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BALANCE OF TRACE METALS (CD, CR, CU, NI, PB, ZN) IN A LYSIMETRIC EXPERIMENT

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ZUSAMMENFASSUNG

In einem dreijährigen Lysimeterversuch wurde die Bilanz für Cd, Cr, Ni, Pb und Zn eines Klärschlamm behandelten Bodens untersucht. Der Klärschlamm war 1985 beigemischt worden und hatte die Konzentration von Zn, Cr, und Cu sehr stark und die Gehalte an Cd, Ni und Pb schwach erhöht. Nach der Zugabe konnte für Weidelgras und Weißklee eine stark erhöhte Aufnahme von Zn und Ni festgestellt werden, sowie eine pozentuale Zunahme aller Metalle im Perkolationswasser. Die Bilanz für Zn, Pb, Cu, Ni und Cr war positiv für einen Kontrollboden, für Cd war sie schwach negativ. Dabei wurde nur die "wet deposition" als input berücksichtigt. Wenn man die "nassen" und "trockeneren" Niederschläge berücksichtigen würde, wäre die Bilanz wahrscheinlich für alle Metalle positiv. Für die Klärschlamm behandelten Böden war die Input/Output-Bilanz deutlich positiv, vor allem für Zn, Cr und Pb.

keywords: *trace metals, lysimetric experiment, soil, atmospheric fall down*

ABSTRACT

A three-year lysimetric experiment was used to study the balance of Cd, Cr, Ni, Pb, and Zn in a sludge-amended soil. Sewage sludge with high concentrations of Cr and Zn was applied to the soil in 1985. The sludge application increased many times the concentrations of Zn, Cr and Cu and to a smaller degree the Cd, Ni, and Pb content of the soil. Following the sludge addition, an increase was observed in the uptake of Zn and Ni by plants (ryegrass and white clover) and in the percentage of all metals leached out from the soil profile.
The balance for Zn and Pb was positive and for Cu, Ni, Cr and Cd was slightly negative for the control soil. It should be noted, however, that for this treatment only the atmospheric fall down (wet deposition) was considered as "input". Taking into consideration both the wet and the dry deposition the balance would probably be positive for all metals studied. The input of the metals with the sludge was so heavy that it exceeded the output by many times at the sludge-amended soil, which resulted in highly positive balance, especially for Zn, Cr, and Pb.

INTRODUCTION

Trace metals enter the soil surface by a number of pathways including direct aerial deposition and waste material utilization (ADRIANO 1986; KABATA-PENDIAS et al. 1984, 1985). Some percentage of the metals is depleted from the soil with crops and leached out to the ground water (DUDKA et al. 1990; LUND et al. 1976; RUSZKOWSKA et al. 1984, 1988; SCHIRADO et al. 1986). The input-output balance of trace metals in soils show that their concentrations in surface soils are likely to increase on a global scale due to technogenic fluxes of metals (KABATA-PENDIAS et al. 1984, 1985; RUSZKOWSKA et al. 1984; TURSKI 1987). The ecological significance of the accumulation of trace metals in soils is greatly enhanced by their concentration mainly in the surface soil layer, by simultaneous increases of several metals, and by their low rate of depletion (KABATA-PENDIAS et al. 1984).
The objective of this research was to estimate the balance of Cd, Cr, Cu, Ni, Pb and Zn in the soils of an unindustrialized area.

MATERIALS AND METHODS

The experiment was set up in lysimeters (size: 0.5 x 0.5 x 0.9 m^3) filled with a pseudopodzolic (loamy sand) soil according to natural genetic horizons to depth of 80 cm. In the spring of 1985, one year after the soil had been deposited to the lysimeters, an air-dried and homogenized sewage sludge of high Cr and Zn contents was applied to the soil at the rate of 5,25 kg/lysimeter (210 Mg/ha). The untreated soil was used as a control (See Tables 1 and 2 for properties and metal contents of the sludge and soils). The sludge was mixed carefully with 20 cm soil layer. Following the sludge addition ryegrass (*Lolium perenne* L.) and white clover (*Trifolium patense* L.) were planted at both sludge-amended and control soil sites. Treatments were replicated four times in a randomized design. During the experiment plants were harvested (ryegrass at the shooting stage and clover at the onset of blooming) 4-5 times and lysimetric percolate waters were collected about 6-8 times a year. The white clover grew only during the first year and then disappeared therefore the plant data for 1986 and 1987 contain only results for ryegrass. After the last crop of the plants had been harvested for each year, soil samples for chemical analysis were taken.

Tab. 1: Some characteristics of the sewage sludge and soils

Treatment	pH		OM	Particles <0.02 mm	CEC	Ca	K	Mg
	H_2O	KCL	%	%	meq/100 g	%	%	%
sewage sludge	6.8	6.7	34.80*	-	-	2.75	0.54	0.25
control soil	6.9	6.1	1.25	20	7.11	0.37	1.08	0.13
soil with sludge	6.9	6.6	2.37	20	10.26	0.50	1.03	0.15

* loss on ignition

Tab. 2: Total concentrations of trace metals (mg/kg) in the sewage sludge and soils; mean values of four replicates*

Treatment	Cd	Cr	Cu	Ni	Pb	Zn
sewage sludge	7.00	1970.0	246.3	92.0	228.0	6100
control soil	1.15	18.1	6.4	12.5	21.5	69
soil with sludge	1.47	137.7	22.6	19.0	38.9	439

* relative standard deviations below 15 %; soil samples taken in the second year of experiment

The sampled plants were washed in deionized water, dried at 70 °C, weighed, and ground in a stainless steel mill. A 5-g subsample was dry ashed at 450 °C for 16 h, dissolved in 10 ml HCl (1:1) and diluted to 50 ml with double-distilled water. The 2-g air-dried and homogenized at agate mortar soil subsamples were digested with $HClO_4$ and HF mixture. Following the evaporation on a hot plate to dryness the samples were dissolved in HCl (1:1) and diluted to 100 ml with 1 % HCL. The water samples were evaporated on a water bath, the residuum was dissolved in HCl (1:1) and subsequently diluted to 50 ml with double distilled water. Zinc was determined in water solution whereas Cd, Cr, Cu, Ni, and Pb were analyzed after a concentration into organic phase (MIBK). Data quality was controlled by insertion of the blank digests, duplicate samples, and internal plant and soil standards into each batch of samples. The physic-chemical and chemical properties of the sewage sludges and the soil were determined by methods conventionally used in soil chemistry. These analyses were performed in the Soil Chemistry Laboratory of IUNG. Cadmium, Cr, Cu, Ni, Pb and Zn in the plant, water, and soil samples were analyzed by flame atomic spectroscopy.
This paper presents results for the period of 1985-1987.

RESULTS AND DISCUSSION

The concentrations of trace metals in the soil (Table 2) were close to the average ranges of the metal content of agricultural soils of Poland (KABATA-PENDIAS et al. 1984). The sludge application increased many times the concentrations of Cr, Cu and Zn in the soil as a result of the much higher concentration of those metals in the sludge than in the soil (Table 2). The amounts of Ni and Pb in the soil increased only slightly in comparison with the control (Table 2). Concentrations of Cr and Zn exceeded values considered as the excessive levels in light soils (KABATA-PENDIAS et al. 1984). Because of the increase in the metal content of the soil the concentration of Zn and Ni increased in ryegrass and white clover remarkably (Table 3).

Tab. 3: Trace metal content (mg/kg) of the ryegrass (R) and white clover (C); mean values for three and one years* for the ryegrass and clover, respectively

Treatment		Cd	Cr	Cu	Ni	Pb	Zn
control	R	0.23	1.0	6.5	2.1	2.4	38
soil	C	0.35	0.9	8.3	2.3	4.0	30
soil with	R	0.33	1.0	10.7	6.2	2.3	289
sludge	C	0.41	1.9	10.1	4.2	4.5	234

* relative standard deviations below 20 %; 4-5 cuts a year

In contrast only slight changes in the Cd, Cr, Cu and Pb concentrations were found in the plants. The differences in the uptake of particular metals by the plants resulted apparently from the different pattern of the metal speciation in the sludge-treated soil (DUDKA et al. 1990; PIOTROWSKA et al. 1985). The concentrations of exchangeable, therefore easily available, Zn and Ni were much higher in the sludge treated than those in the untreated soil, whereas the soil levels of exchangeable forms of the other metals changed little after the sludge had been applied to the soil (DUDKA et al. 1990; PIOTROWSKA et al. 1985). Concentrations of the metals in the lysimetric percolate water and hence their leaching out from the soil profile (being function of the metal concentrations and amount of percolate waters) increased several times at the sludge treated soil sites compared to the control treatment (Table 4).

Tab. 4: Concentrations of trace metals (µg/kg) in rainfall[a] and lysimeter percolate[b] waters; mean values and ranges of three years (1985-1987)

Treatment	Cd	Cr	Cu	Ni	Pb	Zn
rainfall water	0.48 0.2-1.1	1.2 0.6-2.5	1.9 0.8-4.3	2.1 0.7-5.0	4.9 1.5-11.5	159 40-330
control soil	0.69 0.3-1.1	1.4 0.9-1.8	2.8 2.4-3.1	5.0 3.2-8.7	4.8 1.6-6.9	515 177-792
soil with sludge	2.23 1.3-2.9	3.4 2.2-4.4	5.6 3.3-6.3	11.0 6.6-13.6	12.9 7.6-20.8	1052 407-1188

a 12 determinations per year
b 4-6 determinations per year

The balance of the metals is the arithmetic difference between their amounts introduced to the soil with sewage sludge and/or rainfalls (input) and the quantity removed from the soil profile by crops and by the lysimeter percolate water (output). The balance is expressed in mg/lysimeter and can be converted to g/ha by multiplying the original values by a factor of 40 (Table 5 and 6).

Tab. 5: Balance of trace metals (mg/lysimeter*) for the control soil; years 1985-1987

Balance elements	Cd	Cr	Cu	Ni	Pb	Zn
content of soil	88	1384	491	958	1645	5292
			INPUT			
atmospheric falldown	0.2	0.5	0.8	0.9	1.7	71
			OUTPUT			
uptake by plants	0.1	0.6	3.9	1.3	1.2	21
leaching	0.1	0.1	0.4	0.6	0.4	40
total output	0.2	0.7	4.3	1.9	1.6	61
			BALANCE DIFFERENCE			
balance difference	0.0	-0.1	-3.5	-1.0	0.1	10

* 1 mg/lysimeter = 40 g/ha

Tab. 6: Balance of trace metals (mg/lysimeter*) for the sludge treated soil; years 1985-1987

Balance elements	Cd	Cr	Cu	Ni	Pb	Zn
content of soil	125	11726	1784	1441	2842	37317
			INPUT			
atmospheric falldown	0.2	0.5	0.8	0.9	1.8	571
input with sludge	36.8	10342	1293	483	1197	32025
total input	37.0	10343	1294	484	1199	32096
			OUTPUT			
uptake by plants	0.4	1.2	12.2	6.9	2.8	322
leaching	0.2	0.3	0.6	0.8	1.0	55
total output	0.6	1.5	12.9	7.7	3.8	377
			BALANCE DIFFERENCE			
balance difference	36.4	10342	1281	476	1195	31719

* 1 mg/lysimeter = 40 g/ha

A positive balance of Pb and Zn and slightly negative of Cd, Cr and Ni and negative of Cu was found during the period of 1985-1987 in the untreated soil (Table 5). One should point out, however, that at the control soil site only the amounts of the metals falling down as dissolved in rainfall water (wet deposition) were included in the input data. If the total deposition, both dry (contained on particulate matter) and wet, was taken into consideration the balance would probably be positive for all the metals investigated. That hypotheses is strongly supported by results of KABATA-PENDIAS et al. (1985) and other authors (RUSZOWSKA et al. 1984, 1988; TURSKI et al. 1987) that found positive balance also for cadmium and copper in soils of rural and urban areas.

The input of the metals with the sewage sludge was so heavy that it exceeded the output many times at the sludge-amended soil sites, which resulted in highly positive balance of the metals, expecially Zn, Cr, Cu, and Pb (Table 6). Based on the knowledge of low depletion rate of the trace metals from soils it is reasonable to suppose that the metals added to the soil will be continuous source of elements for plant uptake.

The amounts of trace metals falling down from the atmosphere are the significant figures in their cycling in the environment. The results of this paper and other estimations (KABATA-PENDIAS et al. 1985) have shown that a gradual increase of metal concentration can be expected in the surface layer of the soils.

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