EKOLOGIJA. 2004. Nr. 1. P. 42–45

Migration of heavy metals in soil and their concentration in sewage and sewage sludge

Ðarûnas Antanaitis

Lithuanian Institute of Agriculture, Instituto al. 1, LT-58344 Akademija, Këdainiai distr., Lithuania. E-mail: sarunas@lzi.lt

Antanas Antanaitis

Lithuanian Institute of Agriculture, Agrochemical Research Centre, Savanoriø 287, LT-50127 Kaunas, Lithuania. E-mail: analize@agrolab.lt

Concentrations of heavy metals in soil, drainage water and plants were determined in crop rotation fertilization trials at the Lithuanian Institute of Agriculture on sod-gleyic light loam soil. According to leaching from light loam soil as follows heavy metals ranked in a decreasing order: Cd, Cr, Zn, Cu, Ni, Pb.

Concentrations of heavy metals were determined in the sewage sludge from 19 water treatment plants. The concentration of heavy metals (mg kg^{-1}) in the dry matter of sewage sludge ranged as follows: Zn 120–1698, Cr 5.7–4315, Cu 14.5–426, Pb 4.8–475, Ni 7.6–69.8, Cd 0.34–31.98, Hg 0.007–1.045. The main criteria for the use of sewage sludge were determined. Cd and Cr had the greatest effect on sewage sludge contamination due to which it was attributed to category 5, the content of Zn, Cu, Cr, Cd and Pb ranked it to category 4, and of Zn, Cu and Cr to category 3. According to nickel and mercury content the whole sludge could be attributed to the lowest contamination categories (1 and 2).

Key words: sludge, drainage water, heavy metals, soil, plant

INTRODUCTION

Environmental contamination is one of the most important factors destroying the biosphere. Heavy metals play the main part in this destruction. They get into the environment by different ways. Pollution with heavy metals depends on the properties of soil and on economic activities. Therefore, knowledge of the influence of heavy metals on soil and their migration in soil is very important. The content of heavy metals in plants depends on their concentration and migration in soil. Their migration in calcareous soil decreases as follows: Zn > Cd > Pb (Boruvka et al., 1997), Zn ≥ Cu (Zinati et al., 2001). Cr and Pb accumulate in the deeper layer and Cd in the arable layer (Потупаева и др., 2001). Migration of heavy metals depends mostly on the physical and chemical properties of soil (Отаббонг и др., 2001). Interaction among heavy metals has an influence on the amount of heavy metals getting into plants (Фатеев и др., 2001). The amount of heavy metals in the soil of neutral reaction and in plants shows a weak correlation (Tlustos et al., 1997).

At present, when the number of households and industrial sewage is increasing, utilization of sewage sludge is a serious problem. Sewage sludge is used for recultivation of pits and peat-bogs, for fertilization of cultured plants and green plantations. It is necessary to be cautious, because large amounts of heavy metals might be accumulated in sludge and pollute not only soil but also groundwater. When sewage sludge from Panevëþys was spread in the forests, the amount of heavy metals increased 2–3 times and of Ni even 30 times (Katinas, 1999). The levels of heavy metals in sludge collected from different places and at different time vary, so determination of its chemical composition before the use is indispensable.

Sludge was found to be more effective (by 30%) than potassium (sodium) nitrate and its influence lasted longer (Zinati et al., 2001). Compost sludge and wheat straw has increased the variety of the composition of microflora, the total amount of bacteria, the enzymatic activity, the content of humus and the amount of total nitrogen (Bergstrom, Jarvis, 1988). Heavy metals in sludge have a negative influence on plants. According to investigations carried out in Sweden, the abundance of microorganisms was suppressed by heavy metals; the reduction of acetylene was increased (15–80%), though the soil acidity decreased and the amount of organic carbon increased. During a period of 25 years the amount of Cd, Cr, Cu, Pb and Zn increased by 76%, but has not reached the criticial point defined in the EU. The ratio between total C of microorganisms and C in soil increased (Auber, 1976). A complex of fulvic acids and cations of heavy metals was not easily available to microorganisms: the complex with Mn was a source of N and C, and less available was the complex with Fe and Al; the complex with Ni, Cu, Zn stood out for its high resistance (Bloem et al., 1992).

Despite the fact that a lot of investigations in the area of heavy metals have been done, it is impossible to adapt the data directly to a specific region, that is why it is necessary to investigate the environment around us.

The aim of the current research was determination of a relation between levels of heavy metals and their accumulation in plants and water, of the amount of heavy metals in soil, as well as evaluation of the quality of sewage sludge depending on contamination with heavy metals concentrated in the disposal installations of cities and settlements.

MATERIALS AND METHODS

Trials of crop rotation fertilization were carried out during the period 1997–1999 in separate drainage systems of Lithuanian Institute of Agriculture. Sod-gleyic light loam soils prevailed, with pH 7.4 ± 0.19, the amount of P_2O_5 was 128 ± 19.5 – 212 ± 45.6 mg kg^{-1}, K_2O 102 ± 13 – 125 ± 14.3 mg kg^{-1}, N 0.155 ± ± 0.0116 – 0.171 ± 0.0189%, humus 2.62 ± 0.232 – 2.76 ± 0.338. In five separate drainage systems the concentration of heavy metals in soil drainage water and plants was determined. Research data from separate drainage systems were combined, because there was no distinct difference among them.

Investigating the pollution of sewage sludge, samples were taken from 19 places during the period 1996–2000, 1–21 times from different piles loaded at different time.

The content of heavy metals in soil was recalculated in mg kg^{-1}, drainage water – mg l^{-1}, sludge – mg kg^{-1} in dry matter. Heavy metals in soil were determined by extraction 2 M HNO_3, in sludge – by burning, in water and sewage – directly using an atomic spectrometer.

RESULTS

Concentrations of heavy metals in light soil and drainage sewage are presented in Table 1.

The content of zinc and lead in soil was the highest. The concentrations ranked as follows: Zn > Pb > Cr > Ni > Cu > Cd, in drainage sewage: Zn > Cr > Ni > Pb > Cu > Cd. According to the intensity of leaching from light loam soil: Cd > > Cr > Zn > Cu > Ni > Pb. Cadmium leached from the soil even 14.5 times easier than lead.

Larger amounts of heavy metals are accumulated by plants than leached to drainage water (Table 2). Zinc and copper were accumulated by plants most intensively. Almost all plants accumulated the same levels of copper: winter wheat 18.5 ± 2.99 g ha^{-1}, barley 19.2 ± 2.55, potatoes 24.0 ± 3.89. Zinc was accumu-

Table 1. **Content of heavy metals in arable layer, mg kg^{-1}**

Element	In soil mg kg^{-1}	Drainage sewage mg/l	Drainage sewage kg ha^{-1}	Ratio between concentration of drainage water and soil
Cr	9.66 ± 2.005	0.035 ± 0.012	0.083 ± 0.028	0.0036
Cd	0.39 ± 0.08	0.002 ± 0.0003	0.004 ± 0.001	0.0044
Pb	11.01 ± 1.00	0.003 ± 0.002	0.008 ± 0.004	0.0003
Ni	8.09 ± 1.49	0.011 ± 0.002	0.026 ± 0.006	0.0013
Cu	6.21 ± 0.93	0.002 ± 0.001	0.010 ± 0.001	0.0003
Zn	24.91 ± 3.48	0.059 ± 0.021	0.140 ± 0.051	0.0024

Table 2. **Content of heavy metals in the yield and in the soil**

Element	Winter wheat		Summer barley		Potatoes	
	grain mg kg^{-1}	is taken from the soil (0–30 cm)%	grain mg kg^{-1}	is taken from the soil (0–30 cm)%	Potatoe tubers mg kg^{-1}	is taken from the soil (0–30 cm)%
Cr	0.141 ± 0.026	0.0014	0.285 ± 0.079	0.0024	0.239 ± 0.027	0.0033
Cd	0.095 ± 0.013	0.0239	0.089 ± 0.022	0.0125	0.203 ± 0.032	0.0376
Pb	0.417 ± 0.022	0.0037	0.505 ± 0.053	0.0033	0.911 ± 0.082	0.0072
Ni	0.465 ± 0.413	0.0056	0.480 ± 0.312	0.0148	0.524 ± 0.054	0.0235
Cu	4.220 ± 0.643	0.0662	5.180 ± 1.413	0.0688	5.860 ± 0.514	0.0968
Zn	23.52 ± 2.33	0.0922	28.09 ± 1.803	0.0889	15.28 ± 2.025	0.0584

lated as follows: potatoes only 63.3 ± ± 14.58 g ha^{-1}, winter wheat 103.4 ± 13.45, barley 97.5 ± 12.03. Almost the same amounts of zinc, copper and lead were accumulated by winter wheat and spring barley, although winter wheat accumulated by 37% less chromium and 25% more cadmium than barley. Potatoes accumulated cadmium twice as much as wheat and 2.6 times more than barley. Winter and spring barley accumulated heavy metals from the soil as follows: Zn > Cu > Cd > Ni > > Pb > Cr. A different order was observed for potatoes: Cu > Zn > Cd > Pb > Ni > Cr. Potatoes were more sensitive to pollution with Cd and Pb than crops, because potatoes accumulate heavy metals relatively more actively than crops: potatoes – Cd – 0.0376%, Pb – 0.02723%, crops – Cd – 0.001254–0.0239%, Pb – 0.00333–0.0371%.

Concentrations of heavy metals in the sludge investigated during the period 1996–2000 varied in a very wide range not only among different places but also in the same water treatment plant (Table 3).

The variations of average levels of heavy metals in sludge (in dry matter): Cr 21–656, Cd 0.34–7.83, Pb 4.8–475, Ni 7.6–69.8, Cu 14.5–426, Zn 71–1698, Hg 0.110–1.475 mg kg^{-1}. No regular dependence between the concentration of heavy metals in sludge and the volume of industrial works was revealed. Large enterprises have purification equipment, and sewage is more or less cleaned from contamination by heavy metals. Moreover, in big cities industrial sewage is diluted with household sewage.

Sludge containing the highest levels of cadmium and chromium is attributed to category V (Table 4), of zinc, copper and chromium – to category IV. The least influence on pollution have mercury and nickel. 76.6–90.8% of sludge could be attributed to category I.

According to the standard LAND 20–2001, sewage sludge depending on the content of heavy metals is divided into three groups. The possibilities to use sewage sludge are greater when larger amounts of lead, chromium, zinc and cadmium are accumulated in it.

According to the LAND 20–2001 standard, the ratio between the maximum concentration limits is:

Table 4. **Distribution of sewage sludge into pollution categories according to content of heavy metals at water treatment plants in Lithuania, %**

1996–2000

Heavy metals	Sludge pollution categories				
	I	II	III	IV	V
Cr	45.1	8.6	19.4	22.6	4.3
Cd	20.4	44.1	7.5	19.4	8.6
Pb	62.3	12.9	5.4	19.4	0
Ni	76.6	20.4	0	0	0
Cu	27.9	15.1	32.3	24.7	0
Zn	18.3	8.6	39.8	33.3	0
Hg	90.8	9.2	0	0	0

Table 3. **Heavy metals in the sewage sludge at water treatment plants in Lithuania, mg kg^{-1} dry matter**

1996–2000

No	n	Cr	Cd	Pb	Ni	Cu	Zn	Hg
1	21	225 ± 188	1.31 ± 0.63	36.0 ± 14.4	20.7 ± 8.3	389 ± 309	784 ± 266	0.291 ± 0.157
2	18	174 ± 67	3.64 ± 1.78	475 ± 426	69.8 ± 42.3	287 ± 300	1698 ± 1997	0.428 ± 0.289
3	8	6.0 ± 3	0.56 ± 0.27	4.8 ± 2.4	11.3 ± 6.9	39 ± 62	71 ±59	0.035 ± 0.000
4	8	103 ± 16	7.83± 4.73	79.0 ± 10.5	28.1 ± 4.8	205 ± 5	1487 ± 85	0.489 ± 0.000
5	5	49 ± 5	1.45 ± 0.25	191.1 ± 53.7	23.0	186 ± 29	876	0.422
6	5	25 ± 18	1.30 ± 0.81	36.8 ± 26.8	23.3 ± 10.1	228 ± 118	820 ± 182	1.045
7	4	656 ± 234	0.34 ± 0.15	11.7 ± 8.6	7.6 ± 4.0	14 ± 6	156 ± 16	0.029
8	4	17 ± 12	0.73 ± 0.41	20.4 ± 13.0	7.9 ± 4.8	29 ± 27	495 ± 295	0.430 ± 0.317
9	3	34 ± 4	2.50 ± 0.30	17.5 ± 2.5	58.0 ± 6.2	176 ± 36	607 ± 105	0.11 ± 0.141
10	3	27 ± 1	1.77 ± 0.03	42.7 ± 0.4	17.9 ± 0.4	115 ± 18	796 ± 73	0.051 ± 0.020
11	2	40 ± 45	1.49 ± 0.13	32.0 ± 28.6	14.0 ± 1.3	426 ± 493	866 ± 118	–
12	2	27 ± 18	1.78 ± 1.10	44.2 ± 8.2	17.1 ± 1.3	52 ± 53	935 ± 822	–
13	2	6 ± 1	0.70 ± 0.14	42.0 ± 2.8	8.9 ± 1.8	28 ± 4	120 ± 6	0.035 ± 0.007
14	2	21 ± 8	2.60 ± 0.28	69.0 ± 9.9	21.7 ± 5.5	99 ± 24	1145 ± 219	1.475
15	2	28 ± 2	1.50 ± 0.14	40.5 ± 0.7	17.0 ± 0.6	124 ± 1	545 ± 7	0.027 ± 0.005
16	1	34	3.50	77.5	29.5	155	1260	–
17	1	4315	1.98	61.0	46.1	138	659	0.920
18	1	21	2.25	43.5	17.0	203	798	0.219
19	1	21	0.80	23.0	27.4	52	260	–

1 Cd : 56 Cr : 56 Pb : 56 Ni : 41 Cu : 186 Zn : : 0.5 Hg. Meanwhile, in the soil where crop rotation fertilization was carried out, the ratio among heavy metals was as follows: 1 Cd : 28 Cr : 25 Pb : 16 Ni : : 21 Cu : 64 Zn; contamination with cadmium, nickel and lead might be relatively slight.

The ratio among heavy metals varied within the following range: Cd 8–1929, Cr 2–132, Pb 1–34, Ni 4–286, Cu 21–598, Zn 0.01–1.26. Among the lowest levels, especially dangerous is cadmium and from those highest chromium. Using sewage sludge, the least probability to contaminate the soil is by nickel and in most cases by mercury, because even the biggest ratio with cadmium is lower than that calculated according to MLC.

CONCLUSIONS

1. The level of contamination of the soils with heavy metals was found to be not high.

2. The levels of heavy metals accumulated by plants were higher than those leached from soil.

3. The concentration of heavy metals in drainage water decreases as follows: Zn > Cr > Ni > > Pb > Cu > Cd. According to the ability to leach from light loam soil heavy metals are in this decreasing range: Cd, Cr, Zn, Cu, Ni, Pb.

4. Winter wheat and spring barley accumulated heavy metals from soil as follows: Zn > Cu > Cd > > Ni > Pb > Cr. A different order was observed for potatoes: Cu > Zn > Cd > Pb > Ni > Cr.

5. Concentrations of heavy metals in the sludge from water treatment plants varied within the following range: Zn 120–1698, Cr 5.7–4315, Cu 14.5–426, Pb 4.8–475, Ni 7.6–69.8, Cd 0.34–31.98, Hg 0.007–1.045 mg.kg^{-1} (in dry matter).

6. Cd and Cr had the strongest influence on the contamination of sludge. Sludge with the highest content of Cd and Cr was attributed to category 5; Zn, Cu, Cr, Cd, Pb – to category 4, Zn, Cu and Cr – to category 3. According to the content of nickel and mercury, the whole sludge could be attributed to the lowest categories of contamination.

Received
07 July 2003

References

1. Aubert C. *L'agriculture biologique. Pourquoi et comment la pratiquer*. 1976. 367 p.
2. Bergstrom L., Jarvis N. J. Prediction of nitrate leaching losses from arable land under different fertilization intensities using the soil–soil N models. *Soil Use and Management*. 1998. Vol. 7. N 2. P. 79–85.
3. Bloem J., Ruiter P. C., Koopman G. J. Microbial numbers and activity in dried and rewetted arable soil under integrated and conventional management. *Soil Biol. Biochem*. 1992. Vol. 24. N 7. P. 655–665.
4. Boruvka L., Kozk J., Kristoufkova S. Heavy metal accumulation in plants grown in heavily polluted soils. *Folia Microbiologica*. 1997. Vol. 42. Iss. 5. P. 524–526.
5. Katinas V. Research on utilization of Panevëþys wastewater plant sludge. *Heavy metals in the environment: an integrated approach*. Vilnius, 1999. P. 122–124.
6. Tlustos P., Balik J., Pavlikova D., Szakova J. The uptake of cadmium, zinc, arsenic and lead by chosen crops. *Rostlinna Vyroba*. 1997. Vol. 43. Iss 10. P. 487–494.
7. Zinati G. M., Li Y. C., Bryan H. H. Accumulation and fractionation of coper, iron, manganese and zinc in calcerous soil amended with composts. *Journal of Environmental Science and Health. Part B – Pesticides Food Contaminants and Agricultural Wastes*. 2001. Vol. 36. Iss. 2. P. 229–243.
8. Отаббонг Э., Якименко О. С., Садовникова Л. К. Влияние городских осадков сточных вод на доступность биогенных элементов в вегетационном эксперименте. *Агрохимия*. 2001. № 2. С. 55–60.
9. Потупаева Ю. А., Касицкий Ю. И., Сидоренкова Н. К. и др. Распределение подвижных форм тяжелых металлов, токсичных элементов и микроэлементов по профилю дерново-подзолистой тяжелосуглинистой почвы при длительном систематическом применении удобрений. *Агрохимия*. 2001. № 4. С. 61–66.
10. Фатеев А. И., Мирошниченко Н. Н., Самохвалова В. Л. Миграция, транслокация и фитотоксичность тяжелых металлов при полиэлементном загрязнении почвы. *Агрохимия*. 2001. № 3. С. 57–61.

Ðarûnas Antanaitis, Antanas Antanaitis

SUNKIØJØ METALØ MIGRACIJA DIRVOÞEMYJE BEI JØ KONCENTRACIJA NUOTËKOSE IR DUMBLE

S a n t r a u k a

Lietuvos þemdirbystës instituto sëjomainininiuose træðimo bandymuose árengtame velëniniame glëjiðkame lengvo priemolio dirvoþemyje nustatytos sunkiøjø metalø koncentracijos dirvoþemyje, drenaþo vandenyje ir augaluose, iðneðamø elementø kiekiai. Pagal savybæ iðsiplauti ið lengvo priemolio dirvoþemio sunkieji metalai iðsidëstë ðia maþëjanèia eile: Cd, Cr, Zn, Cu, Ni, Pb.

Nustatyta sunkiøjø metalø koncentracija 19-oje valymo árenginiø nuotekø dumble. Jø koncentracija ávairavo tokiose ribose: Zn 120–1698, Cr 5,7–4315, Cu 14,5–426, Pb 4,8–475, Ni 7,6–69,8, Cd 0,34–31,98, Hg 0,007–1,045 mg kg^{-1} sauso dumblo. Nustatyti pagrindiniai kriterijai, ribojantys dumblo panaudojimà. Didþiausià átakà valymo árenginiø dumblo uþterðtumui turëjo Cd ir Cr, dël kuriø dumblas priskirtas 5 kategorijai, 4 kategorijai – Zn, Cu, Cr, Cd ir Pb, 3 kategorijai – Zn, Cu ir Cr kiekiai. Dël nikelio ir gyvsidabrio visà dumblà galëtume priskirti maþiausiai uþterðto dumblo kategorijoms (1 ir 2).

Raktaþodþiai: drenaþo vanduo, nuotekø dumblas, sunkieji metalai, dirvoþemis, augalai