STUDY OF HEAVY METAL POLLUTION OF THE UPPER-TISZA FLOODPLAIN USING XRF TECHNIQUES

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ABSTRACT. The increased level of heavy-metals in the sediments of floodplains is strongly related to the Romanian metalwork. Different heavy metals (eg. Cu, Zn, Pb) often accumulate in the silt of the ore spoil bank and they can become a serious source of environmental pollution. In this study the heavy metal content of the floodplain of the Tisza-Kraszna crossing was determined with the help of energy-dispersive X-ray fluorescence spectrometry (ED-XRF), and particle induced X-ray emission (PIXE) method. Cu and Zn concentration values were compared with data obtained from Flame Atomic Absorption Spectrometry (F-AAS). The depth profile of the sampling territory was determined for Cu, Zn, and Pb concentrations. We carried out toxicological experiments with *Synapis alba* germination and root elongation to decide how the exceedance of the limit of geological agent affected the vegetation.

Keywords: heavy metal content, PIXE, ED-XRF, F-AAS

INTRODUCTION

The Tisza origins in the Northeast-Carpathians, as a left-side feeder of the river Danube, and it passes the territory of Ukraine, Hungary and Serbia. The river crosses the Hungarian border at Tiszabecs. Leaving the Carpathians, the characteristic of its first stage changes and in Hungary the stage of the river can be characterized medium and low. Because of the increased amount of floating sediment the Tisza performs a significant accumulation activity at its Hungarian section. Contamination can be presented as permanent contamination and there are sources that pose continuous, potential threat mainly because of bypassing the rules of environment protection. For example the metalwork in Baia Mare and Baia Borsa are such sources; these were responsible for the notorious cyanide contamination and heavy-metal pollution that happened several years ago (Szabó et al., 2008).

The increased levels of heavy-metals in the sediments of floodplains are strongly related to the Romanian ore mining and processing. Different heavy metals (Cu, Zn, Pb etc.) are often accumulated in the silt of the refused ore and they can become a serious source of environmental pollution. Heavy metals are released into aquatic and soil environments due to various anthropogenic activities and pose a serious threat to plants, animals and even human beings because of their bioaccumulation, nonbiodegradable properties and toxicity even at low concentrations (Rabnecz et al., 2007). The plants of contaminated areas can mobilize and uptake the heavy metals without showing any syndrome of metal toxicity, and they can get into food chains. (Keresztúri et al., 2008, Csatári et al., 2009)

The aim of the study was to observe the heavy metal load in the floodplain of the Tisza-Kraszna estuarine region beside Vásárosnamény. Cu, Zn and Pb concentration depth profile of the sampling territory was determined. Based on this study we got information about the degree and type of heavy-metal pollution. For the elemental analysis of sediments and other environmental samples usually flame-atomic absorption spectrometry (F-AAS) or ICP-AAS techniques are used (Djingova, 2000). In this study we introduced energy-dispersive X-ray fluorescence spectrometry (ED-XRF) for sediment analysis.

ED-XRF is a very efficient and widely used method in the determination of elemental composition. The method is non-destructive, sensitive, multielemental and the sample preparation is simple, inexpensive (Bacsó, 1998). The investigation and development of ED-XRF method began in the ATOMKI-HAS in the 1970's (Kis-Varga, 1976). In order to control the ED-XRF results F-AAS technique was also used. The F-AAS is a destructive, very sensitive and one elemental technique. We could also compare the differences between a non-destructive and a destructive tecnique (Somogyi, 1997) by using both types of methods. We compared the mass and trend of data, which we got from the two methods.

In addition toxicological experiments with *Synapis alba* germination and root elongation were carried out to decide how the exceedance of the limit of the geological agent (KöM-EüM-FVM-KHVM joint decree 6/2009) affected the vegetation and how we should rely on toxicity.

MATERIALS AND METHODS

Our samples were taken from the Tisza-Kraszna floodplain near Vásárosnamény in 10.10.2007 (Chart. 1). On this territory the Tisza and the Kraszna deposit a significant amount of sediment that varies in space. The UG4SZ soil profile is located on the left side of the Tisza 560 m far from the current riverbed and 120 m from the current line of the Kraszna. EOV coordinates were: x=893630, y=314960. The main wall of the segment was greyish brown and genetically belonged to the Fluvisols. The upper layer of the profile had aggregated structure and the lower was homogeneous and structure-less.
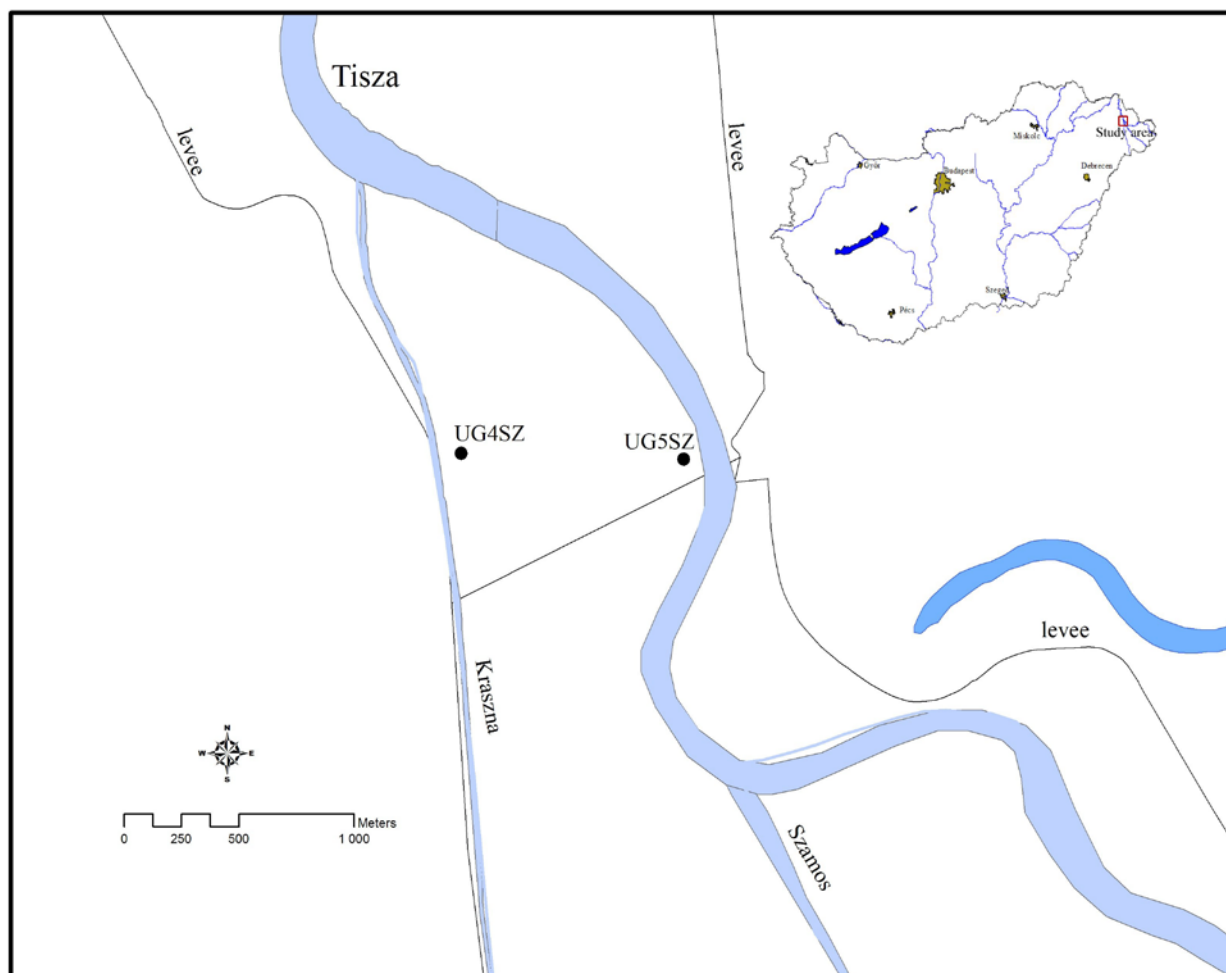

Chart 1. Location of soil profiles

The UG5SZ soil profile was located on the left side of the Tisza 70 m from its current line. EOV coordinates were: x=894805, y=314453. At the time of sampling the segment was 20 meters far from the river Tisza. This in turn, basically influenced the vegetation coverage too. The main wall of the profile was greyish brown and genetically belonged to the Fluvisols. It was homogeneous towards the bottom of the profile without visible layers. The structure of it was aggregated and tabular.

The ideal sampling area should not be covered with water permanently but if the river floods, it had to be covered because of the forming of new sediments and the consolidation of heavy metals. Moreover it is also necessary to be prevented from disturbance and from ecological activities that could contribute to the accumulation of heavy metals in the soil.

The samples were taken from two soil segments. We sampled a 1m deep profile from the surface at every 2 cm with the use of a slick-spoon. We obtained 0.25 kg of sample from each depth. All together 25 layer-samples were analysed. The next phases of sample preparation were done in the laboratory of a DE-ATOMKI- Department of Environmental Physics. We transported the sample to the laboratory and let them to dry at room temperature. After this we made pulverizing process in a mortar. We grinded the sample in a ball grinder mill for 5 minutes. With this method particle size below 5 μm was achieved, thus we could reduce the particle size effect. We took out 650 ± 100 mg from the grinding sample and we prepared pellets with 10 mm diameter and 0,850 g/cm^2 layer thickness. The size was determined according to saturation sample thickness requirement of X-ray fluorescence

analyses. We prepared 2 pastilles from each sample in order to minimise the measurement error, and some ore to the analysis of homogeneity. 108 pastilles were prepared altogether. The measurement of the pastilles was made by the ED-XRF equipment in the DE-ATOMKI on 30 kV anode potential and on 0.4 mA anode current with 1800s measuring time.

The light element content of the matrix (C, O, Si, Mg, Al, K, Na, Fe) was determined by particle induced X-ray emission (PIXE) techniques. The PIXE analysis was performed at the nuclear microprobe facility of ATOMKI-HAS (Rajta, 1996). A focused 2 MeV proton beam which was obtained from the 5 MeV Van De Graaf accelerator was used for the measurements. The bio-PIXE set up (Kertész et al. 2005) was used, which was developed for the analysis of biological and environmental samples (Kertész et al, 2009). The setup includes two Si(Li) detectors with which the simultaneous measurement of X-rays originating of light (C-Fe) and heavy (Ca-U) elements is solved (Uzonyi et al. 2001). In order to check the reliability of the XRF measurements the elemental content of some pastilles was determined by bulk-PIXE using the PIXE setup at the 45° beam line of the VdG accelerator (Kertész et al, 2010).

For the quantitative analysis of ED-XRF we used the AXIL evaluation software with the Elemental Sensitivity Module. The evaluation of PIXE spectra was made with the help of PIXEKLM program package (Szabó, 1993, Szabó, 2009). We determined the concentration of the following elements: K, Ca, Ti, Cr, Mn, Fe, Cu, Zn, As, Sr, Y, Zr, Pb.

F-AAS study was made at University of Debrecen, Department of Landscape Protection and Environmental Geography. For the measurements 30ml solution was prepared from the samples. 2 grams of each samples was used. The excavation was performed according to the MSZ-08-1722/3- 1989 Hungarian standard with the use of $H_2O_2+HNO_3$. After that we determined the Co, Cu, Ni and Zn elements from soil solution with Perkin-Elmer 3000 F-AAS instrument.

The samples were prepared to the toxicology test after the regulation of the Hungarian National Standard regarding to the F2 biological analyzing toxicology examination prescription. We were working with the samples prepared for the ED-XRF analysis. The samples were shake-mixed with sterile tap water in 1:10 mass balance on a GFL 3015 shooking-gear. Then it was left to settle. We determined the conducting ability and the pH of it on a CONSORT C853 appliance, since the complete salt content could influence the outcome of the test, so we proceeded with extreme care. The samples were centrifuged in an IEC CENTRA MP4 set for 5 minutes on 3000 rpm. Right after it the samples were strained on a filter paper, and the filtrate was used to the test. 3 ml was taken with a pipette from the filtrate mentioned above and then it was poured on a filtrate paper put in a Petri-dish. The test was adjusted with 30 *Synapses alba* germination and root elongation.

RESULTS AND DISCUSSIONS

The average concentration values of heavy metals of the sampling territories obtained from the three different methods are presented in Table 1.

The average heavy-metal concentrations of the 2 sampling territories in mg/kg

		Cr	Mn	Fe	Ni	Cu	Zn	Pb	Sr	Zr	As	Y
ED-XRF	**UG4SZ**	390	1130	47400	*	92	288	118	126	200	25	32
	UG5SZ	430	1540	49000	*	141	514	186	140	230	40	33
F-AAS	**UG4SZ**				62	53	230					
	UG5SZ				70	85	330					
PIXE	**UG4SZ**	116	1011	51813	61	96	371	72	130	208	39	*

The UG5SZ soil profile had higher heavy metal concentration values than the UG4SZ soil profile. We could not estimate the accumulation velocity and distribution of the colloid part because of the complicate hidrology and plant(vegetation) system of the sampling area. However, we could suppose, that the cause of the higher heavy-metal concentration value of the UG5SZ soil profile was the smaller distance to the River Tisza.

We established the depth profile of the UG4SZ and UG5SZ soil sections for the Cu, Zn, Pb elements on the basis of ED-XRF, PIXE and F-AAS results. The results are shown in figure 1 and 2. The vertical axis is the depth in centimetres and the horizontal axis is the concentration value in mg/kg unit. On the figures the red broken line indicates the threshold limit of the geological medium (based on KöM-EüM-FVM-KHVM joint decree 6/2009 Cu-75 mg/kg, Zn-200 mg/kg, Pb-100 mg/kg). The error of the ED-XRF and PIXE is 5-10 per cent, depending on the element.
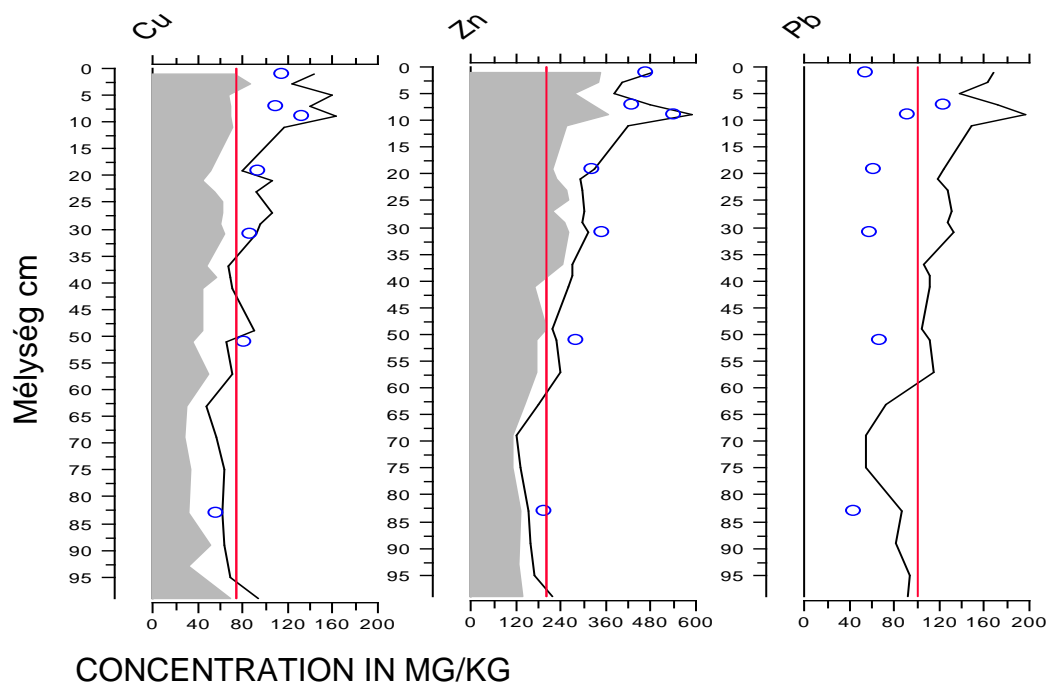
Fig. 1 Depth distribution of UG4SZ's soil profile according to ED-XRF (black line), FAAS (grey silhouette) and PIXE (blue circle) results of Cu, Zn, Pb elements

Based on the depth distribution (Fig. 1) of Cu, Zn, Pb we could conclude that in the case of UG4SZ's soil profile their the heavy metal concentration in the upper 50-60 cm layer is higher than the threshold limit. In the case of the F-AAS analysis concentration values exceeding the limit could be found in 0-40 cm in for Zn and 3 cm in the case of Cu. The highest concentration values were found in the upper 10 layers.
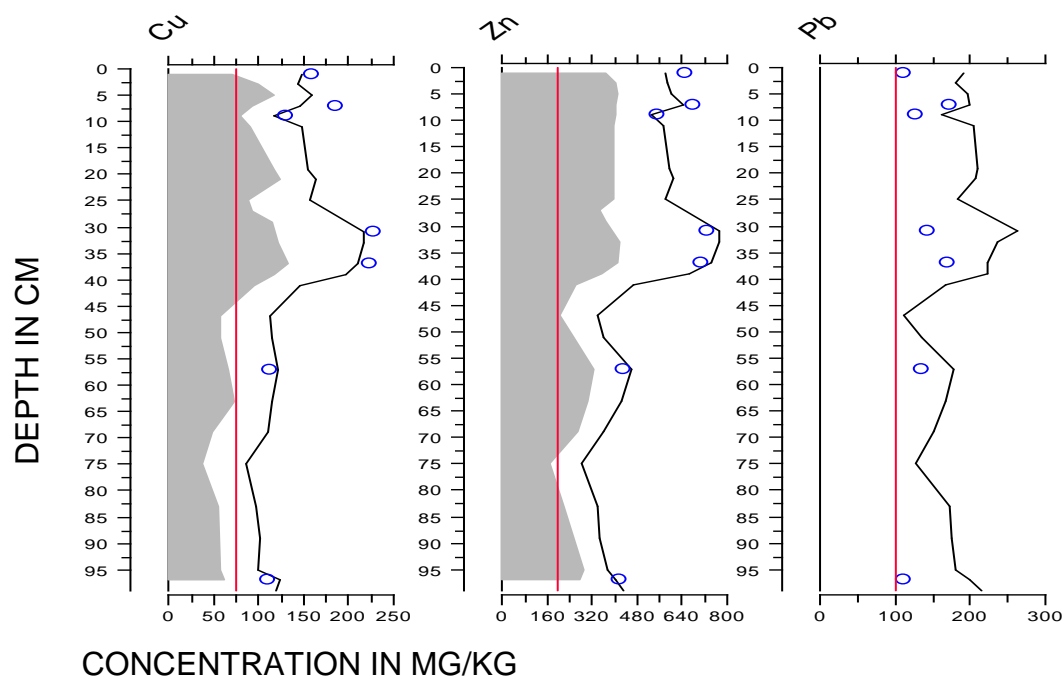

Fig. 2 Depth distribution of UG5SZ's soil profile according to ED-XRF (black line), FAAS (grey siluet) and PIXE (blue circle) results of Cu, Zn, Pb elements

Based on ED-XRF results in the case of Cu, Zn, Pb elements the concentration values exceeded the threshold limit in the whole UG5SZ segment. The F-AAS results showed that the highest concentrations were in the upper 45 cm. Moreover we could observe one marked peak in the depth profile of all elements in the 30-40 cm depth. In order to determine the origin of Cu, Zn and Pb pollution correlation analysis were made on the ED-XRF data (Fig. 3; see Fig. 2).
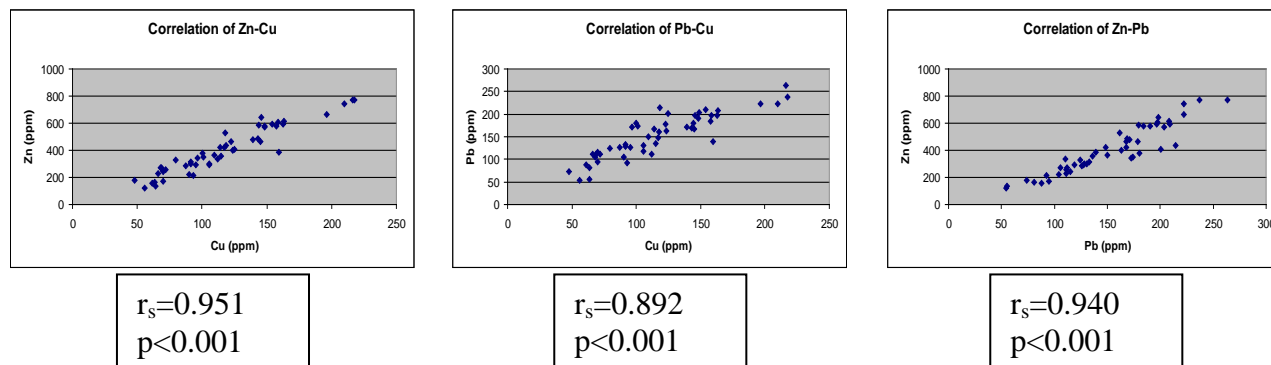

Correlation of Zn-Cu
$r_s=0.951$
$p<0.001$

Correlation of Pb-Cu
$r_s=0.892$
$p<0.001$

Correlation of Zn-Pb
$r_s=0.940$
$p<0.001$

Fig. 3 Correlation between of Cu, Zn, and Pb elements
(Spearman's Rhos and significant levels are reported inside the frames).

The connection between Cu, Zn and Pb concentrations was proved to be very strong (correlation coefficients were 0.951, 0.892, 0.940 on the $p<0.001$ significant level). On this bases we could suppose, that the three elements come from the same pollution source. Considering the anthropogenic activity of the catchments area and source area of river Tisza it is supposed that the non-ferrous metal and their technique in Romania was the top source of the elevated concentrations of Cu, Zn, Pb. Most probably the peaks in the 30-40 cm depth in the UG5SZ soil profile belonged to the heavy-metal pollution originating from Baia Borsa in March, 2000. This means that the velocity of accumulation in the upper 40 cm in the UG5SZ soil profile varied between 4.3-5.7 cm/year. It is a real rate if we consider the relief condition.

On the data of figure 1 and 2 we can compare the different analytical methods. Data obtained from ED-XRF and PIXE were very similar for Cu, Zn. In the case of lead a systematic error could stand behind the difference, which we would like to clear during following measurements. Concentration values obtained from the F-AAS measurement were proved to be systematically lower than from the X-ray analytical techniques. The results of the correlation analysis between ED-XRF and F-AAS for Cu and Zn are shown on Fig 4 and 5.
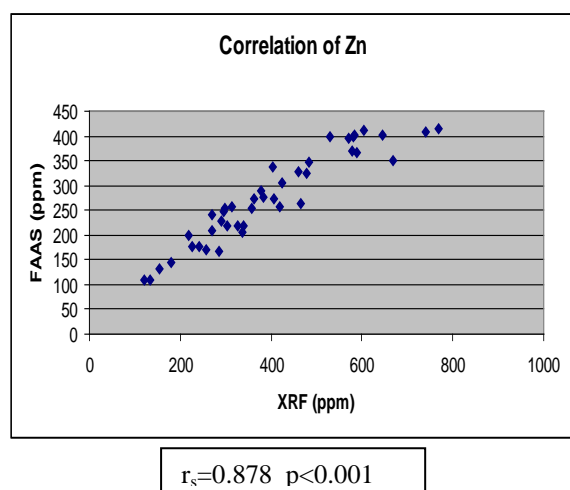

Correlation of Zn

$r_s=0.878$ $p<0.001$

Fig. 4 Comparison of XRF and FAAS methods about Zn

Correlation of Cu
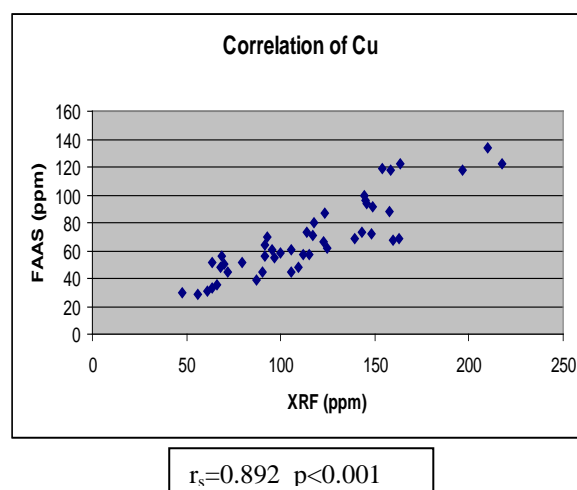
$r_s=0.892$ $p<0.001$

Fig. 5 Comparison of XRF and FAAS methods about Cu

The connection between ED-XRF and F-AAS in the case of Cu, Zn was found to be very strong ($r_s=0.878, 0.892$) and significant ($p<0.001$). Because of

concentrations from ED-XRF and F-AAS were similar in tendency, but the F-AAS method give lower values, we supposed that the cause of difference was that the

ED-XRF is a non-destructive analytical method providing absolute concentrations while and the F-AAS is a destructive analytical method using dissolved material. In case of F-AAS method the solution we used, resulted lower values than the real ones determined by ED-XRF.

Next step was to study the effect of the heavy-metal contamination on the vegetation. For the toxicological study 6-6 samples from the two soil segments with the highest concentrations were chosen and mustard-seed test was performed on them.

Table 2. contains the results of the toxicological analysis. The results showed that in the case of the two segments the accumulation of heavy-metal contaminants did not caused decrease in growth. Moreover, the growth of the sprouts transcended the growth of the sprouts in the control group.

Table 2

Summary of toxicological results of UG4SZ and UG5SZ's soil profile

Name of layer sample	pH	Conductivity (µ S)	%	Evaluation 1.	%	Evaluation 2.
UG4SZ4-6	7.83	550	118	stimulating	87	non toxic
UG4SZ8-10	7.77	534	110	non toxic	99	non toxic
UG4SZ36-38	8.14	522	134	stimulating	178	stimulating
UG4SZ50-52	8.02	517	116	stimulating	106	non toxic
UG4SZ74-76	8.19	514	136	stimulating	110	non toxic
UG4SZ98-100	8.21	515	117	stimulating	112	non toxic
UG5SZ8-10	8.15	535	106	non toxic	161	stimulating
UG5SZ32-34	8.02	537	103	non toxic	145	stimulating
UG5SZ36-38	8.29	548	149	stimulating	94	non toxic
UG5SZ50-52	8.25	535	109	non toxic	88	non toxic
UG5SZ68-70	8.08	524	129	stimulating	117	stimulating
UG5SZ90-92	7.97	524	113	non toxic	137	stimulating

The toxicological analysis showed that the permanent heavy-metal concentration in the area did not block the growth of the plants. The answer to the question why it could happen was simply the favourable elemental composition and the neutral pH of the soil. The pH was considered to be neutral in the whole segments and the mobilisation of heavy-metals through these segments was limited for plant uptake.

CONCLUSIONS

This study confirmed that the Tisza-Kraszna floodplain suffered heavy-metal pollution from year to year. This assumption was confirmed by the depth profile of Cu, Zn, Pb elements (figure 1, 2). Strong correlations were found between Cu, Zn and Pb concentrations, which refers to common origin. The marked peak at 30-40 cm depth in the UG5SZ soil profile most probably belonged to the heavy-metal pollution from Baia Borsa in March in 2000.
We showed that the multielemental ED-XRF method well applicable in sediment's investigation studies. The sample preparation (grinding, pastille doing) was rapid and cost-effective. Although the ED-XRF technique proved to be a reliable analytical tool for the investigation of heavy metal content of sediments, the use of complementary analytical techniques is recommended for the complex study of sediments.

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