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EXAMINATION OF HEAVY METAL ACCUMULATION IN THE SEDIMENTS AND PLANTS OF AN ACTIVE FLOODPLAIN NEAR THE RIVER TISZA

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ABSTRACT. Several sources of pollution can be found in the catchment area of the River Tisza and some of them significantly contribute to the pollution of the river and its active floodplain. In this paper the accumulation of four metals (Zn, Cu, Co, Ni) in soil and plant (*Zea mays, Urtica Dioica L.)* samples and their relations to the soil characteristics were studied near Gulács (Hungary). Since the metal availability is also an important factor, the Lakanen-Erviö (NH_4-acetate + EDTA) extractable metal content of the soil was also determined. Summarizing the results we can say that, considering the metal accumulation, the granulometric composition plays the most important role among the soil characteristics. Significant correlation was found between the acid-soluble and the Lakanen-Erviö extracted metal concentrations, but in most cases (Co, Cu, Zn) no connection was found between the easily soluble metal content and the concentrations accumulated by the plants. Regarding the land use more Co and Zn was found in the soil samples of orchards, but more Cu and Ni accumulated in the soils of ploughlands.

Keywords: River Tisza, active floodplain, metal uptake, *Zea mays*, *Urtica Dioica* L.

INTRODUCTION

The problem of soil contamination is increasing due to the human activities. Near the bank of the River Tisza and its tributaries, several mines and industrial plants can be found that can contaminate the water and active floodplain of the rivers. Mainly mining (barrows) and ore refining (the use of polluting technologies) cause the most significant environmental risk (Lakatos et al. 2003). One of the largest accidents occurred in 2000 when a great quantity of mine sewage got into the River Viso (and then to the River Tisza) from the ore refining plant of Baia Mare and Baia Borşa. The sewage was contaminated mainly with Cu, Pb and Zn. Moreover, this contamination occurred together with the flood of the River Tisza. Besides, contaminated slurry from mines is drained off from time to time, generally at the high-water stage of rivers and brooks so the diluted (even below the limit) contaminants get into the surface water bodies. Contaminants in water can appear in two different ways: (1) in dissolved state and (2) attached to suspended matters. Thus, dissolved contaminants can become diluted, and the concentration of suspended materials is also lower in higher river flows. However, the concentration of contaminants attached to colloidal particles can be very high and settling onto the active floodplain it can exceed the limit value concerning soils and sediments (Szalai 1998, Hum and Matschullat 2002, Braun et al. 2003, Szalai et al. 2005, Papp et al. 2007). The contaminants in soils do not cause significant harm while the pH of the soil remains alkaline. However, if the soil pH decreases, these metals can be mobilized, thus their bioavailability increases and getting into the food chain the living organisms can accumulate them (Papp and Kümmel, 1992). Some of these heavy metals are essential trace elements for plants but the excessive accumulation of them can be harmful and toxic for the living beings (Fodor, 2002). The traces of river pollution can be found in the sediment of the river bed or the active floodplain, and it can be proven that the contaminations in 2000 were not single cases (although they certainly resulted in high concentrations). In this paper we examine the heavy metal concentration (Co, Cu, Ni, Zn) in surface soil samples of the active floodplain of the River Tisza, near Gulács (Upper Tisza region). Furthermore, our aim was to study what metal concentrations plants (*Zea mays*, *Urtica dioica* L.) are able to accumulate.

MATERIALS AND METHODS

10 surface soil samples were collected from the active floodplain of the River Tisza near Gulács (approx. 701 river km, Fig. 1) in the summer of 2006. The samples derive from ploughlands and orchards (5-5 samples). They were taken from the depth of 0-25 cm and we homogenized 8-10 subsamples to make composite samples in order to decrease the errors originated from the microheterogeneity of soil. Furthermore, maize (*Zea mays*) from ploughlands and stinging nettle (*Urtica dioica L.*) from orchards were also collected in order to examine the metal uptake of these plants. *Zea mays* was chosen because of its common presence throughout the ploughlands (see the picture below) and *Urtica dioica L.* was the other species from orchards because, according to earlier experiments, it can be used as a biomonitor of bioavailable metal concentrations (Otte, 1991).

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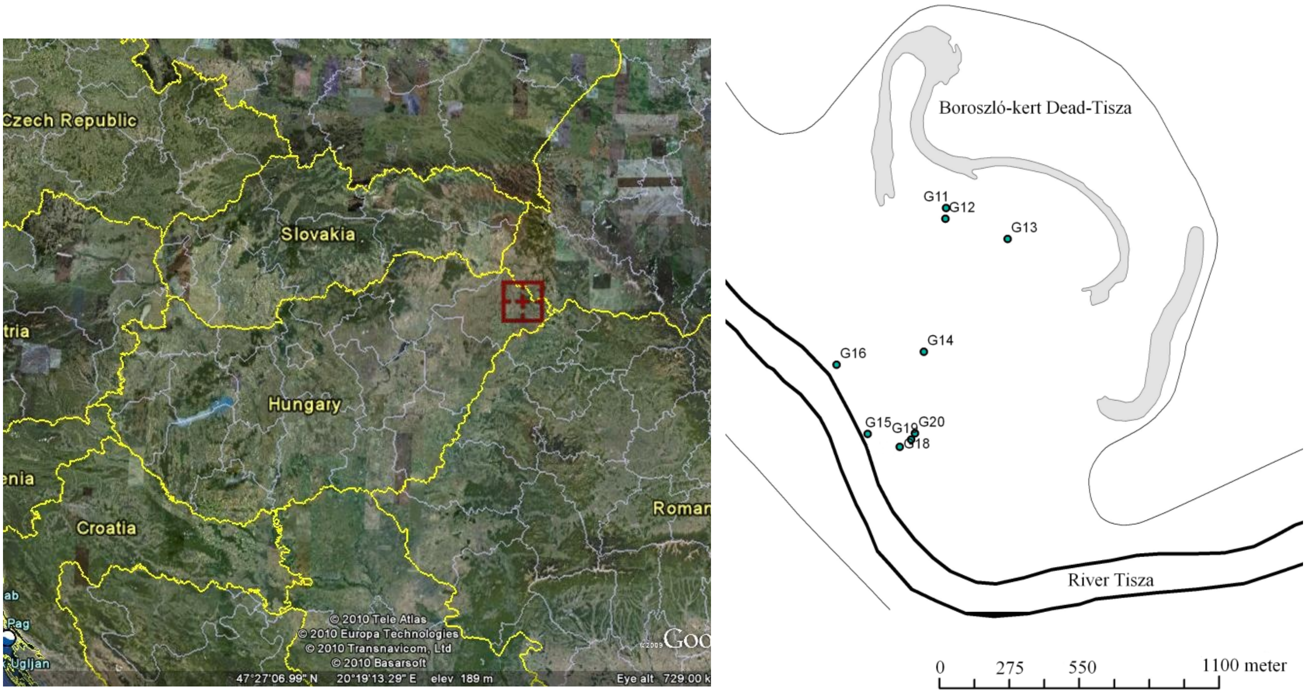

Fig. 1. The situation of the examined area and the sampling points of the Boroszlókert Dead Tisza region.
Legend: G11-20: surface soil samples; —: levee

A photo of the active floodplain near Gulács (Boroszló-kert Dead Tisza region)

The soil samples were cleaned from the organic matter pieces and were dried at 105 °C, then passed through a 2 mm sieve. Granulometric composition (with Köhn-pipette), humus content (after Tyurin's scheme) and active and potential acidity (pH_{H2O}, pH_{KCl}) of soil samples were determined according to the valid Hungarian standards (MSZ-08-0210:1977, MSZ-08-0205:1978, MSZ-08-0206-2:1978).

The metal content of soils was determined according to the MSZ-08-1722-3:1989 Hungarian standard (cc. HNO_3+H_2O_2 acid digestion).

Since the total metal content by itself does not give enough information about the dangers caused by metals, therefore in the case of surface samples the available concentration for plants was also determined with Lakanen-Erviö extraction (NH_4-acetate + EDTA, Lakanen and Erviö 1971).

The plant samples were washed with distilled water and they were also dried. Then, we separated them into root and shoot. The samples were digested with cc. $HNO_3+H_2O_2$ and the metal content of them was measured with an FAAS appliance.

All experiments (both with the soil and plant samples) were performed in triplicate and blanks were run simultaneously. The metal analyses were carried out with Perkin-Elmer 3000 FAAS instrument at the University of Debrecen, Department of Landscape Protection and Environmental Geography.

The data processing was executed with Microsoft Excel, and SPSS for Windows 16.0 was used for the statistical analyses. Since the distributions of the examined variables (Zn, Cu, Co, Ni) granulometric composition fractions, humus content, pH and $CaCO_3$-content) were normal, Pearson correlation analysis was carried out.

RESULTS AND DISCUSSION

Soil characteristics, such as pH, organic matter and clay content, significantly influence the metal content and its availability in soils (Salomons and Förstner, 1984). In Table 1 the characteristics of the soil samples can be seen. The samples are rather sandy-silty, the clay content is low. They have varied humus content and the pH values are slightly acid. $CaCO_3$ content is important in terms of the buffering capacity of the soils. It is observable that the samples from orchards contain less $CaCO_3$ therefore these soils have worse buffering capacity than the soils of ploughlands.

Table 1.

Characteristics of soil samples (means of 5-5 samples)

landuse	sand %	silt %	clay %	humus %	pH (H_2O)	$CaCO_3$ %
ploughland	40.0 ± 9.2	48.3 ± 7.4	11.4 ± 2.3	4.5 ± 1.5	6.82 ± 0.5	6.02 ± 0.4
orchard	45.4 ± 9.7	43.5 ± 8.6	11.0 ± 2.6	5.2 ± 1.6	6.94 ± 0.2	4.77 ± 0.2

The zinc content of the soil and plant samples

The **zinc** concentrations of the soil samples varied from 89.5 to 174.5 mg·kg^{-1}. Table 2 shows the mean zinc concentrations in the soil samples, split by the land use. This concentration is more than the background level but does not reach the critical contamination level (200 mg·kg^{-1}, joint decree no. 6/2009 KvVM-EüM-FVM).

The concentration of zinc extracted by the Lakanen-Erviö reagent is 5-10 mg·kg^{-1}, i. e. less than 10% of the acid-extractable concentration. The relative standard deviation of both is 18%.

It is observable in Fig. 1 that the zinc concentrations measured in the different plant organs exceed the concentrations of the Lakanen-Erviö solutions. Since zinc is an essential trace element and can be harmful only at high concentrations, plants can accumulate more zinc than the zinc content of the soil (Szabó, 2006). It also can be seen that maize accumulated more zinc than stinging nettle, on average (maize roots: 67.7 mg·kg^{-1}, 41.5 mg·kg^{-1}; stinging nettle roots: 22.3 mg·kg^{-1}, shoots: 19.6 mg·kg^{-1}). In the case of the maize samples the grain crop can also be the place of accumulation, but according to earlier investigations the distribution of zinc is constant in the different organs of maize plants so maize did not accumulate zinc in the crop (Szabó, 2000).

The copper content of the soil and plant samples

The mean concentration of **copper** in the soil samples is 53.1 mg·kg^{-1}, the most extreme value is 80.3 mg·kg^{-1}. In Table 2 the copper concentration of soil samples can be seen according to the land use. Similarly to zinc, this amount is also beyond the background level (30 mg·kg^{-1}) but does not exceed the contamination level.

The available copper content is varies between 5.2 and 11.5 mg·kg^{-1}. The relative standard deviation of both extractions is approximately 25%.

Examining the Fig. 2 it is observable that none of the plants or the plants' organs accumulated more copper than the Lakanen-Erviö extractable concentration. Comparing the plants, maize accumulated more copper, on average, and this plant accumulated more cooper in its roots (roots: 6.4 mg·kg^{-1}, shoots: 0.9 mg·kg^{-1}). It can be explained by the fact that sometimes plants can not transport the heavy metals from their roots to the other plant organs since these metals are often bound only to the surface of the cell walls (Szabó, 2008). However, the opposite is typical of the stinging nettle (roots: 0.9 mg·kg^{-1}, shoots: 4.6 mg·kg^{-1}).

Table 2

The Zn and Cu concentrations in the soil samples according to the land use (means of 5-5 samples)

Land use	Zinc (mg/kg)		Copper (mg/kg)	
	Total acid extractable	LE-soluble	Total acid extractable	LE-soluble
Ploughland	126.1	5.0	55.2	7.0
Orchard	153.8	10.1	51.0	10.3

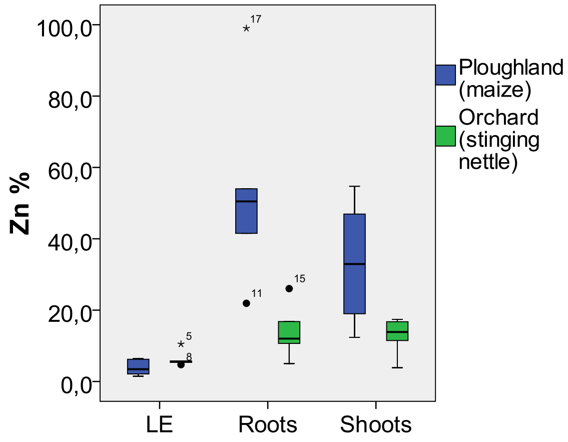

Fig. 1. The percentage of the Lakanen-Erviö soluble (LE) zinc and the zinc concentration of the plants' organs compared to the total acid-extractable zinc content of soils

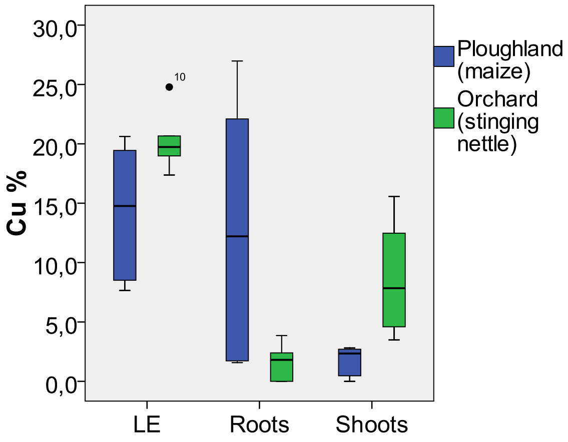

Fig. 2. The percentage of the Lakanen-Erviö soluble (LE) copper and the copper concentration of the plants' organs compared to the total acid-extractable copper content of soils

The cobalt content of the soil and plant samples

Similarly to the previous cases, the **cobalt** concentrations determined by us in the soil samples (Table 3) do not exceed the critical contamination level (30 mg/kg, according to the joint decree no. 6/2009 KvVM-EüM-FVM). The relative standard deviation of these data is the smallest (9%).

The easily soluble concentration of cobalt is less than 15% of the total metal content of the soil. The values are varied between 2.6 and 4.9 mg·kg^{-1}. Here, when the relative standard deviation does not correspond with that of the acid-extractable amounts (13%).

Regarding the plant accumulation (Fig. 3), both of the examined plants accumulated less cobalt than the Lakanen-Erviö soluble cobalt concentration. On average, maize accumulated a bit more cobalt (1.5 mg·kg^{-1}) than stinging nettle (1.1 mg·kg^{-1}) and higher Co concentrations were measured in the root of the examined plants than in the shoots.

The nickel content of the soil and plant samples

The mean concentration of the **nickel** measured in the soil samples is 75.8 mg·kg^{-1} (Table 3). Since the critical contamination level of nickel is 40 mg·kg^{-1} (joint decree no. 6/2009 KvVM-EüM-FVM), the concentrations measured by us can be considered as 'contaminated'.

The Lakanen-Erviö extractable metal content is less than 10% of the total acid extractable nickel concentration of the soil samples and the relative standard deviation of the data is 24%. Although the total Ni content of the soil exceeds the contamination level, it does not necessarily indicate potential danger to the living being since the available metal concentration is not that high.

The mean nickel concentration in maize is 3.9 mg·kg^{-1}, and in stinging nettle it is 4.2 mg·kg^{-1} (Fig. 4). It is observable that only maize roots accumulated more nickel than the Lakanen-Erviö extractable amount. However, stinging nettle accumulated more nickel in its shoots.

Table 3.

The Co and Ni concentrations in the soil samples according to the land use (means of 5-5 samples)

Land use	**Cobalt (mg/kg)**		**Nickel (mg/kg)**	
	Total acid extractable	**LE-soluble**	**Total acid extractable**	**LE-soluble**
Ploughland	20.0	2.8	78.0	3.6
Orchard	21.4	2.7	73.6	4.7

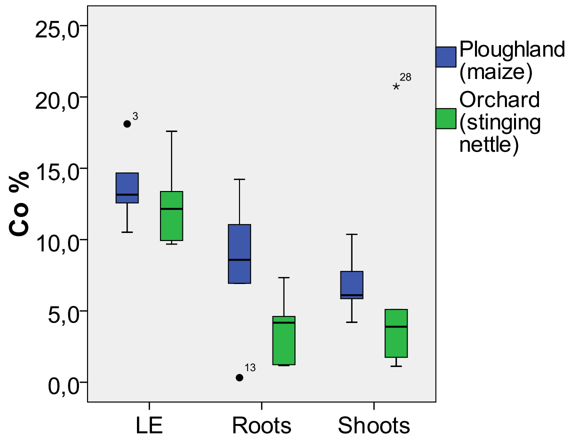

Fig. 3. The percentage of the Lakanen-Erviö soluble (LE) cobalt and the cobalt concentration of the plants' organs compared to the total acid-extractable cobalt content of soils

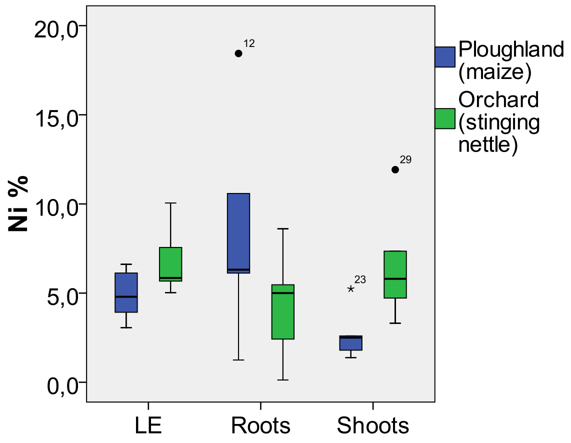

Fig. 4. The percentage of the Lakanen-Erviö soluble (LE) nickel and the nickel concentration of the plants' organs compared to the total acid-extractable nickel content of soils

Correlations - the connections between the metal concentrations and the soil characteristics

Since the distribution of the examined data was normal (according to the Shapiro-Wilks test), Pearson correlation was carried out in order to examine the correlation between the different data. The probability level of every given correlation coefficients is $p<0.05$.

Regarding the total metal content of the soil samples Zn and Co concentrations have positive significant correlation with the silt fraction of the soil (the coefficients are 0.78 and 0.75, respectively). However, these metals also have negative correlation with the sand fraction (Zn: r=-0.80; Co: r=-0.68). The specific surface of the sand grains is small so the metal adsorption is more difficult (Stefanovits et al. 1999). The best adsorption occurs on the surfaces of the clay minerals, but since our soil samples contain only a little clay, the silt fraction act as inorganic. Besides, Zn also has positive connection with the pH_{H2O} and the humus content of the soil (r=0.80 and r= 0.64). These correlations can be explained by the facts that the availability of the Zn depends on the soil pH and this metal is strongly attached to the humus materials of the soil (Szegedi, 1999). Earlier investigations reported that humus plays a significant role in the preservation of metals and the regulation of their uptake (Livens 1991). Considering Cu and Ni, no connection was found with the soil characteristics and the metals do not correlate with each other.

Examining the Lakanen-Erviö soluble metal content, Cu and Ni have positive significant correlation with the silt fraction (r=0.68 and r=0.78, respectively) and the humus content of the soil (the coefficients are 0.65 and 0.69). However, negative connection was found with the sand fraction in both cases of these metals. These results are also confirmed by the facts mentioned above. Besides, Zn has positive connection with the pH_{H2O} (r=0.69).

In this case we also found connection between the different metal concentrations. Cu strongly correlates with both Ni (r=0.84) and Zn (r=0.79) and the correlations are significant at the 0.01 level. This result proves that the adsorption of Cu antagonizes the adsorption of Zn (Sipos, 2004). Lakanen-Erviö extractable cobalt concentration does not correlate any of the metals or soil characteristics.

Considering the metal uptake of maize, two significant correlations were observed: the cobalt content of the maize has negative connection with the humus content of the soil (r=-0.89), but the Ni concentration of the plant correlates positively with the clay fraction of the soil (r=0.92). The cobalt concentration of the stinging nettle also has negative correlation with the clay fraction of the soil (r=-0.98) and the zinc concentration of the plant correlates with the pH_{H2O} positively (r=0.88).

Correlations - the connections between the metal concentrations of the soil and plant samples

In the case of ploughlands significant correlation was observed between the cobalt and copper content of the soil. The correlation coefficient is 0.89. Moreover, the Ni concentration of the maize correlates with the Co content of the soil and positive connection was also found between the Lakanen-Erviö soluble Ni and Cu content (r=0.94 and r=0.95, respectively). The correlations between Co and Ni can be explained by the fact that these two metals have similar physiologic characteristics; they can make chelates and displace other metals from important centres (Mengel, 1976).

Regarding orchards, the Cu concentration of the soil correlates with both the Zn content of the soil (r=0.97) and the Ni content of the stinging nettle (r=0.88). The copper content of the stinging nettle also has significant connection with the Ni concentration of the soil samples (r=0.94).

CONCLUSIONS

The different pollutions affect soils directly or indirectly. In the course of our work the heavy metal (Zn, Cu, Co, Ni) content of soil and plant samples was examined in the active floodplain of the River Tisza.

Summarizing the results we can say that the examined metal concentrations exceeded the contamination level only in the case of nickel. Examining the connections between the characteristics and the metal concentrations of the soil we found that the granulometric composition is the most determinant factor. The samples have little clay content thus silt fraction acts as inorganic colloid in these soils. Humus content also plays an important role in the metal adsorption, especially in the case of Cu, but we found correlation with this characteristic only in the case of Zn.

Lakanen-Erviö extraction was carried out in order to examine the plant available metal concentration of the soils. According to our results this easily soluble metal content did not exceed 20% of the total acid-extractable heavy metal concentration of the soils. These metal concentrations are higher in the orchards than in ploughlands, except Co, but the difference between the two land use types is not significant here.

Both of the examined plants accumulated more Zn than the Lakanen-Erviö extracted amount. In general, the roots of the maize (*Zea mays*) samples accumulated the most of the examined metals, but stinging nettle (*Urtica dioica L.*) accumulated more nickel, on average. Regarding the Cu and Co concentrations, the difference between the two plants is not significant.

Based on these results we can say that the examined plants are not hyperaccumulator species, the measured concentrations do not threaten the living organisms.

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