The content of Pb, Zn and Cd in hydroameliorated soil and drainage water and their uptake by plants

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ABSTRACT

The goal of the investigations was to assess the average contents of heavy metals (Pb, Zn and Cd) in the surface soil layer (0–30 cm), in drainage water and their uptake by growing plants, in the experimental amelioration field for four different variants of drainpipe spacing (15, 20, 25 and 30 m) during the three-year period. Maize and winter wheat were grown in all variants throughout the trial period. In all variants of drainpipe spacing, heavy metals in soil, drainage water and plant material were within the limits. The highest average level of Pb was 13.5 mg.kg^{-1}, Zn 88 mg.kg^{-1} and Cd 0.7 mg.kg^{-1} in soil. Drainage water concentration of heavy metals was below 50 μg.dm^{-3} for Pb, below 2 μg.dm^{-3} for Cd, while the highest average value of Zn amounted to 20 μg.dm^{-3}. In grain of the crops grown, the concentration of Pb was below 0.4 mg.kg^{-1} and that of Cd below 0.1 mg.kg^{-1}.

Keywords: heavy metals (Pb, Zn, Cd); drainage water; plants; hydroameliorated Gleyic Podzoluvisol

Metals such as lead (Pb), zinc (Zn) and cadmium (Cd) belong to the class of toxic metals. They are present in soil in the form of minerals. Content of trace elements in soil depends on its mineral composition and texture (Pospišilová and Laštincová 1998) and on the parent substrate from which the soil was formed (Mengel and Kirkby 1979). Heavy metals in soils constitute an important source for their uptake by plants and subsequent input into the food chain (Borůvka et al. 1996, 1997). In various soil plant systems they may represent a potential risk to the environment (Mikanová et al. 2001). Besides being constituents of the mineral part of soils, another substantial source of heavy metals is the environment contaminated by industrial and agricultural pollutants. According to Barbier (1979), most lead in the air results from the running automobile engines. Zinc is leached in high concentrations in the vicinity of its ore sites (Walker 1971), while cadmium is predominantly introduced into soil with mineral fertilizers, that is, cadmium containing phosphate raw materials (Förstner 1980, O'Neil 1985). Beneš and Benešová (1993) report that atmospheric precipitation accounts for 82% of total lead input, and 60% of total cadmium input. According to Královec and Slavík (1997), metals supplied by atmospheric precipitation are generally regarded as the main source of heterogeneous substances, much more significant than inorganic or organic fertilizers applied.

Unlike many organic pollutants, metal ions cannot be transformed into inert forms, so their environmental presence is permanent. Their concentration in water is reduced through dilution and precipitation in sediments, while in soil they can form complexes with organic and inorganic substances (Garison 1981).

As heavy metals Pb, Zn and Cd are dangerous to the environment, research involving their quantitative assessment in different human environments is of the utmost importance. The danger ensuing from these metals derives from their tendency to accumulate in the vital organs of humans, animals and plants. For this reason, one of the methods of environmental protection involves efficient determination of toxic metals by reliable and sensitive analytical procedures. As most soils in Croatia, notably the hydroameliorated areas – 161 530 ha, are clean, great attention should be paid to the protection of these soils (sites).

Investigations carried out in the 1996–1998 period had the following goals:

To determine soil contents of heavy metals (Pb, Zn and Cd) in drained Gleyic Podzoluvisol (0–30 cm), concentration of heavy metals in drainage water and concentration and total output of heavy metals with plants in four different variants of drainpipe spacing.

MATERIAL AND METHODS

The trial was set up on the Jelenščak field (Central Sava Valley) on ameliorated Gleyic Podzoluvisol and for its purposes drainpipe spacing variants of 15 m (area = 1425 m^2), 20 m (1900 m^2), 25 m (2375 m^2) and 30 m (2850 m^2) were studied (four variants each with four replications). All variants were combined with contact hydraulic material – gravel. Drainpipes have the following characteristics: length 95 m, diameter 65 mm, average slope 3‰ and average depth 1 m, and they discharge directly into canals. Drainage discharge was measured continually by means of automatic electronic gauges – limnimeters, which were set up in each variant, at the drainpipe outlet into the open canal.

The same crop was grown under unified agricultural management practices in all pipe drainage variants and in each trial year (Table 1).

Table 1. Agricultural management and application dates for crops grown during the trial period

Year	Crop	Sowing date	Fertilizer formulae	Fertilizer supplied amount (kg.ha^{-1})	total amount (kg.ha^{-1}) N	P	K	Harvest date
1996	maize	May 22	NPK 7-20-30	400	28	34.9	99.2	November 28
			UREA (46%)	190	87			
			KAN (27%)	110	30			
					145			
1997	maize	May 6	NPK 7-20-30	450	31.5	39.3	111.6	October 27
			UREA (46%)	195	89.5			
			KAN (27%)	200	54			
					175			
1998	winter wheat	October 29	NPK10-30-20	400	40	52.4	66.1	July 21
			UREA (46%)	150	69			
			KAN (27%)	200	54			
			KAN (27%)	150	40.5			
					203.5			

Table 2. Major characteristics of ameliorated Gleyic Podzoluvisol

Depth (cm)	Content of particles (%)		Porosity (%)	Capacity (%)		Permeability (m.day^{-1})	Bulk density (g.cm^{-3})	pH		Humus (%)	mg.kg^{-1} soil	
	silt	clay		water	air			H_2O	1M KCl		P	K
0–35	47	46	48	44	4	0.011	1.35	6.7	5.3	3.0	25.8	62.8
35–75	45	48	49	45	4	0.010		6.5	5.2			
75–115	55	39	46	42	4	0.011		7.9	7.1			
115–130	63	25	49	45	4			8.1	7.2			

Samples of drainage water were taken in spring, autumn and winter and soil samples in spring, summer, autumn and winter, following the seasonal dynamics.

The total content of metals in soil samples was determined by the procedure of digestion in aqua regia using the microwave technique with an MLS-1200 Mega instrument.

Concentrations of metals in solutions were measured with flame AAS (spectrometry of atom absorption) in acetylene-air mixture using an AAS Perkin Elmer 3110 instrument. Flame sensitivity: Pb – 500 μg.dm^{-3}, Zn – 20 μg.dm^{-3} and Cd – 25 μg.dm^{-3}.

Samples of plant material (grain and straw) were taken at the end of the growing season. Samples were dried (at 105°C), ground, and then burned (1 g) by the wet procedure in a $HNO_3/HF/HClO_4$ mixture. Pb, Zn and Cd were then determined by the AS method by blowing the prepared sample into the flame of the acetylene-air mixture.

Statistical analysis of variance MSTAT-C (1990) was applied.

Soil properties

Major characteristics of ameliorated Gleyic Podzoluvisol are presented in Table 2.

The soil is of silty clayey texture to the depth of 0.75 m, and of lighter texture at depths of 0.75–1.15 m. Soil texture at depths below 1.15 m is silty loam. The soil is porous, with the total pore volume of 48–49%. Soil water capacity is 42–45%. Air capacity is low – 4%. Vertical

Table 3. Total quantity and distribution of monthly precipitation (mm)

Year	January	February	March	April	May	June	July	August	September	October	November	December	Total
1996	54	32	41	70	71	31	91	83	191	46	135	79	924
1997	44	55	26	45	73	81	103	63	30	76	127	86	809
1998	65	5	58	59	103	107	121	87	174	120	51	49	999

Measurements were made at the Meteorological Station Kutina, which is 15 km from the trial field

Table 4. Total yearly quantities of drainage discharge (mm)

Variants	1996	1997	1998
15 m	220	160	272
20 m	222	159	269
25 m	224	164	283
30 m	225	164	284

Table 5. Quantity of heavy metals supplied into soil by atmospheric precipitation ($g.ha^{-1}.year^{-1}$)

Year	Pb	Zn	Cd
1996	59.44	385.56	13.91
1997	47.67	206.60	11.58
1998	110.10	120.00	11.31

Measurements were made near Sisak, which is 15 km from the trial field

hydraulic conductivity is very low (0.011 m/day). Bulk density is 1.35 $g.cm^{-3}$ (0–35 cm).

Availability of macro biogenic elements P and K is very poor whereas the humus content and soil reaction are moderate.

Climate characteristics

Weather characteristics are presented in terms of the quantity and distribution of monthly precipitation (mm) in Table 3.

During the three-year trial period, the total annual precipitation ranged between 807.3 mm (1997) and 999.2 mm (1998). Unevenly distributed annual precipitation was accompanied by uneven monthly precipitation. Air temperatures ranged from 10.3°C (1996) to 11.1°C (1998).

Hydrological relations

It can be seen from Table 4 that there are certain differences in the quantity of drainage discharge, both between the tested variants in each year and between the trial years. In our opinion, there are several reasons for these differences in drainage discharge, primarily the different total annual quantity and distribution of precipitation, the crop grown and its different water requirements (evapotranspiration), as well as different efficiency of each particular pipe drainage system.

Air quality

Contents of heavy metals in sediments and their quantity supplied into soil by atmospheric precipitation are presented in Table 5. It can be seen that there are differences in the levels of heavy metals within each year.

Fertilizer quality

Table 6 presents the concentration of metals in mineral fertilizers applied in the trial field.

Based on the mineral fertilizer formulation, namely its Pb, Zn and Cd concentrations, and the total fertilizer supplied in a particular year (Table 1), the total input of Pb, Zn and Cd into soil was estimated for each year.

RESULTS AND DISCUSSION

Heavy metals in hydroameliorated soil

The obtained average results did not indicate contamination of hydroameliorated soil by heavy metals (Table 7) and results are relatively lower also in comparison with other studies (Královec and Slavík 1997, Romić and Romić 1998), which are attributed to the short time that this soil has been used for agricultural production and relatively small total incoming components.

Average three-year research results for each metal reveal differences between particular years as well as between the tested variants within each year. Namely, it is evident that there was an imbalance between the total incoming components (Tables 5 and 6) and the total outgoing components (Tables 4 and 11), and it had influenced probably the content of elements in individual years. Differences between the tested variants within each year are attributed to the time of sampling. According to Vidaček et al. (1994), the functionality of drainage systems (discharge, its intensity or the period without

Table 6. Concentrations of heavy metals in applied mineral fertilizers ($mg.kg^{-1}$) and their total quantity introduced into soil ($g.ha^{-1}$)

Year	Fertilizer formulae	Fertilizer supplied amount ($kg.ha^{-1}$)	Concentration of metals ($mg.kg^{-1}$)			Total quantity introduced into soil ($g.ha^{-1}$)		
			Pb	Zn	Cd	Pb	Zn	Cd
1996	NPK 7-20-30	400	2.1	0	25.0	0.8	0	10.0
1997	NPK 7-20-30	450	2.1	0	25.0	0.9	0	11.3
1998	NPK 10-30-20	400	2.6	0	20.3	1.0	0	8.1

Table 7. Average yearly concentration of heavy metals in soil (mg.kg^{-1}) per variants

Variants	Pb			Zn			Cd		
	1996	1997	1998	1996	1997	1998	1996	1997	1998
15 m	12.5	9.0	12.0	77	70	82	0.6	0.6	0.7
20 m	13.5	9.5	11.0*	88	88	84	0.7	0.6	0.7
25 m	13.0	10.0	10.0**	82	84	86	0.7	0.6	0.7
30 m	12.0	8.5	13.0	78	88	87	0.6	0.7	0.7

P 5%(1.8), ** *P* 1% (2.5) *F*-test not significant *F*-test not significant

Table 8. Average yearly concentration of heavy metals in drainage water (µg.dm^{-3}) per variants

Variants	Pb			Zn			Cd		
	1996	1997	1998	1996	1997	1998	1996	1997	1998
15 m	< 50	< 50	< 50	18	15	8	< 2	< 2	< 2
20 m	< 50	< 50	< 50	18	10**	9	< 2	< 2	< 2
25 m	< 50	< 50	< 50	19	12*	9	< 2	< 2	< 2
30 m	< 50	< 50	< 50	20	14	9	< 2	< 2	< 2

**P* 5% (2.26), ***P* 1% (3.25)

Detection limit for Pb = 50 µg.dm^{-3}, for Cd = 2 µg.dm^{-3}

discharge) at the time of sampling may influence the differences in results, both in particular years and within each test variant.

Heavy metals in drainage water

Results of average concentrations of heavy metals in drainage water recorded in the three-year trial period are presented in Table 8. Concentrations of heavy metals in drainage water did not indicate pollution (Table 10), which is in agreement with the results obtained by Moore (1981) and Moore and Sutherland (1981), Đumija et al. (1989) and Čoga et al. (1998). Different average Zn concentrations were recorded in the three-year trial period (the same may be assumed for Pb and Cd, due to detection limit flame AAS) per years and per drainage system variants. The differences between particular years probably had influenced the total incoming and the total outgoing components (like soil) and the differences between the tested variants within each year the time of taking water samples, i.e. the functionality of drainage systems at that moment. The concentration of drainage water depends on the time of sampling (Vidaček et al. 1994).

Heavy metals in dry grain and harvest residues (maize stalks and straw)

Table shows the differences in heavy metal concentrations in crops grown, years and different variants of drainpipe spacing. Highest Pb concentrations (in all

Table 9. Concentration of heavy metals in dry grain and in harvest residues (mg.kg^{-1} dry matter)

Variants	Maize (1996)			Maize (1997)			Winter wheat (1998)		
	Pb	Zn	Cd	Pb	Zn	Cd	Pb	Zn	Cd
In dry grain (mg.kg^{-1} dry matter)									
15 m	0.21	25.25	0.073	0.24	10.15	0.094	0.38	12.15	0.098
20 m	0.27	25.52	0.064	0.26	10.41	0.083	0.35	12.75	0.085
25 m	0.26	26.14	0.075	0.22	11.05	0.084	0.36	11.14	0.085
30 m	0.29	26.93	0.068	0.29	11.13	0.087	0.36	13.28	0.090
In harvest residues-maize stalks or straw (mg.kg^{-1} dry matter)									
15 m	2.14	12.23	0.109	2.10	5.19	0.110	4.15	5.23	0.412
20 m	2.65	11.82	0.099	2.12	5.74	0.125	4.19	5.78	0.455
25 m	2.32	12.46	0.088	1.74	5.25	0.130	4.86	5.11	0.471
30 m	2.89	12.98	0.095	2.25	5.79	0.124	4.64	5.15	0.513

Table 10. Yield of dry grain and weight of harvest residues (maize stalks or straw), kg.ha^{-1}

Variants	Maize (1996)		Maize (1997)		Winter wheat (1998)	
	dry grain yield	weight of residues	dry grain yield	weight of residues	dry grain yield	weight of straw
15 m	5820	6460	8453	10059	3843	3459
20 m	5343	5877	8018	9541	3888	3538
25 m	4915	5407	7803	9676	3283	3152
30 m	4348	5087	7268	9303	3088	3242

Table 11. Total quantity of heavy metals (g.ha^{-1}) taken out with yield and harvest residues

Variants	Maize (1996)			Maize (1997)			Winter wheat (1998)		
	Pb	Zn	Cd	Pb	Zn	Cd	Pb	Zn	Cd
15 m	15.0	218.1	1.1	23.2	138.0	1.9	15.8	64.8	1.8
20 m	16.0	205.8	0.9	22.3	138.2	1.9	16.2	70.0	1.9
25 m	13.8	195.9	0.9	18.6	137.0	1.9	16.5	52.7	1.8
30 m	16.0	183.1	0.8	23.0	134.8	1.8	16.2	57.7	1.9

drainpipe spacing variants) were recorded in 1998 (in wheat grain), the year with the highest input of Pb into soil by precipitation and fertilizers (Tables 5 and 6). Highest Zn concentrations were found in 1996 (in maize grain) at the time of the highest Zn deposition by precipitation (Table 5), while the highest concentration of Cd was recorded in 1998 (in wheat grain), the year with the overall lowest input of Cd into soil by precipitation and fertilizers. As can be seen, the highest concentrations of Pb and Zn in crop grain were recorded in the years of their highest availability to plants, though Němeček and Podlešáková (2001) maintain that the uptake of trace elements by crops correlates not so much with the total content but with the content of mobile or potentially mobilizable species. Contrary to Pb and Zn, in which their highest concentrations in crop grain coincided with their highest input into soil, the opposite was found for Cd, i.e. the highest concentrations in grain (wheat) were recorded at the lowest input of Cd into soil. According to Mortvedt (1987), differences in the uptake and transport of Cd into aboveground plant parts are considerable, depending on the species.

Pb and Cd concentrations were in all years and in all variants about 10 times lower in grain than in harvest residues, while the Zn concentration was about twice lower in maize grain than in maize stalks (1996 and 1997), and about 2.5 times lower in wheat grain than in straw (Table 11). According to Mortvedt (1987), this may be due to the smaller transport of heavy metals, and thereby also lower risks of their getting into the food chain and also due to necessity of Zn for improvement of enzyme activity.

The quantity of heavy metals taken out of soil (Table 11) was calculated on the basis of their concentration in grain and harvest residues (Table 9) and the yield of dry matter of grain and harvest residues (Table 10). As can be seen from Table 11, the highest output of the studied metals occurred in the year with its highest availability to plants, either through fertilization or air deposition. Similar results were obtained by Iserman (1983) and Christensen et al. (1998).

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REFERENCES

American Public Health Association (1992): Standard methods for the examination of water and wastewater. 18th ed.

Barbier M. (1979): Introduction to chemical ecology. Inst. Chim. Subst. Nattur. CNRS, Gif-sur-Yvette, France, Longman, London, New York.

Beneš S., Benešová J. (1993): Bilance rizikových prvků ve sférách životního prostředí. Rostl. Výr., *39*: 941–958.

Borůvka L., Huan-Wei Ch., Kozák J., Krištoufková S. (1996): Heavy contamination of soil with cadmium, lead and zinc in the alluvium of the Litavka River. Rostl. Výr., *42*: 543–550.

Borůvka L., Krištoufková S., Kozák J., Huan-Wei Ch. (1997): Speciation of cadmium, lead and zinc in heavily polluted soils. Rostl. Výr., *43*: 187–192.

Christensen T.H., Lorenz S.E., Hamon R.E., Dominigues H.C., Sequeira E.M., Megrath S.P. (1998): Measured soil water concentrations of cadmium and zinc in plant pots and estimated leaching outflows from contaminated soils. Wat., Air Soil Pollut., *102*: 105–115.

Čoga L., Vidaček Ž., Poljak M., Kovačević V. (1998): Cadmium and lead in the system drained soil-plant-water in the

Drava-Danube catchment area. 16th World Congr. Soil Sci., Vol. I, No. 113 (Summ.), Montpellier.

Đumija L., Manitašević J. (1989): Determination of heavy metals and inorganic pollutants in water of canals on experimental field Ježevo. Agrohemija (Beograd), (1–3): 69–77.

FAO (1990): Guidelines for soil description. Soil resources, management and conservation service land and water development division. 3rd ed. Rome.

Förstner U.G. (1980): Cadmium. In: Hatzinger O. (ed.): Handbook of environmental chemistry, Part A. Springer-Verlag, Berlin, Heidelberg, New York, Vol. 3: 59–107.

Garison S. (1981): Trace metals in contaminated waters. Envir. Sci. Technol., *13*: 396.

Isermann K. (1983): The extent to which agriculture is involved in environmental problems in modern industrial society. IFA Report A/83/60.

Královec J., Slavík L. (1997): Transfer of lead, cadmium and mercury in the system soil-plant-animal. Rostl. Výr., *43*: 257–262.

Mengel K., Kirkby E.A. (1979): Principles of plant nutrition. 2nd ed. Int. Potash Inst., Bern.

Mikanová O., Kubát J., Mikhailovskaya N., Vörös I., Biró B. (2001): Influence of heavy metal pollution on some soil-biological parameters in the alluvium of the Litavka river. Rostl. Výr., *47*: 117–122.

Moore J.W. (1981): Influence of water movements and other factors on distribution and transport of heavy metals in a shallow bay (Canada). Arch. Envir. Contam. Toxicol., *10*: 715.

Moore J.W., Sutherland D.J. (1981): Distribution of heavy metals and radionuclides in sediments, water and fish in an area of great bear lake contaminated with mine wastes. Arch. Envir. Contam. Toxicol., *10*: 329.

Mortvedt J.J. (1987): Cadmium levels in soils and plants from some long-time soil fertility experiments in the United States of America. J. Envir. Qual., *16*: 137–142.

Němeček J., Podlešáková E. (2001): The main features of the transfer of trace elements into plants. Rostl. Výr., *47*: 7–13.

O'Neil P. (1985): Environmental chemistry. Georg Allen & Unwin, London, Boston, Sydney.

Pospíšilová L., Laštincová J. (1998): Determination of some trace elements in soil using ICP-AES method. Rostl. Výr., *44*: 427–429.

Romić M., Romić D. (1998): Contents of metals Pb, Cd, Zn and Cu in agricultural soils of Zagreb and its surroundings. Poljopriv. Znan. Smotr., *63*: 147–154.

Vidaček Ž., Drevenkar V., Husnjak S., Sraka M., Karavidović P. (1994): Nitrates, pesticides and heavy metals in drained soils and water in the area of catchment basin rivers Karašica and Vučica. Agric. Wat. Proc. Worksh. Bizovačke Toplice (Croatia): 211–222.

Walker C. (1971): Environmental pollution by chemicals. Hutchinson Educational, London.

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ABSTRAKT

Obsah Pb, Zn a Cd v meliorované půdě a drenážních vodách a jejich transport do rostlin

Cílem výzkumu bylo stanovit průměrný obsah těžkých kovů (Pb, Zn a Cd) v orniční vrstvě půdy (0–30 cm) a v drenážní vodě a jejich koncentrace v rostlinách pěstovaných na hydromeliorované půdě ve variantách se čtyřmi různými roztečemi drenážních trubek. Pokusy probíhaly na experimentálním meliorovaném pozemku na oglejené podzolové Luvizemi. Rozteč drenážních trubek byla 15, 20, 25 a 30 m. Během celého pokusného období byla pěstována kukuřice a ozimá pšenice a byla použita stejná agrotechnika. Koncentrace těžkých kovů v půdě, v drenážní vodě a v rostlinné hmotě vyhověla ve všech variantách definovaným limitním hodnotám. Největší průměrný obsah Pb v půdě byl 13,5 $mg.kg^{-1}$, Zn 88 $mg.kg^{-1}$ a Cd 0.7 $mg.kg^{-1}$. V drenážní vodě byla koncentrace Pb nižší než 50 $\mu g.dm^{-3}$, Cd nižší než 2 $\mu g.dm^{-3}$ a průměrná hodnota Zn nepřesahovala 20 $\mu g.dm^{-3}$. V zrnu pěstovaných plodin nepřesahovala koncentrace Pb 0.4 $mg.kg^{-1}$ a Cd 0.1 $mg.kg^{-1}$.

Klíčová slova: těžké kovy (Pb, Zn, Cd); drenážní voda; rostliny; meliorovaný podzolový luvisol

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