present in the soil (Bujtás et al. 1995). A likely explanation is that during the alternate irrigation and drying periods more metals have been fixed in the soil when tomato was grown, than with corn. It was shown before that release of heavy metals from soil samples experimentally contaminated with heavy metal salt solutions, then dried for 1 month an rewetted to its previous water content, was about 30-50 % smaller than the release from soil samples not subjected to drying (Csillag et al., 1994). The repeated irrigation-drying sequence in the soil monolith experiments

was about 2 months longer when tomato was grown than for maize because of the different vegetation period of the two species.
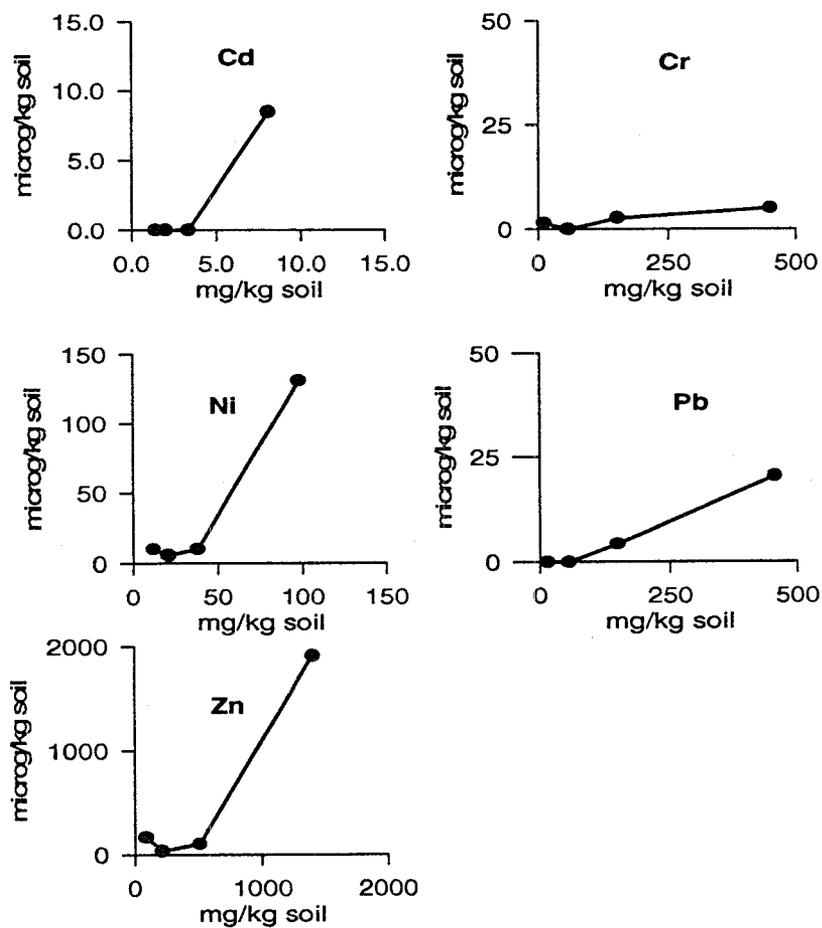

Figure 1: Correlations between total potentially available concentrations of the metals in the soil (X-axis) and their soil solution concentrations (Y-axis) in the experiment with tomato

Table 2: Soil solution concentrations of the metals [µg/kg soil] at the end of the vegetation period

	depth (cm)	experiment with maize loading		experiment with tomato loading	
		control	100L	control	100L
Cd	0-10	*	90.2	*	8.5
	10-15	*	11.6	*	*
	15-20	*	*	*	*
Cr	0-10	1.9	7.0	1.5	5.1
	10-15	0.6	2.3	1.7	3.8
	15-20	*	*	1.0	3.4
Ni	0-10	4.3	2600	10.1	131
	10-15	2.1	225	4.7	5.4
	15-20	5.6	13.7	4.4	2.6
Pb	0-10	*	7.8	*	20.5
	10-15	*	11.5	5.9	7.0
	15-20	*	*	4.9	2.7
Zn	0-10	50.8	28600	165	1910
	10-15	81.0	2920	87.5	140
	15-20	130	232	52.0	126

note: * concentrations below determination limit

The *gas composition of the soil* showed specific changes when the environmental conditions were altered. There was a distinct increase in CO_2 concentration when the soil columns were saturated with water at the start of the experiment in order to bring the 4 columns to a fairly uniform physical state (between the measurement points 16. and 31. of Figure 2.); this was followed by a decrease of CO_2 concentrations during the subsequent drying of the monoliths. The magnitude of the CO_2 concentration changes reflected the length of the saturation period (e.g. in the soil of the experiment with tomato, Figure 2., here the monolith of the 30L treatment was saturated for a shorter time because of technical reasons). Mixing of the sewage sludge into the top 10 cm soil layer (see values at the measurement point 106. in Figure 2.), and planting of tomato seedlings about one week afterwards (see values at the measurement point 121. in Figure 2.) are also reflected by a temporary increase in CO_2 concentrations, which was longer when the sludge was enriched with metals than when original, control sludge was applied. However, CO_2 levels in the soil did not fully return to their original values, when plants were present during the later stages of the experiment.

The *gas composition inside the plants* was markedly different from that of the soil. In the control treatment CO_2 concentrations slowly and monotonously decreased during the maturing

of the plants, the CO_2/O_2 ratios remained mostly below 1 in both plant species. The higher intensity of the peaks of the various gases in maize as compared to the tomato plants may reflect inherent differences between the two species (Figure 3.). In earlier experiments the ratio of CO_2/O_2 measured in the stem and regarded as analogous to the respiration quotient, RQ, was found to reflect well various physical and chemical stress situations for the plants. Under unfavourable conditions the ratio exceeded a value of 1 and was higher when the stress was stronger. In normal physiological status of the plants the CO_2/O_2 ratio in the stem is slightly below 1 (Pártay et al., 1987). In the present experiment maize and tomato responded differently, when substantial amounts of metals were present in the root environment. In maize the CO_2 concentrations remained above O_2 levels during the whole vegetation period (CO_2/O_2 ratios were above 1), with substantial oscillation phenomena. This type of response curve may be interpreted as a result of the repeated struggling of the plants against metal stress. In contrast, CO_2 concentrations in tomato showed recovery at about 10 days after the initial stress. After this point, CO_2/O_2 ratios remained below 1 for the whole experiment, indicating a normal physiological status of the plants.
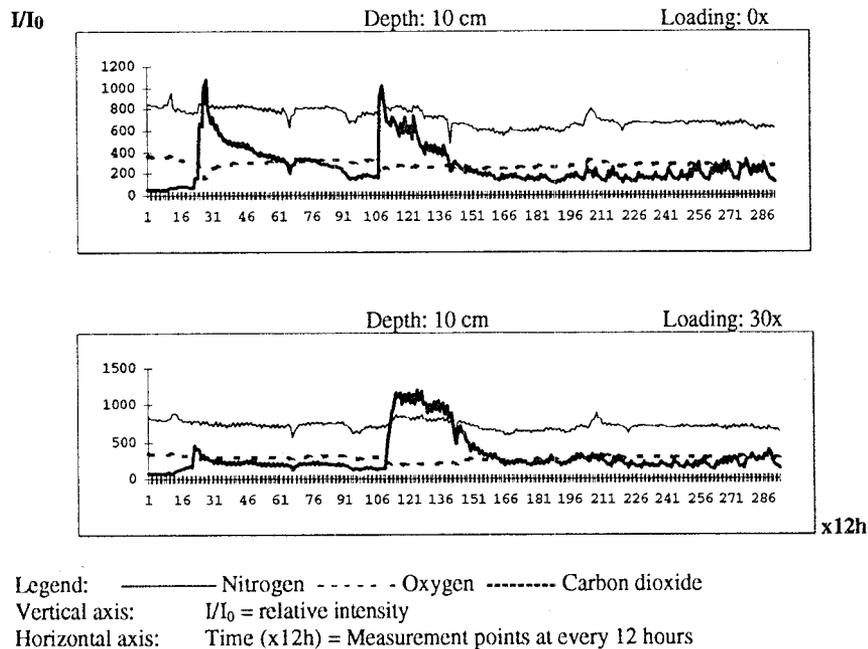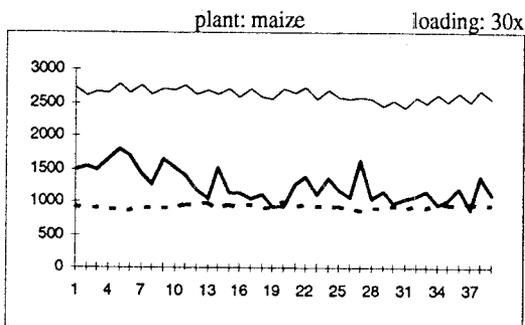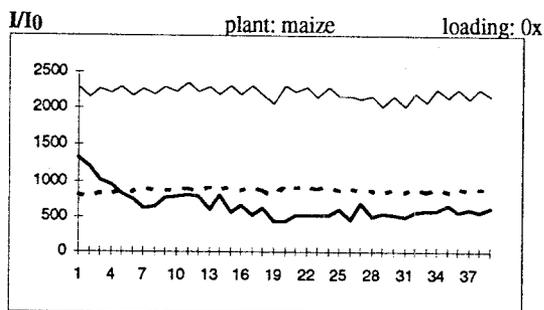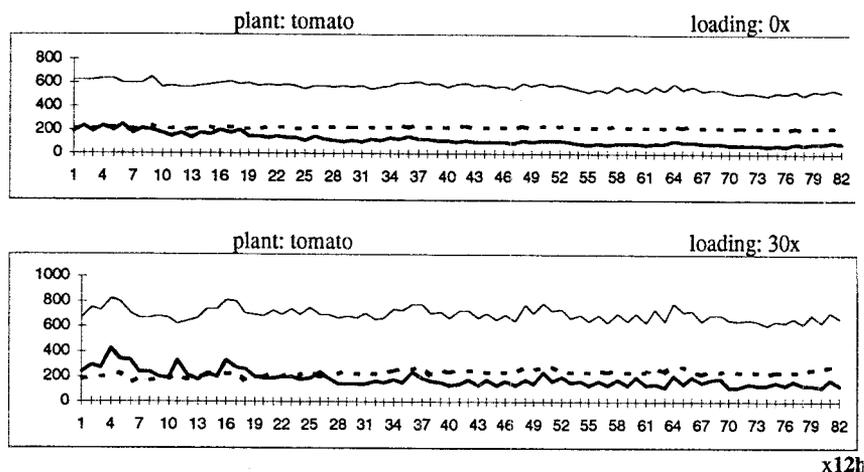

Legend: ——————— Nitrogen - - - - - - Oxygen --------- Carbon dioxide
Vertical axis: I/I_0 = relative intensity
Horizontal axis: Time (x12h) = Measurement points at every 12 hours

Figure 2: Relative gas concentrations in the soil of the experiment with tomato

Conclusions

Differences in the release of metals into the soil solution were in agreement with literature data. Even the more mobile metals added to the sludge entered the soil's liquid phase in appreciable amounts only after extreme overloadings. Soil solution concentrations were of several magnitudes smaller than total potentially available concentrations. However, since the solubility of the heavy metals in soils has great significance in their bioavailability and their migration (Kabata-Pendias and Pendias, 1992), relatively small increases in solution metal concentrations may have an impact on the environment.

This was indicated also by the results of the QMS measurements, which were shown to be a suitable methodology to follow changes in the soil gas phase under the influence of physical (soil water content) and chemical (presence of sewage sludge) factors.

Legend ————— Nitrogen - - - - - - Oxygen -------- Carbon dioxide
Vertical axis: I/I_0 = relative intensity
Horizontal axis: Time (x12h) = Measurement points at every 12 hours

Figure 3: Relative gas concentrations in the plants

Although increasing amounts of metals in the sludge (and the consequently increasing available amounts of the metals in the soil solution) did not seem to have any significant effect on the gas phase in the contaminated soil layer, changes in the gas phase inside the plants indicated stress situation at elevated metal levels. The onset and dynamics of plant stress may be established on the basis of changes in CO_2/O_2 ratios in the plants during their life-cycle.

Although the results of this laboratory experiment may not be directly applicable to field situations, comparison of the total and plant-available metal concentrations in the soil with the actual metal uptake by the test plants (Bujtás et al., 1995) and with the plants' stress response may give a complex model about the interdependence of the bioavailability and effects of excess metals in the soil-plant system.

Acknowledgement

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