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MEASURE OF HEAVY METAL LOAD IN THE FLOODPLAIN OF THE RIVER TISZA

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Abstract: The quality of the River Tisza is significantly influenced by the industrial activity of Ukraine and Romania. The main problem is the heavy metal pollution which can be in dissolved form in the water or attached to colloidal particles in the sediments. In this paper an investigation of soil samples taken from the floodplain of the river was carried out. Surface samples were collected and profiles were created. As, Cd, Co, Cu, Ni, Pb and Zn concentrations were determined. The results show significant and continuous heavy metal load. ANOVA test was carried out and the metal concentration in the upper layer of the active floodplain is proved to be considerably higher than in the reclaimed side. Regarding copper and zinc, in addition to the total metal content, their percentage available for plants (Cu and Zn percentages measured in the Lakanen-Erviö solution) is also more in the active floodplain than in the reclaimed side (copper: 27%, zinc: 47%). Discriminance analysis can identify the location of the soil samples (correlate to the levee) with 92% accuracy. Soil profile shows increased heavy metal loads in the top layer of the soil and proved that the accident in 2000 was not the only pollution occurrence. Based on the results we came to the conclusion that the pollution comes constantly with the sediments from the over arm of the River Tisza and its tributaries.

Keywords: Tisza, floodland, heavy metals, accumulation, statistical analysis

1. Introduction

The different anthropogenic productive and social activities load our environment with various contaminations. A great quantity of pollutants can get into the environment especially in the course of industrial production. It often occurs that the wastes and by-products containing toxic materials in large quantities are not properly treated, namely without adequate technical protection the contaminants can get unlimited into the environment. The contaminations can occur in two ways: (1) continuous pollution in various concentrations; or (2) occasional pollution in high concentrations.

In this work the metal contamination of the sediments of the River Tisza was examined so in the followings contaminants getting into the surface water streams will be studied. These contaminants can occur in dissolved form and attached to colloidal particles transported in different quantities depending on the speed of the flow (i. e. the sediment transporting ability).

The River Tisza originates from Romania and, passing Ukraine, enters Hungary near Tiszabecs. Stepping out from the Carpathians, the morphological type of the river changes from upper- and middle-course type to lower-course type. This is an important information in addition to the fact that the River Tisza transports a great deal of floating sediment so contaminants can occur both in dissolved form and attached to the sediment. There are not considerable pollution sources in Hungary that can contaminate the river's water. However, near the bank of the River Tisza and its tributaries several industrial (mining and ore processing) plants can be found in other countries, their technical protection is not always adequate and, based on the accidents happened in the last few years, we can say that we should not keep these plants in mind only as potential pollution sources. In addition to the sudden, unexpected contaminations mentioned by the media, we should also take the minor pollutions into consideration. Metals can get into the water in dissolved form and attached to colloidal particles. During the floods metals attached to colloids are deposited. Thus the metal concentration is significantly influenced by the quantity of the deposited sediment during the flood and the percentage of the colloids. The quantity of the deposited colloids and the rate of the deposition depend on the flow rate. Sluggish stream is favourable for the accumulation and the plant coverage is also important since it increases the roughness and decreases the speed of flow (Szalai, 1998; Braun et al., 2003; Sándor and Kiss, 2009).

The metal pollution examination of the active floodplain of the River Tisza is not new, publications related to this topic can be found from the early years of the 1980s (e. g. Győri and Végvári, 1981; Black and William, 2001; Hum and Matschullat ,2002).

In this research examinations were carried out in a sample area of the Boroszló-kert Holt-Tisza region (near Gulács) – near the River Tisza. Our aim was to demonstrate how the transported sediments contaminated with metals affect the active floodplain compared to the reclaimed side and how effectively the higher concentration of the contaminants can be identified with high-resolution vertical sampling. Moreover, confirming the contaminations water quality data were analyzed to show contamination periods between 2003 and 2009.

2. Materials and methods

Water quality data were taken from Tisza Water Quality Warning System (TWQWS). The network consists of 4 measuring stations in the border sections of the River Hernád, the River Berettyó, the River Szamos and the River Tisza. The data of the monitoring station of Técső (River Tisza) were analysed in terms of the hygienic threshold limits.

In 2006 and 2007 91 surface soil samples were collected from the active floodplain of the River Tisza in Boroszló-kert (Fig. 1). The soil samples were taken from the depth of 0-25 cm and, homogenizing 8-10 subsamples, composite samples were made in order to decrease the errors originated from the microheterogeneity of soil.

High-resolution vertical sampling was also carried out: a 1-meter-deep profile was dug and sampled in every 2 cm (according to Ciszewski, 2003).

The majority of the samples (71) derive from the active floodplain and 20 samples were collected from the reclaimed side (Fig. 1).

The soil samples were dried at 40 °C and then passed through a 2 mm sieve. The granulometric composition (with Köhn-pipette), the humus content (after Tyurin’s scheme), the $CaCO_3$-content

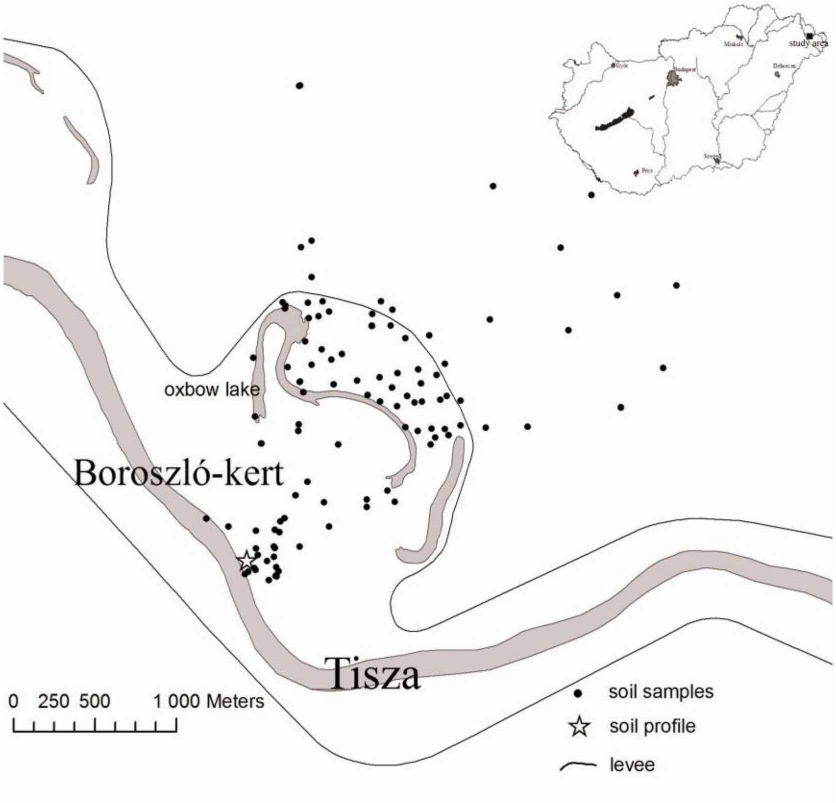

Fig. 1. The locality of the soil samples in the Boroszló-kert Holt-Tisza region.

(with calcimeter, Scheibler method) and the active and potential acidity (pH_{H2O}, pH_{KCl}, y_1, y_2) of the soil samples were determined according to the valid Hungarian standards (MSZ-08-0210:1977, MSZ-08-0205:1978, MSZ-08-0206-2:1978). The humus quality was measured based on Hargitai's method (1981): absorbances of 1% NaF (E_{NaF}) and 0.5% NaOH (E_{NaOH}) extracts were measured at 533 nm (with spectrophotometer).

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) with FAAS and ICP-OES. Analyses of the surface samples were carried out with Perkin-Elmer 3000 FAAS appliance (Co, Cu, Ni, Zn) at the Department of Landscape Protection and Environmental Geography (University of Debrecen). The samples from the soil profile were analysed for the same elements as well as As, Cd and Pb at the Central Chemical Laboratory of the Centre of Agricultural Sciences (University of Debrecen). Detection limits are shown in Table 1.

Table 1. Detection limits of the applied methods.

	Detection limits	
Elements	ICP-AES	FAAS
As	12.0 μg/l	300.0 μg/l
Cd	1.5 μg/l	2.0 μg/l
Co	5.0 μg/l	5.0 μg/l
Cu	2.0 μg/l	3.0 μg/l
Ni	5.5 μg/l	10.0 μg/l
Pb	14.0 μg/l	10.0 μg/l
Zn	0.9 μg/l	1.0 μg/l

Total metal content by itself does not give enough information about the dangers caused by metals since they are available for plants to a different extent depending on their form of occurrence. Therefore, in the case of surface samples the available quantity for plants was also determined with Lakanen-Erviö extraction (NH_4-acetate + EDTA, Lakanen and Erviö 1971).

During the data processing the normal distribution of the data was analysed with D'Agustino test. Variance analysis (ANOVA) and discriminance analysis were carried out. Regarding the data of the soil characterizations the distribution is not normal; therefore Mann-Whitney test was applied. TANAGRA software and SPSS for Windows 15.0 were used for the analysis. The data were visualized by C2 (Juggins, 2003) and ArcGIS 9.0 software.

3. Results and discussion

3.1. *The heavy metal load of the River Tisza by the industrial activity*

Regarding the dissolved metal content the data of the Tisza Water Quality Warning System station in Técső proves the facts described above in the introduction. In this station the dissolved zinc, copper, lead and cadmium content are measured and the data are available from November, 2003 to December, 2009. In this period the measured metal content exceeded at least four times both the warning and the alarming limit values (Table 2): between 21 November 2003 and 14 December 2003; between 9 October 2004 and 15 November 2004; in 3 December 2005; between 2 March 2006 and 17 April 2006. The pH values were under 5.5 (normally they are above 7.2) from 4 May 2008 to 25 June 2008 – heavy metal measurements were not carried out in this period. Since the measurements (because of technical reasons) are not constant, the limit values could often be exceeded.

Table 2. Values of warning and alarm limits in the TWQWS at Técső.

Element	Values of	
	warning (μg/L)	alarm (μg/L)
Zn	600	1800
Cd	10	30
Pb	200	600
Cu	200	600

3.2. *Physical and chemical properties of the soil*

There is no significant difference in the sand content and the amount of polymerized humic acids (E_{NaF}) between the two sides of the levee. However, significant difference was found in the values of silt and clay content, humus content, the amount of the short carbon chain humic acids, humus quality and pH_{H2O} regarding the two side of the levee (Table 3).

The percentages of the sand and silt fractions are the most considerable ones in the granulometric composition of the sediment. The effect size is average (approximately r=0.3 – see Field 2009) both in the cases of the silt and the clay fraction but extremely significant differences (i.e. the effect of

Table 3. Soil properties and the results of Mann-Whitney test.

Soil properties	Situation	Lower quartile	Median	Upper quartile	Mann-Whitney's U	Effect size (r)
Sand content (%)	floodland	31,2	38,9	47,9	619,5	-0,09
	reclaimed side	32,1	42,3	56,7		
Silt content (%)	floodland	43	48,5	56,8	452,5	-0,26
	reclaimed side	33,8	43,6	50,3		
Clay content (%)	floodland	9,1	10,9	12,9	418,5	-0,29
	reclaimed side	10,3	13,4	17,3		
Humus (%)	floodland	3,2	4,1	5,3	295	-0,33
	reclaimed side	4,9	5,3	5,7		
E(NaF)	floodland	0,25	0,33	0,52	206	-0,12
	reclaimed side	0,16	0,32	0,56		
E(NaOH)	floodland	0,13	0,19	0,28	500	-0,46
	reclaimed side	0,29	0,41	0,61		
Humus quality	floodland	1,41	1,85	2,81	228	-0,46
	reclaimed side	0,37	0,83	1,4		
pH(H_2O)	floodland	6,7	7	7,4	68	-0,64
	reclaimed side	4,9	5,3	5,7		
$CaCO_3$ content (%)	floodland	1,5	2,4	3	-	-
	reclaimed side	0	0	0		

the levee is not noteworthy considering the granulometric composition) are not expected since, before the river regulations, the granulometric composition of the sediment was determined only by the distance from the river (farther from the river bank finer sediments were deposited) and the intensity of the floods. This pattern was also influenced by the shifting of the river channel. However, after the construction of levees and the cut-offs (see the oxbow in Fig. 1) closer to the channel coarser sediments but closer to the levee finer sediments were deposited. The areas outside the levee were always farther from the channel so the sediments are finer there. This also has effects on the chemical linkage of the metals since fine particles as inorganic colloids play an important role in the metal adsorption (Stefanovits et al., 1999). Due to the intensive agricultural activities in the reclaimed side, there is more humus - as organic colloids (Szabó, 2000; Filep, 1999; Farsang et al., 2007) – in the active floodplain than outside the levee. This is proven by the higher concentration of the short carbon chain humic acids. It is important also because the humus quality of the Fluvisols in the active floodplains is generally unfavourable (Stefanovits et al., 1999) but we have got better results in our samples. The pH and quantity of the $CaCO_3$ can be the explanation: the calcareous sediments of the active floodplain result in higher pH (Table 3) and make more advantageous conditions for humification. On the other hand, another factor also affects the pH and the humus quality of the soil: the draining capability of the soil can be improved due to the tillage of the agricultural areas. Thus the leaching is also more intense, which leads to the decrease of the pH and results in the humus of poor quality. The most definite effect size occurs in the case of the pH.

3.3. Heavy metal content of the surface samples

Analyzing the surface soil samples we can get information about the root zone of the plants. The measured metal concentrations are shown in Table 4.

Table 4. The total acid extractable and the Lakanen-Erviö extractable (LE) metal content of the samples from the active floodplain and the reclaimed side (mean ± standard deviation).

Element	Active floodplain	Reclaimed side
Co-LE (mg/kg)	6.7±1.0	4.9±0.8
Co (mg/kg)	18.9±2.7	16.3±2.1
Cu-LE (mg/kg)	15.6±5.8	7.24±1.1
Cu (mg/kg)	32.9±8.3	19.3±4.0
Ni-LE (mg/kg)	10.3±1.3	8.5±1.5
Ni (mg/kg)	46.1±6.9	38.3±7.4
Zn-LE (mg/kg)	15.5±9.8	7.5±6.7
Zn (mg/kg)	118.4±24.2	84.3±30.1

According to the result of the variance analysis zinc, copper and nickel concentrations are higher in the upper 25 cm of the soil in the active floodplain than in the cases of the control samples from the reclaimed side (Fig. 2-3). Regarding copper and zinc, in addition to the total metal content, their percentages available for plants are also more in the active floodplain than in the reclaimed side (copper: 27%, zinc: 47% more). This can be explained by the fact that the metals are bound to the soil particles in different chemical forms inside and outside the active floodplain. Inside the active floodplain metals are more easily mobilizable and can be accumulated in plants and get into the food chain – in close correlation with the different soil characteristics (pH, humus quality – see above). Regarding the samples from the active floodplain and the reclaimed side discriminance analysis was carried out with zinc, cobalt, copper and nickel as independent variables. After excluding the outstanding values, we can estimate from the results with 92% accuracy ($p<0.01$) whether the sample is from the active floodplain or the reclaimed side (Table 5). The order of the metals based on the structure matrix (Pearson correlation coefficient matrix) values is the following: copper (0.978), zinc (0.703), nickel (0.547) and cobalt (0.444). (As our unpublished results show, the high amount of zinc comes to Hungary by the River Túr where we found 400 mg/kg Zn in the floodplain soil.) Therefore copper and zinc concentrations are very significant in the function and the other two metals are certainly subordinated but their participation in the examination is reasonable since they increase the accuracy of the estimation. Based on the canonical correlation coefficient (0.746) the function explains 55% of the variance of the independent variable.

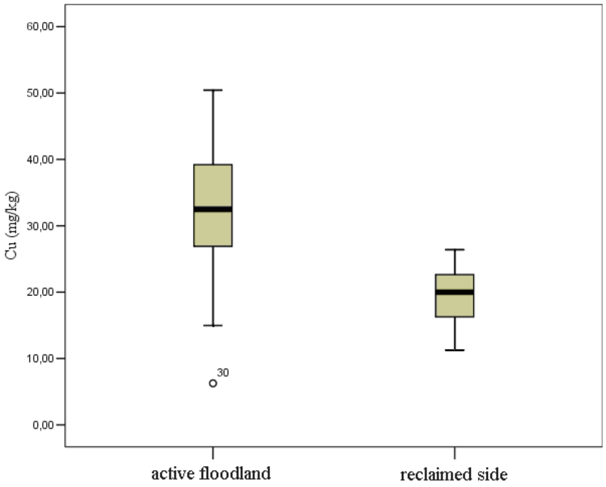

Fig. 2. The copper content of the samples from the floodplain and the reclaimed side (mg.kg^{-1}).

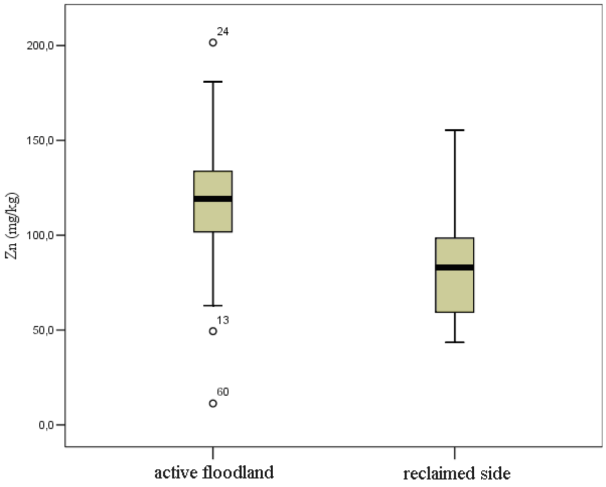

Fig. 3. The zinc content of the samples from the floodplain and the reclaimed side (mg.kg^{-1}).

3.4. Heavy metal content in the soil profiles

The analysis of the profiles made the examination of the vertical distribution of the pollutions possible. In Figure 4 the arsenic, cadmium, lead, copper, zinc, nickel and cobalt concentrations of the soil profiles can be seen.

The elemental analysis proves that the accident in 2000 was not the only contamination (Fig. 4). Gamma spectroscopic analyses (Dezső et al., 2009) showed that the ^{137}Cs isotopes, got into the atmosphere by the Chernobyl disaster in 1986 then fallen out, can be found now in the depth of 26 cm in the soil profile (Fig 4/A-line); therefore, the sedimentation rate is approximately 1-1.2 cm/year in this locality of the active floodplain. The highest metal concentrations were measured in this layer – deposited during the last 20 years – and it is exactly the same layer as the plants' root zone. In the cases of As and Cd the limit values (contamination limit value according to the joint decree No. 10/2000; vertical grey line shows the concerned elements in Fig. 4) were exceeded remarkably and the concentrations of the copper, nickel and zinc also approach the limit value. The highest Pb concentration (63 mg/kg) exceeds the background value (25 mg/kg) but does not reach the contamination limit (100 mg/kg). The situation is similar regarding Co: the contamination limit value is 30 mg/kg but all the measured values in the profiles are below 20 mg/kg.

Concerning the essential metals, high metal concentrations in the sediments of active floodplains do not cause problems, we should reckon with deficiency instead (especially in cultivated agricultural areas). However, the concentration of the toxic As and Cd exceeds the limit value, and this is very disadvantageous in terms of the floodplain farming but arsenic is not mobilizable in the soil-plant system (Kádár and Pálvölgyi, 2005). If soil contains humus of good quality, cadmium is bound in insoluble chelates (Livens, 1991; Szabó et al.,

Table 5. The classification table of the discriminance analysis

			Estimated group membership		
			Active floodplain	Reclaimed side	Total
Original	pc	Active floodplain	57	3	60
		Reclaimed side	3	17	20
	%	Active floodplain	95	5	100
		Reclaimed side	15	85	100
Cross-validated	pc	Active floodplain	57	3	60
		Reclaimed side	4	16	20
	%	Active floodplain	95	5	100
		Reclaimed side	20	80	100

92.5% of original grouped cases correctly classified.
91.3% of cross-validated grouped cases correctly classified.

2008a). In the examined floodplain the polymerized long carbon chain humic acids dominate thus either cadmium can not pose any threat. In the course of our examination considerable metal accumulation of plants was not experienced but these examinations are not completed.

4. Summary

At least 4 significant pollution periods can be identified by analyzing the data of the station in Técső so in addition to the well-known contaminations the river is relatively often contaminated by heavy metals. The examination of our samples revealed that the metal concentration is significantly higher in the upper layer of the soil in the active floodplain, and the percentage available for plants is also higher here than in the reclaimed side. Based on the analysis of the soil profiles we proved that sediments contaminated with heavy metals are continuously deposited into the active floodplain. The quantity of the deposited sediment and the metal concentration in the layers depend on the characteristics of the flood: how large area is flooded by the water, what the rate of the flow is in the floodplain and how long the flood lasts. The flow rate is also important in terms of the sediment composition thus the vegetation coverage can also increase indirectly the metal concentration attached to the clay fraction. The effects were shown by the examination of the soil profile.

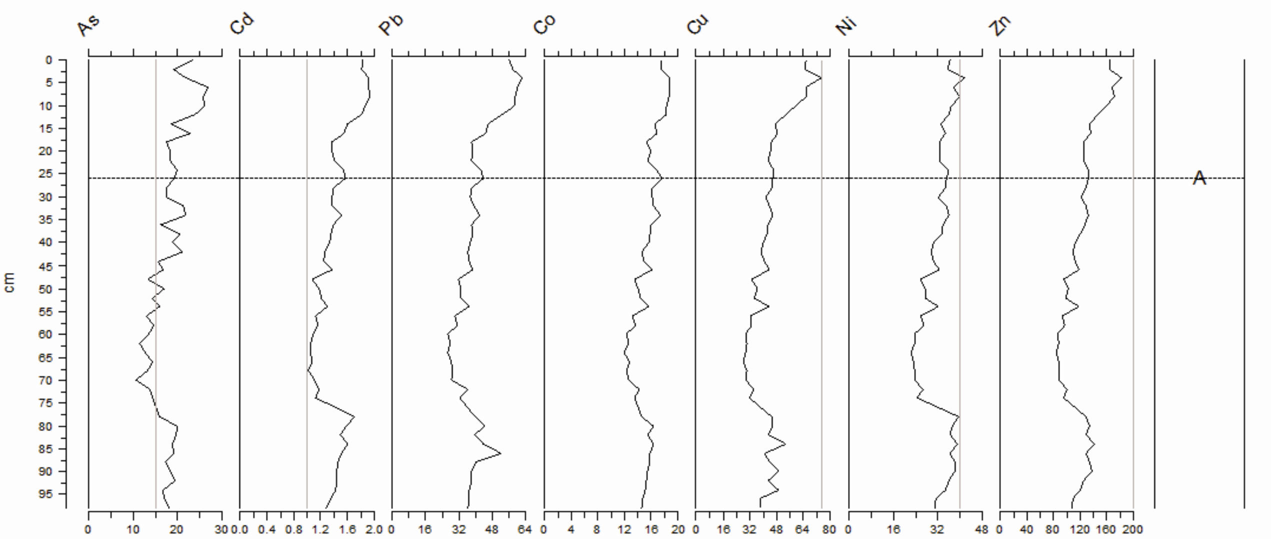

Fig. 4. The metal distribution of the soil profile regarding the arsenic, cadmium, cobalt, copper, lead, nickel and zinc (mg.kg^{-1}).

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