

CHANGES OF AVAILABILITY OF SOME MICROELEMENTS IN HEAVY METAL AMENDED SOIL

Lajos SZABÓ – László SZEGEDI

Department of Environmental Management and Agronomy
Károly Róbert College, H-3200 Gyöngyös, Mátrai str. 36., Hungary

Introduction

Environmental pollution is placing an ever-increasing load on various environmental resources, including soil. There is increasing interest in potentially toxic microelements and hazards related to heavy metals and environmental pollution (Szabó-Fodor 1998, Fodor 2000). The loading threshold values for soils is a function of the soil properties (pH, soil organic matter content, clay content, type of clay materials, etc.) (Kádár-Morvai 1998, Fodor 2002).

There are no universal solvents or methods that provide a satisfactory characterization of the exchangeable or plant available fractions of all harmful materials in various soil types. At the present time, the total content is used to estimate the level of microelement contamination (Fodor-Szabó 2003). As most microelements and heavy metals are strongly bonded to soil particles (minerals and oxides), the total content does not indicate the actual availability and/or mobility of elements. From physiological, ecological and hazard aspect, the more soluble fractions are more important (Fodor 1998, Fodor-Szabó 2003, Kádár et al. 2000). Our objective was to follow the changes of mobility of various microelements after heavy application rates to the soil.

Methods

A long term field experiment on microelement loading was initiated at Tass-pusztá Model Farm of the Károly Róbert College in November 1994. The experiment was designed as a split-plot, where the eight applied elements (Al, As, Cd, Cr, Cu, Hg, Pb, Zn) were the main plots and the three application rates (0/30, 90 and 270 kg element ha⁻¹) were the sub-plots. Water soluble salts of the above elements were mixed into the 20-30 cm cultivated layer of the soil. The soil textural class is clayey-loam with a bulk density 1,21 g cm³ (vertic cambisol). The main soil properties are the following: pH_(H₂O)=6,2; pH_(KCl)=5,4; γ_1 =9,5; no CaCO₃; 3% humus; upper limit plasticity (K_A)=45; 30-35% clay content).

Samples were taken from the upper horizon of the soil (0-30 cm) in 1995, 1996 and 1997. The soil samples were subjected to the NH₄-acetate+EDTA extraction solution to determine the amount of available elements. Total element content was also determined using the extracting solution cc.HNO₃+cc.H₂O₂. ICP AES was used to analyze the element concentration in the soil samples.

Results and discussion

Treatments increased the plant-available element concentrations significantly in the plow layer. Rate of 270 kg ha⁻¹ resulted in a more than 10-fold increase in concentration of exchangeable elements in tilled depth. The concentration increase was even more pronounced for Cd, Cr, As and Hg based on the soil tests conducted in 1995 (Table 1).

Table 1 Effect of treatments on the available element content in the ploughed layer

Element	in the control soil	Rate of application in the fall of 1994, mg kg ⁻¹			LSD _{5%}	Average
		1994, mg kg ⁻¹				
		0*/30	90	270		
<i>NH₄-acetate+EDTA extraction, mg kg⁻¹, 1995</i>						
Al*	127	119	156	188	24	148
Cu	7	22	32	98	24	40
Pb	6	18	35	96	32	39
Zn	7	24	58	75	25	41
Cd	0,2	13	37	117	35	42
As	0	14	38	98	29	38
Cr	0,2	2	5	12	4	5
Hg	0	3	4	17	4	6
<i>NH₄-acetate+EDTA extraction, mg kg⁻¹, 1997</i>						
Al*	110	113	110	126	14	115
Cu	7	9	25	47	10	22
Pb	6	12	23	36	8	19
Zn	7	16	20	37	6	20
Cd	0,2	8	22	43	12	18
As	0	0,2	7	14	7	5
Cr	0,1	0,1	0,3	0,7	0,2	0,3
Hg	0	0,1	0,3	0,6	0,2	0,3
<i>Available fraction as a percentage of the added amount, 1997</i>						
Al*	-	30	0	18	36	16
Cu	-	20	60	44	22	41
Pb	-	60	57	33	22	50
Zn	-	90	43	33	40	55
Cd	-	80	73	48	32	67
As	-	2	23	16	22	14
Cr	-	1	1	1	2	1
Hg	-	1	1	1	2	1

* 30 kg ha⁻¹ of Al was not applied. This plot received no application and served as the control for the Al application rates.

In two years the concentrations of elements extractable by NH₄-acetate+EDTA decreased significantly in the tilled layer. Chemical bonding in the soil was most pronounced with Cr and Hg, the NH₄-acetate+EDTA extraction of the following elements all decreased by the indicated amounts in these two years: As-85-90%, Pb and Cd-50-60%, and Cu and Zn-45-50%. Transformation rate of elements from that in the NH₄-acetate+EDTA extractable form to the less soluble forms was different for all elements.

It is considerable interest to examine the proportion of the elements that were present in the HN_4 -acetate+EDTA soluble form three years after application. Practically all of the Cr and Hg added in the soluble form were transformed into the in-soluble forms in the soil. Immobilization (bonding) of Al and As was also significant, averaged across all application rates only 16 and respectively, of the added material was detectable with this method. Between 40-60% of the Cu, Zn and Pb was extracted with NH_4 -acetate + EDTA, while more than 67% of the added Cd remained soluble to this extraction agent. It seems that this important micro-contaminant remains more soluble in the soil than other elements for a longer time. The NH_4 -acetate+EDTA soluble sequence of the element three years after application, based on the percent of applied elements, was: Cd, Zn, Pb, Cu, Al, As, Hg, Cr. The proportion of "total" and available concentration within a soil sample varied for the different elements (Table 2). Available Cr and Hg forms are rapidly transformed into insoluble forms in the soil. The soil test carried out in 1996 provided additional evidence of the higher solubility of Cd, Pb and Cu in the soil compared to the other added elements. The available Cd forms represented 85% of the "total" as compared with 64% Pb and 61% Cu. Exchangeable/soluble forms in proportion of the "total" expressed in percent gave the following series: 85% Cd, 64% Pb, 61% Cu, 33% Zn, 26% As, 8% Hg and 2% Cr.

Table 2 Results of soil analysis in the 0-30 cm layer of plots
with 270 kg ha^{-1} element load, 1996

Element	Total amount (mg kg^{-1})	Available (mg kg^{-1})	Available fraction (% of total applied)
As	75	19,9	26
Cd	90	76,6	85
Cr	101	2,2	2
Cu	82	49,9	61
Hg	39	3,3	8
Pb	46	29,4	64
Zn	150	49,2	33

Conclusions

The majority of microelements (micro-contaminants) that enter the soil accumulate in the upper 30 cm. The rate of transformation and bonding in the soil was different for each element. The proportion of exchangeable forms in the soil decreases with time, but the series based on NH_4 -acetate+EDTA extraction practically remains the same. The extractable contaminants (Cd, Zn, Pb, Cu) in the soil can be separated from those that are readily transformed into insoluble/non exchangeable, bonded forms (As, Hg, Cr).

References

- Fodor, L. (1998): Effect of heavy metals on wheat and maize crop on brown forest soil. *Agrokémia és Talajtan.* 47. 1-4.; p. 197-205.
- Fodor, L. (2000): Plant uptake of some micropollutants from contaminated soil. *Proc. of 11. Conf. of ISCO, Buenos Aires, Argentina.*
- Fodor, L. (2002): Nehézfémetek akkumulációja a talaj-növény rendszerben. Doktori disszertáció. VE Georgikon MTK, Keszthely, p. 141.
- Fodor, L. – Szabó, L. (2003): Mikroelemek a talaj-növény rendszerben. III. Növénytermesztési Tudományos Nap. Akaprint. Budapest. p. 163-167.
- Kádár, I. – Morvai, B. (1998). Effect of micropollutants on soil and crop on calcareous sandy soil. *Agrokémia és Talajtan.* 47. 1-4.; p. 207-214.
- Kádár, I. – Konecz, J. – Gulyás, F. (2000): Mikroelem-terhelés hatása a kukorica összetételére és a talaj könnyen oldható tápelemtartalmára karbonátos csernozjom talajon. *Agrokémia és talajtan.* 49. 1-2.; p. 205-220.
- Szabó, L. – Fodor, L. (1998): Investigation of mobility and availability of some heavy metals in field conditions. In. *Soil Pollution, Filep, Gy. Ed. Agricultural University, Debrecen,* p. 132-137.
- Kádár, I. (2004): Szennyvíziszap-adagok hatása a növény (*Triticum vulgare* L.)-talaj rendszer néhány mikrobiológiai és biokémiai tulajdonságára (Impact of sludge treatments on some microbiological and biochemical properties of plant (*Triticum vulgare* L.)-soil system. – in *Hungarian*). *Agrokémia és Talajtan.* 53. 3-4. 331-342 pp
- Svetková, K.; Henselová, M.; Morvová, M. (2005): Effects of a carbonization product as additive on the germination, growth and yield parameters of agricultural crops. *Acta Agron. Hun.* 53. (3). 241-250 pp
- Tanács, L., Matuz, J., Gerő, L., Petróczi, I.M. (2005): Effect of NPK Fertilizers and Fungicides on the Quality of Bread Wheat in Different Years. *Cereal Res. Commun.* 33 (2-3): 627-634 pp