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BEHAVIOR OF HEAVY METALS IN THE SOIL-PLANT SYSTEM

Nehézfémek viselkedése a talaj-növény rendszerben

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Abstract

Relationships between heavy metals, soils and plants may be studied in objective manner in field conditions. A long-term field experiment was set up with some microelements at Károly Róbert College on a slightly acidic clay soil. Four levels (0, 30, 90 and 270 hg element·ha^{-1}) of microelements were added to plots separately at initiation. Different crops (winter wheat, maize and sunflower) were grown each year. In addition to yield evaluation, soil tests and plant analyses were completed yearly. In the first year of the experiment nearly the total amount of applied elements could be detected in the ploughed layer in mobile form. Two years later only about one-third of the applied elements were traced in available forms. With time there was a fixation of these elements in less mobile/soluble forms and they stayed mainly in the cultivated soil layer. Cd remains mobile in the soil-plant system for a long time. It accumulated both in the vegetative and generative parts of plants with no observed symptoms of toxicity and yield loss. Pb can enter both the vegetative and generative plant organs, however its accumulation cannot be increased with increasing Pb loads of the soil. Pb has low mobility in the soil-plant system. Hg and As cannot translocate into the grain even their extremely high concentration in the soil. Grain, as a generative organ, proved to be resistant tot these micropollutants. The non-essential elements Cd, Cr and Pb can translocate into the grain, so they can pollute the food chain.

Keywords: microelements, heavy metals, soil pollution, crop accumulation.

JEL: Q15

Összefoglalás

A nehézfém-talaj-növény kapcsolatrendszer egzakt szabadföldi kísérletekben tanulmányozható megbízhatóan. A Károly Róbert Főiskolán szabadföldi nehézfém-terhelési tartamkísérletet állítottunk be gyengén savanyú agyag talajon, 8 mikroelemmel négy terhelési szinten (0/30, 90 és 270 kg elem/ha). A parcellákon minden évben más-más jelzőnövényt termesztettünk (őszi búza, kukorica, napraforgó). A termés mérése mellett évente talaj- és növényvizsgálatokat végeztünk. A kísérlet első évében a kiszórt elemek csaknem teljes mennyisége mobilis formában volt kimutatható a szántott rétegben. Két évvel később már csak kb. kétharmad részük volt kimutatható felvehető formában. Idővel az elemek oldhatósága/felvehetősége csökkent és a művelt talajrétegben maradtak. A Cd hosszú ideig megtartotta mozgékonyságát a talaj-növény rendszerben. Dúsulása a vegetatív és generatív növényi részekben is megfigyelhető volt fitotoxikus tünetek és *termés csökkenés nélkül. Az Pb beépült a vegetatív és a generatív növényi részekbe, de talajterhelés hatására dúsulása nem volt igazolható. Csak kis mértékben mozgékony a talaj-növény rendszerben. Az As és a Hg még extrém magas talajterhelés esetén sem épült be a szemtermésbe. A szem, mint generatív szerv genetikailag védett e szennyezőkkel szemben. A növény számára nem esszenciális elemek közül a Cd, Cr és az Pb bekerültek a szemtermésbe, és így terhelhetik a tápláléki láncot.*

Kulcsszavak: mikroelemek, nehézfémek, talajszennyezés, növényi akkumuláció.

Introduction

Nowadays, pollution is a serious threat to all part of the environment including the soil. The industrialization, urbanization and intensification of agricultural production have caused adverse environmental effects in North Hungarian Region: in fact polluted areas cover about 15% of the region, but affect nearly 40% of the population (Németh-Kádár 1991, Kádár 1993, Szalai et al. 2002).

Contaminated soils mostly are found in industrial and urban areas, in surrounding of metal-mines, along motorways and in arable lands treated with heavy application of sewage sludge. The accumulation of potentially hazardous chemical compounds and elements, particularly toxic trace elements result irreversible changes in the environment (Kádár 1995, Simon et al. 1999). The monitoring of dynamics of harmful trace elements (eg. heavy metals), their accumulation in the topsoil and transfer into the field corps can be studied objectively in long-term field experiments. The field experiment that was initiated at model farm of Károly Róbert College (KRC) and belongs to a country-wide research program started and conducted by the Research Institute for Soil Science and Agricultural Chemistry of Hungarian Academy of Sciences. This research program ("Contamination of the environment with heavy metals") covers three different experimental sites representing three of the main soil types of Hungary: such as calcareous loamy chernozem, calcareous sandy soil and brown forest soil. Research stations adopt the same methodology.

Károly Róbert College is the center of agricultural and rural development education and research in the North Hungarian Region. The environmental research and education are one of the most important activities of the College. Recent research priorities mostly concern sustainable soil management and fertilizer use, control of movement and accumulation of trace elements in the soil-plant system and development of sustainable cropping systems. Main goals of the research:

- to study fixation, transformation, plant availability, leaching of some heavy metals in the soil,
- to follow element uptake by and transport within the plants,
- to monitor heavy metal accumulation in different plant organs (especially in the edible parts),
- to study their phytotoxicity and effect on the quality and quantity of the crop yield.

Materials and methods

The soil type of the experiment field is a slightly acidic chernozem brown-forest soil (vertic cambisol), which represents the determinative soil type of the region. Its main characteristics are as follows: $pH_{(H2O)}$ 6,4; $pH_{(KCl)}$ 5,4; y_1 9,5; $CaCO_3$% 0; humus content 3%; upper limit of plasticity (K_A) 45; L% 70; hy 4,8. This is a silty-clay soil, its bulk density is 1.21 $g \cdot cm^{-3}$. The cation exchange capacity of the soil is 40 meq/100 g soil. Total amounts of the exchangeable cations are 36 meq/100 g soil. The main exchangeable cations are Ca^{++} (83%), Mg^{++} (10%), Na^+ (6%), K^+ (1%). The soil profile is presented in Figure 1.

Figure 1 The profile of the chernozem brown forest soil
Photo: Fodor (1994)

The field trial was set up in 1994 with 8 elements (Al, As, Cd, Cr, Cu, Hg, Pb, Zn), on 3 levels each (0, 30, 90, 270 kg element·ha^{-1}), i.e. 24 treatments all in triplicate with 72 plots altogether. Plot sizes were 35 m^2 each. In the experiment arranged in split-plot design the main plots included the 8 selected elements and sub plots represented the 3 load levels. Treatments were carried out once at initiation using soluble salts of examined microelements (Table 1).

Table 1 Treatments of the field trial

Element	Loading levels kg element·ha^{-1}			Form of applied salts
	1	2	3	
Al	0	90	270	$Al(NO_3)_3 \cdot 9H_2O$
As	30	90	270	$NaAsO_2$
Cd	30	90	270	$3CdSO_4 \cdot 8H_2O$
Cr	30	90	270	K_2CrO_4
Cu	30	90	270	$CuSO_4 \cdot 5H_2O$
Hg	30	90	270	$HgCl_2$
Pb	30	90	270	$Pb(NO_3)_2$
Zn	30	90	270	$ZnSO_4 \cdot 7H_2O$

Source: own construction

The experimental plants were winter wheat, maize and sunflower. Experimental plots were cultivated with commonly used agrotechnics.

Soil samples were collected from the ploughed layer (0-30 cm) of each plot. The mobile element fraction of soil samples was determined by NH_4-acetate+EDTA extraction (Lakanen-Erwiö 1971). The total amount of the elements in homogenized soil samples was measured using cc.HNO_3+cc.H_2O_2 extractions. Plant samples were taken yearly during the vegetation period at phenophases characterized by intensive nutrient uptake. The total element content

was determined in the plant samples after microwave digestion using cc.HNO_3+cc.H_2O_2. The composition of soil- and plant samples was determined using inductively coupled plasma mass spectrometry (ICP-MS) detecting 25 elements in the lab of RISSAC.
Mathematical, statistical analyses of data were carried out using variance analysis of split-plot experiments, and the $LSD_{5\%}$ was calculated.

Results

Change of element content in the soil

The extractable element contents were increased considerably in the ploughed layer by treatments. In time, the amount of NH_4-acetate+EDTA soluble fractions somewhat decreased, but the fixation was different for each element. Cr and Hg showed the most expressed fixation in the soil. Soluble fractions transformed very quickly into less available forms. The available element content in the ratio of total amount was only 2% and 8% in case of these elements. According to results of soil analysis presented in Table 2, Cd, Pb and Cu showed high mobility in the soil. Mobile fractions expressed in the percentage of the total amount, the mobility order of investigated elements was as follows: Cd (85%) > Pb (64%) > Cu (61%) > Zn (33%) > As (26%) > Hg (8%) > Cr (2%).

Table 2 Transformation and bonding of heavy metals in the soil after two years of application

Element	Total amount $mg \cdot kg^{-1}$	Available amount $mg \cdot kg^{-1}$	Available fraction (% of total applied)	Recovery %	
				cc.HNO_3+cc.H_2O_2 digestion	NH_4 acetate+EDTA extraction
As	75	19,9	26	73	22
Cd	90	76,6	85	99	85
Cr	101	2,2	2	79	2
Cu	82	49,9	61	63	48
Hg	39	3,3	8	43	4
Pb	46	29,4	64	29	25
Zn	150	49,2	33	72	43

Source: own construction

On the basis of results of cc.HNO_3+cc.H_2O_2 digestion it can be stated that

- Cd was almost totally detectable (90%),
- Cr, As, Zn and Cu were well detectable (60-90%),
- Hg was middling detectable (30-60%),
- Pb was poorly detectable (10-30%)

by this analytical method after two years of application.

As for Lakanen-Erviö's method (NH_4-acetate+EDTA extraction), it can be stated that

- Cd was well detectable (60-90%),
- Cu and Zn were middling detectable (30-60%),
- Pb and As were poorly detectable (10-30%),
- Hg and Cr were hardly detectable (under 10%).

Because significant amount of applied Cd was detectable by both analytical methods, so Cd contamination of the soil can be qualified even by NH_4-acetate+EDTA extraction.

Vertical movement of Cr(VI) in the soil profile was already detected in the second year of the experiment (Table 3). Cr contamination was expressed in the 30-60 cm as well as 60-90 cm layers. Cr content in deeper layers was less than one-tenth of that in the ploughed (0-30 cm) layer. To check toward movement of Cr(VI), soil samples must be taken from deeper layers in the future.

Table 3 Effect of 270 kg·ha^{-1} heavy metal load on the element composition of soil profile

Element and depth of sampling (cm)	Total content, mg·kg^{-1}		Available content, mg·kg^{-1}	
	control soil	treated soil*	control soil	treated soil*
As				
0-30	9	75	0	19,9
30-60	9	12	0	0,3
60-90	9	11	0	0,1
Cd				
0-30	0,6	90	0,3	76,6
30-60	0,6	0,6	0,2	0,2
60-90	0,6	0,4	0,2	0,1
Cr				
0-30	30	101	0	0,2
30-60	26	36	0	0,4
60-90	26	34	0	0,2
Cu				
0-30	25	82	7	49,9
30-60	22	22	5	5,1
60-90	20	18	5	3,6
Hg				
0-30	0	39	0	3,3
30-60	0	0	0	0
60-90	0	0	0	0
Pb				
0-30	20	46	7	29,4
30-60	20	21	6	9,4
60-90	15	14	5	3,8
Zn				
0-30	85	150	10	49,2
30-60	85	82	7	6,9
60-90	70	71	6	3,2

* averages of replications
Source: own construction

As and Pb were basically detected in the upper 0-30 cm layer in the second year. Only slight contamination was detected in the 30-60 cm layer. Dynamics of As and Pb leaching was not evaluated after second year of application. More examinations are needed to describe the leaching processes of these elements. The elements Cd, Hg, Cu and Zn were fixed in the ploughed layer. Both the total content and available fraction were detected in the upper 0-30 cm layer. These contaminants seem to be resistant to leaching.

Change of element content in crops

In the first year of the experiment considerable As accumulated in the vegetative organs of wheat with increasing As load of the soil. The 270 kg·ha^{-1} As load resulted about a hundred times enrichment of As content in the green sprout and straw. As was not detectable in the grain even in case of the highest As application rate. The As content of maize straw seemed related to application rate, but significant accumulation was measured only at the 270 kg·ha^{-1} application rate. Corn was not contaminated with As. Higher As concentration were measured in vegetative parts of sunflower compared with cereals, but As was less than the detectable level in sunflower seeds (Table 4).

Table 4 Effect of increasing As loads on the As content of crops, mg·kg^{-1}

Sampling		Application rates mg·kg^{-1}				LSD$_{5\%}$	Average
date	part of crop	0	30	90	270		
			Winter wheat				
05.05.	Shoot[1]	0,0	0,4	2,0	2,8	1,2	1,7
31.07.	Straw[4]	0,0	0,1	1,1	5,2	0,9	1,6
31.07.	Grain[4]	0,0	0,0	0,0	0,0	0,0	0,0
			Maize				
07.06.	Shoot[2]	0,0	0,0	0,0	1,0	0,5	0,2
17.07.	Leaf[3]	0,0	0,0	0,0	0,0	0,0	0,0
08.10.	Straw[4]	0,0	0,3	0,6	1,5	0,7	0,6
08.10.	Grain[4]	0,0	0,0	0,0	0,0	0,0	0,0
			Sunflower				
24.06.	Shoot[2]	0,2	0,7	5,2	12,8	3,3	4,7
05.08.	Leaf[3]	0,1	0,3	0,8	2,3	0,3	1,1
15.09.	Straw[4]	0,0	0,4	1,3	3,3	1,1	1,2
15.09.	Seeds[4]	0,0	0,0	0,0	0,0	0,0	0,0

[1]- at shooting, [2]- at 4-6 leaf stage,
[3]- at flowering, [4]- at harvest
Source: own construction

Cd accumulation increased significantly both in vegetative and generative parts of crops with increasing Cd applications to the soil. The 0,1-0,5 mg·kg^{-1} Cd content of control crops suggests that the background levels with Cd were rather high in soils of the Gyöngyös area. Each treatment resulted in wheat grain unsuitable for human consumption. The Hungarian Standard (8/1995. (X. 21.) EüM.) allows 0,1 mg·kg^{-1} Cd in ground cereals and flour. Cd content was about 10-40 times higher in treated sunflower seeds than in the control, so the seeds were not usable for food. Cd remains mobile in the soil-plant system for a long time. It can accumulate in the generative tissues, so it is a real risk for the food chain (Table 5).

Table 5 Effect of increasing Cd loads on the Cd content of crops, mg·kg^{-1}

Sampling		Application rates mg·kg^{-1}				LSD$_{5\%}$	Average
date	part of crop	0	30	90	270		
			Winter wheat				
05. 05.	Shoot^1	0,1	1,0	1,7	2,2	0,9	1,6
31. 07.	Straw^4	0,2	1,6	2,7	7,7	2,2	3,0
31. 07.	Grain^4	0,1	0,6	0,9	1,0	0,1	0,6
			Maize				
07. 06.	Shoot^2	0,5	9,9	16,4	21,8	1,3	12,2
17. 07.	Leaf^3	0,3	5,4	8,8	12,2	0,6	6,7
08. 10.	Straw^4	0,4	5,7	9,0	11,6	0,6	6,7
08. 10.	Grain^4	0,1	0,6	0,9	0,9	0,2	0,6
			Sunflower				
24. 06.	Shoot^2	0,3	14,7	26,3	38,6	8,0	21,2
05. 08.	Leaf^3	0,3	3,7	6,3	11,6	1,0	5,5
15. 09.	Straw^4	0,3	1,2	2,8	4,8	1,8	2,3
15. 09.	Seeds^4	0,3	3,8	6,4	12,8	4,2	5,8

^{1}- at shooting, ^{2}- at 4-6 leaf stage
^{3}- at flowering, ^{4}- at harvest
Source: own construction

Although Pb showed only moderate enrichment in crops, it was near, or exceeded, the 0,5 mg·kg^{-1} limit values set in the Hungarian Standard (8/1995. (X. 21.) EüM) for winter wheat grain. There was no evidence of the effect of treatments. Pb concentration in corn remained at the same level, and Pb was not detected in sunflower grain (Table 6). Pb was immobile in the soil-plant system.

Table 6 Effect of increasing Pb loads on the Pb content of crops, mg·kg^{-1}

Sampling		Application rates mg·kg^{-1}				LSD$_{5\%}$	Average
date	part of crops	0	30	90	270		
			Winter wheat				
05. 05.	Shoot^1	0,5	1,7	2,6	3,0	2,7	2,4
31. 07.	Straw^4	0,8	1,0	1,4	4,3	1,1	1,9
31. 07.	Grain^4	0,6	0,4	0,7	1,1	0,8	0,7
			Maize				
07. 06.	Shoot^2	0,4	1,0	1,2	2,7	1,6	1,3
17. 07.	Leaf^3	0,1	0,1	0,6	0,9	0,9	0,4
08. 10.	Straw^4	1,1	2,1	2,6	2,0	1,0	2,0
08. 10.	Grain^4	0,1	0,2	0,3	0,2	0,4	0,3
			Sunflower				
24. 06.	Shoot^2	0,4	0,9	1,4	1,2	0,8	1,0
05. 08.	Leaf^3	0,2	0,3	0,2	0,6	0,4	0,3
15. 09.	Straw^4	0,1	0,3	0,3	0,6	0,4	0,3
15. 09.	Seeds^4	0,0	0,0	0,0	0,0	-	0,0

^{1}- at shooting, ^{2}- at 4-6 leaf stage
^{3}- at flowering, ^{4}- at harvest
Source: own construction

The Zn content in winter wheat shoots was not significantly affected by Zn treatments. Only the highest application rate caused significant Zn enrichment in winter wheat straw. Moderate Zn enrichment was observed in vegetative parts of maize and sunflower. Zn accumulation was expressed mostly in the grain by increasing doses. The Zn content in the control wheat grain was higher than the Hungarian standard values (30 mg·kg^{-1}). There was moderate Zn accumulation in maize, whereas treatments doubled Zn content in sunflower seeds as compared to the control (Table 6). Zn was also less mobile element in the soil-plan system, but its accumulation can be significant in grain.

Table 7 Effect of increasing Zn loads on the Zn content of crops, mg·kg^{-1}

Sampling		Application rates mg·kg^{-1}				LSD$_{5\%}$	Average
date	part of crop	0	30	90	270		
				Winter wheat			
05. 05.	Shoot^1	31	34	38	39	8	35
31. 07.	Straw^4	16	16	22	40	8	24
31. 07.	Grain^4	38	42	46	54	7	45
				Maize			
07. 06.	Shoot^2	37	49	74	80	20	60
17. 07.	Leaf^3	38	52	88	88	30	66
08. 10.	Straw^4	25	37	57	64	28	46
08. 10.	Grain^4	43	46	49	55	15	48
				Sunflower			
24. 06.	Shoot^2	42	54	61	66	12	56
05. 08.	Leaf^3	45	52	69	70	17	59
15. 09.	Straw^4	7	11	26	31	5	19
15. 09.	Seeds^4	42	52	49	87	8	58

^{1}- at shooting, ^{2}- at 4-6 leaf stage
^{3}- at flowering, ^{4}- at harvest
Source: own construction

Conclusions

The rates of transformation and fixation of toxic elements in the soil was different for different elements. The mobile contaminants (Cd, Zn, Pb, Cu) can be separated from those that are readily transformed into unavailable forms very quickly. Leaching of Cr, applied as Cr(VI) is a quick process on a slightly acid brown forest soil. Cr can be dangerous for the ground water, because of its quick vertical movement into the soil. There is no relation between the plant uptake and available/soluble element content of the soil. These are varied depending on microelements and crop plants.

Cd remains mobile in the soil-plant system for a long time. It accumulated both in vegetative and generative parts of plants with no observed toxic symptoms and yield loss. Pb can enter the vegetative and generative plant organs; however, accumulation does not increase with increasing concentration in the soil. Pb has low mobility in the soil-plant system; its plant-uptake is impeded. As apparently is not translocated into the grain even with very high concentration in the soil. Grain, as a generative organ apparently was protected against this micropollutant. Accumulation of Zn, which is an essential element, can be considerable in the grain.

Environmentally hazardous elements (Cd, As, Cr, Pb) accumulate mostly in the vegetative straw. Using appropriate management practices (e.g. incorporation of straw into the soil), it is possible to decrease the concentration of hazardous elements in the agronomic cycle. Pb is less mobile in the soil-plant system. The main source of the Pb pollution of crop plants is the areal deposition. Therefore cereals and corn production is suggested along the M-30 motor road and M-3 motorway. Vegetable production and maize growing for silage are not allowed. On the As- and Hg-contaminated soil production of cereals and corn is suggested because these metals are not translocated into the grain.

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