

## GIS DATABASE OF HEAVY METALS IN THE FLOODPLAIN OF THE TISZA RIVER

Szilárd SZABÓ<sup>1</sup>, Gyöngyi GOSZTONYI<sup>1</sup>, Beáta BABKA<sup>1</sup>, Nikoletta DÓCS<sup>1</sup>, Mihály BRAUN<sup>2</sup>  
Péter CSORBA<sup>1</sup>, Gábor TÜRK<sup>1</sup>, Lajos Szabolcs MOLNÁR<sup>1</sup>, Beáta BAKOS<sup>1</sup>, György SZABÓ<sup>1</sup>,  
István FUTÓ<sup>3</sup>, Sándor GÖNCZY<sup>4</sup>, Csaba ÁGOSTON<sup>5</sup>, Magdolna SZABÓ<sup>1</sup>, Gergely SZABÓ<sup>6</sup>,  
József PROKISCH<sup>7</sup>

<sup>1</sup> University of Debrecen, Hungary, Department of Landscape Protection and Environmental Geography

<sup>2</sup> University of Debrecen, Debrecen, Hungary, Department of Inorganic and Analytical Chemistry

<sup>3</sup> Institute of Nuclear Research of the Hungarian Academy of Sciences, Debrecen, Hungary, Ede Hertelendi  
Laboratory of Environmental Studies

<sup>4</sup> Ferenc Rákóczi II. Transcarpathian Hungarian Institute, Berehovo, Hungary, Department of Geosciences

<sup>5</sup> KVI-PLUSZ Ltd., Budapest, Hungary

<sup>6</sup> Department of Physical Geography and Geoinformatics, Hungary

<sup>7</sup> Institute of Bio and Environmental Energetics, University of Debrecen, Hungary

**ABSTRACT.** Since it is Hungary's second largest river, the River Tisza is important both as a river and because of its active floodplain. The contaminations endanger the aquatic and the related living nature as well as the farming in the active floodplain. The water quality of the river is examined regularly by the competent authority but far less information is available about the active floodplain. More data is necessary in order to estimate the potential danger. In this paper the River Tisza and its tributaries were examined, especially considering the metal accumulation and its relation to the soil characteristics. We started to create the database in 2004 and several tasks were achieved: the metal content of the root zone in the active floodplain (horizontal distribution); the metal content of the upper 1 m zone in the active floodplain (vertical distribution); the general water chemical and isotope analyses and the metal content of the oxbow lakes near the River Tisza; the metal content of the sediments of the oxbow lakes. More than 300 surface soil samples, 18 soil profiles (18 x 50 samples) and 45 oxbow lakes were examined up to now. Cu, Co, Fe, Ni, Mn, Zn contents were determined in every case and As, Cd, Pb determinations were also carried out in reasonable cases. ArcGIS 9.0 was applied in order to create the spatial database and the statistical analyses of the data were carried out with SPSS. In this paper some case studies will be presented.

**Keywords:** Tisza, heavy metals, soils, oxbow lakes, accumulation

### INTRODUCTION

The River Tisza is Hungary's second largest river and it plays an important role both in natural and economic respects. The quality of the water, the sediments and the soil samples determines utilization possibilities so it is especially important to know the contaminations. Since the river derives from beyond the frontier, most of the potential and the actual contamination sources that affect the quality concentrate there. The mine accident of Baia Borșa (March 2000) drew the attention to the endangerment of the active floodplain since the contamination occurred together with the flood of the River Tisza. This contamination came forth and several researches dealt with the active floodplain.

Before this accident only a few sources are available regarding the active floodplain of the river. After 2000, some work informs us of the metal content of the surface sediments and soils (Alapi et al., 2003, Black et al., 2001. Hum, 2002, Hum, 2005a, Hum, 2005b, Szalai et al., 2005, Farsang et al., 2007, Cser, 2008) and this is very important since the root zone of the plants are here so it is significant in terms of the

potential available metal content. Other authors (Braun et al., 2003, Szalai, 2007, Braun et al., 2008, Sándor et al., 2008, 2009) dealt with the vertical distribution of the metals thus we can conclude on the rate and the depth of the earlier contaminations, and we can also estimate the rate of the sedimentation as an indirect benefit – if we can identify the time of the deposition of the sediments containing extreme metal concentrations.

We should note that in many instances – in the case of some metals (mostly essential metals) – it is improper speaking of metal contamination in the active floodplain since most of the excess consist of essential trace elements so it is more accurate to use the term 'metal loading'. However, it is not true in the cases of the toxic metals.

The water quality of the river is monitored regularly by the competent authority but far less information is available about the active floodplain and the oxbow lakes. Our aim is to create a geoinformation database that covers the characteristics and the metal concentration of the soils in the active floodplain as well as the water quality of the oxbow lakes. In this

paper we intended to present the database prepared up to now and the results that can be gained with its use.

## MATERIALS AND METHODS

The creation of the database has begun in 2004 in the framework of the NKFP-3B0019/2002 tender and has not completed yet. Currently, the research is carried out in the section of the River Tisza between Tokaj and Tiszabecs, including the active floodplain of the River Szamos, Kraszna and Túr, with the support of the No. 68566 Hungarian Scientific Found (OTKA).

### Soil sampling

In the course of our work surface and profile samples were collected. Considering the micro-heterogeneity of the alluvial soils, surface soil samples were collected from the active floodplain and the reclaimed side. 8 subsamples were homogenized to make composite samples. 1-meter-deep soil profile was dug and sampled every 2 centimetres (according to Ciszewski, 2003) to examine the vertical distribution of the metal content. The sampling of the layers belonging to different floods would be more ideal, but it is very altering depending on the distance from the river: the thickest sediment deposited close to the river and it can be more than 10 cm there, but near the levee the thickness of the sediment is only some millimetres. Due to this, the 1-meter-deep profiles show different periods of time of the floodplain (approaching the levee more and more). Therefore, the 2 cm thickness is not related to floods, but the aim of the sampling is to

examine the distribution of the metal concentrations. If we can add a date to the extreme values (either minimums or maximums), we can also estimate the rate of the sedimentation as an indirect benefit.

### Soil examinations

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<sub>3</sub>-content (with calcimeter, Scheibler method) and the active and potential acidity (pH[H<sub>2</sub>O], pH[KCl], HAC, EAC) 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 (ENaF) and 0.5% NaOH (ENaOH) 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<sub>3</sub>+H<sub>2</sub>O<sub>2</sub> 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

Elements	Detection limits	
	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 the surface samples the available quantity for plants was also determined with Lakanen-Erviö extraction (NH<sub>4</sub>-acetate + EDTA, Lakanen et al., 1971).

### Water sampling of oxbow lakes

Water and sediment samples were taken from every oxbow lake. The water samples were taken in polyethylene bottles from 20 cm depth, approximately 5 metres distance from the river bank.

### Water examinations

After the sampling the water samples were stored in a freezer bag till the transport to the laboratory and the quantity of nitrite, nitrate, ammonium and orthophosphate ions, the chemical oxygen demand (COD), the stable isotopes ( $\delta$ D and  $\delta^{18}$ O) and the heavy metal content were determined within 24 hours.

The alteration of the oxygen and hydrogen isotope ratios can help to trace the path of the water (Schoeller 1990). The water of the Earth is mainly derived from precipitation. Since the water infiltrating into the ground preserves its original isotope ratios, the  $\delta$ D és  $\delta^{18}$ O values of the waters can prove the origin of the water. It is an important factor for our research since

we can conclude on the origin of the water of oxbow lakes (precipitation, the floods of the river or the ground water).

#### *Sediment sampling of oxbow lakes*

Sediment sampling of the oxbow lakes was also executed in 2007. The sediment samples were taken from various points close to the river bank. The upper decomposing plant materials were removed in order to reduce the effect of the local concentration heterogeneity.

#### *Geoinformation background*

The coordinates of the samples were determined with GPS, generally as the mean of 60 positions (with approximately 1 m accuracy). DGPS was applied (with approximately 30 cm accuracy) in the sample area of Mezőladány because of the small grid distance (~20 m). The database was created in ArcGIS 9.0. The sample points form the geometric data of the database and the laboratory measurements give the descriptive data. *In situ* data collection was carried out with DigiTerra Explorer in \*.shp format. The programme facilitates the immediate *in situ* record of the descriptive data so if we define the descriptive data then the integration and the addition of the new data to the existing data is very simple. Thus, beside the coordinates and the sample identifier we can record *in situ* the information related to the roughness, the geomorphology and the situation from the levee.

## RESULTS AND DISCUSSIONS

#### *Soil examinations*

The soil characteristics are examined with various methods.

High resolution sampling was carried out in 5 areas (in the surroundings of Gulács, Vásárosnamény, Mezőladány, Cigánd and Túrricse, Fig 1-2). Its main goal is the determination of the metal distribution in the

root zone of the active floodplains and its comparison to the reclaimed side. Besides, we also had a secondary goal and it was different in every area (detailed in Table 2).

Transects were made in order to examine the effect of the distance from the river on the metal accumulation. The sample analyses of 8 transect are completed, 54 samples were collected up to now. In the cases of the River Kraszna, Szamos and Túr approximately 30-30 composite samples were taken along the rivers, from the frontier to the estuary. 20 soil profiles were dug up to now: mainly in the active floodplain of the River Tisza (15), 2-2 profiles near the River Szamos and Túr, and 1 profile near the Kraszna. Two of the profiles near the River Tisza were situated near Técsó (Ukraine); the others were created in Hungary. Moreover, nine 40-centimetres-deep profiles were sampled every 2 centimetres in the area of the high-water overflow in Cigánd. The descriptive data consist of the soil characteristics and metal concentrations described in the chapter 'Materials and methods'.

#### *The examinations of oxbow lakes*

From 2005, samples were taken 6 times from 35-45 oxbow lakes near the River Tisza, between Rakamaz and Tiszabecs (Fig 3). In the different sampling times the lakes contained different volume of water, sometimes they were dried – especially in the end of summer – thus we could not take samples from every oxbow lake in every sampling time. Both water and sediment samples were taken.

The times of the samplings were: October 2005, May 2006, August 2006, November 2007, November 2008, November 2009 and February 2010. Moreover, samples are planned to take in May and August, 2010. The descriptive data consist of the general water chemical parameters, the metal concentrations and stable isotopes described in the chapter 'Materials and methods'.

Table 2

The areas of the high resolution sampling

Sample area	Number of samples	Secondary goal
Gulács (R. Tisza, 701 river km)	91	The examination of the effect of the roughness on the metal accumulation
Vásárosnamény (R. Tisza, 684 river km)	90	The comparison of the sediments of the River Tisza and the River Kraszna, the characteristics of the metal accumulation near the estuary
Mezőladány (R. Tisza, 658 river km)	160	The examination of the soil micro-heterogeneity in ploughlands and grasslands
Cigánd retention basin (R. Tisza, 591 river km)	27	The survey of the original state in order to trace the change of the metal concentration after the floods
Túrricse (R. Túr, 15.5 river km)	30	The characteristics of the metal accumulation, the correlations between the soil characteristics and the metal concentrations

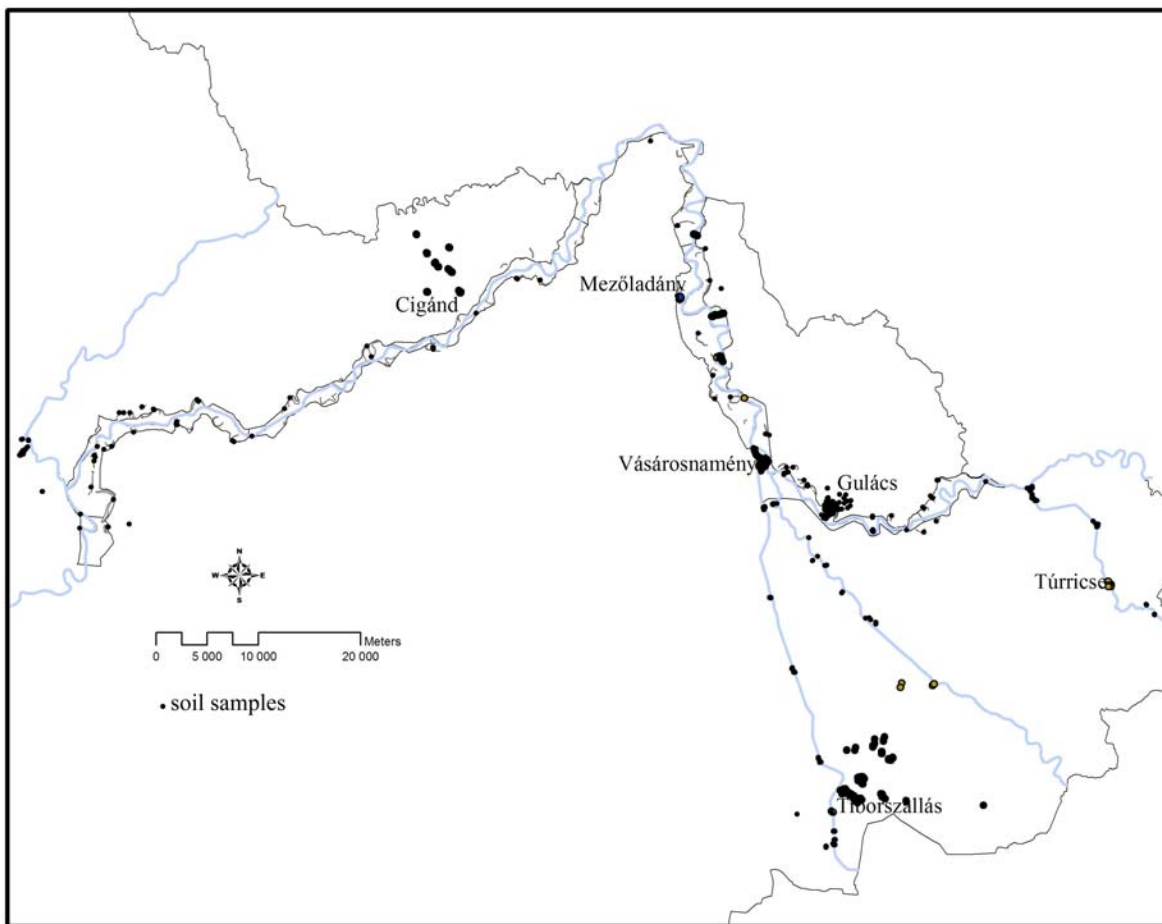


Fig. 1 The map of the examined area

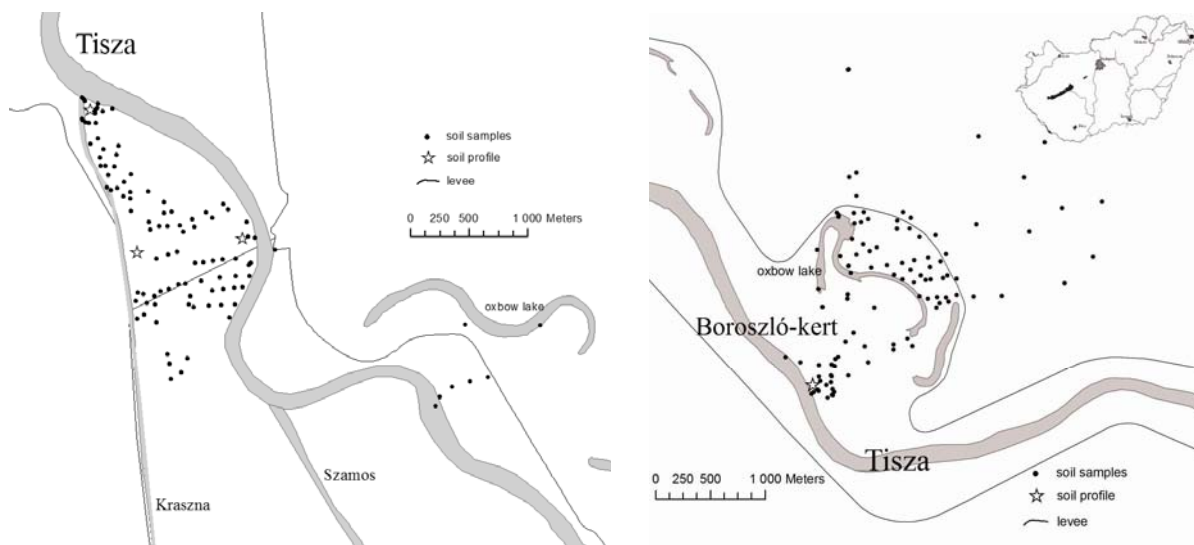


Fig. 2 Detailed maps of sample areas near Vásárosnamény (a) and Gulács (b)

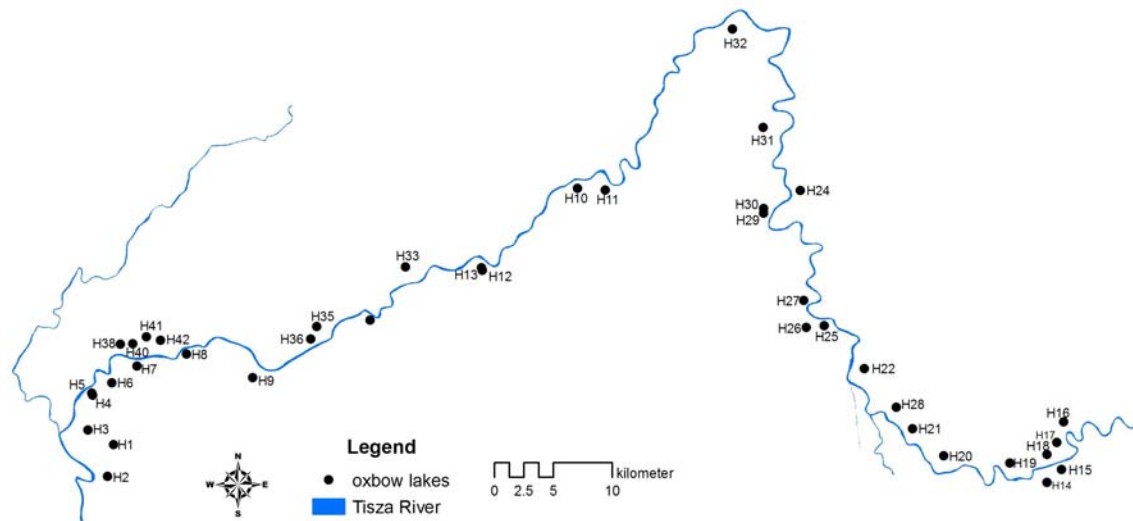


Fig. 3 The sampled oxbow lakes along Tisza

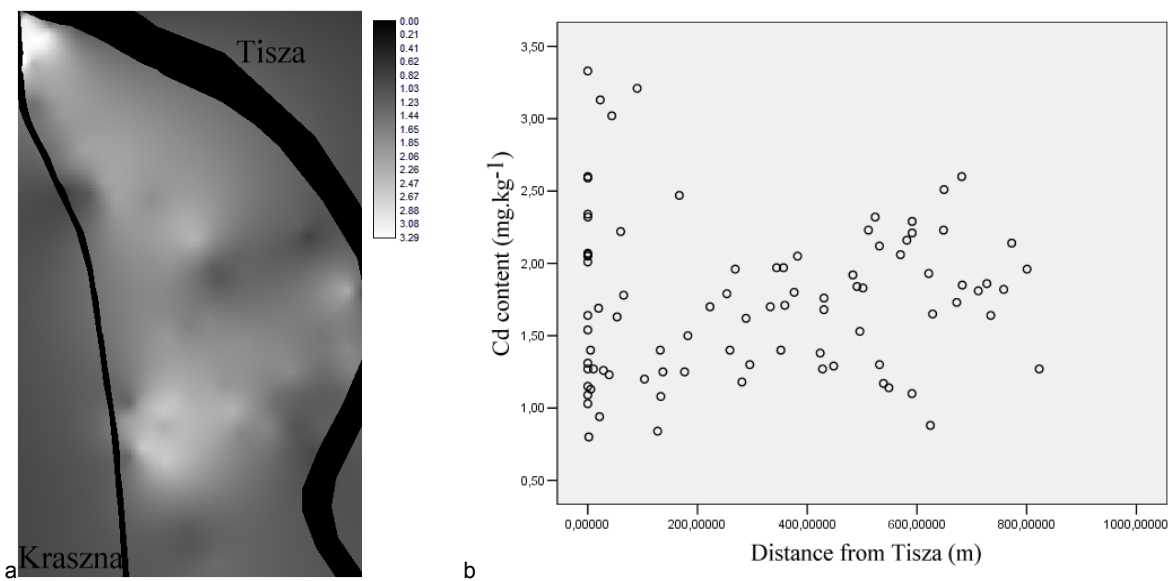


Fig. 4 Map of the Cd content ( $\text{mg.kg}^{-1}$ ) of the soil samples near Vásárosnamény (a) and the relationship between the distance and the accumulated Cd (b)

### The geoinformation system

According to our goals, we created a geoinformation system where the surface soil samples, the water samples and the soil profiles can be represented as overlays. This geoinformation system makes the realization of the following goals possible. The data are stored in one, well-arranged environment. The geoinformation environment makes the quick query (depending on the demands) and the data export of the result possible. We can simply add the results of the new examinations to the database. We can add data that derive from the relative situation of the sample points (e. g. distance from the river). By a proper

sampling plan, continuous surface can be created from the point data with spatial interpolation (e. g. minimum curvature, kriging). In the followings some examples are presented about what the geoinformation system can be used for.

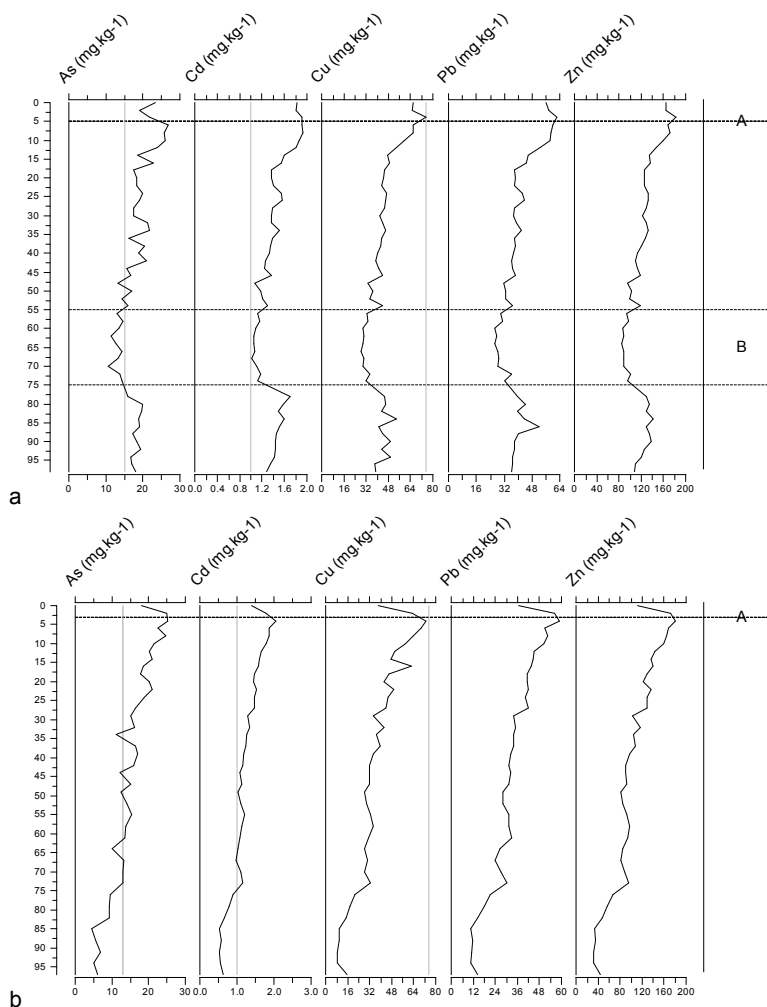
### Case studies

#### Cadmium distribution near the estuary of Kraszna and Tisza (Vásárosnamény)

We can conclude on the distribution of the metals by the statistical surfaces derived from the point surface samples. An example of this can be seen in the map of the Cd-distribution in the sample area near

Vásárosnamény. It is complemented with a diagram of the Tisza shoreline – sample point distance (also created using geoinformation methods). In Fig. 4/a it is observable that the cadmium concentration exceeds the contamination limit ( $1 \text{ mg}\cdot\text{kg}^{-1}$ , according to the joint decree no. 6/2009) everywhere, except some smaller areas. The cadmium concentration of the sediments is

significantly higher in the case of the active floodplain than in the reclaimed side. The distance from the river is not a determinant factor (Fig. 4/b) and this is owing to the sediments of the River Kraszna, the roughness (Manning's  $n$  values), and the causeway of the road in the area and particular flow relations under it.



**Fig. 5** The metal distribution of the soil profile Nr. 1(a) and Nr. 2(b) regarding the arsenic, cadmium, copper, lead, and zinc ( $\text{mg}\cdot\text{kg}^{-1}$ ); grey line: pollution level based on 6/2009 decree; dashed line: marker layers

#### *The analysis of the soil profiles near Gulács*

The concentration of arsenic, cadmium, copper, lead and zinc are shown in the two soil profiles of Gulács (Fig 5). Based on the results we can say that the metal concentration of the root zone is higher in both profiles. It does not pose real threat in some cases since these metals are mainly essential trace elements and the measured concentrations cannot be considered as 'contaminated'. However, the As and Cd concentrations are alarming. Comparing the two figures it can be seen that in the profiles the zone 'A' is situated almost in the same depth, the difference is minimal. However, it is observable that in the case of

the profile 1 the maximum is in the 4-6 cm layer – supposedly the trace of the heavy metal contamination of 2000 - and examining the profile 2 this maximum can be found in the 2-4 cm layer. The low metal concentration of the zone 'B' is in 55-75 cm deep, but it is not clear regarding the profile 2. It would be simple to declare that this zone is in the 86-100 cm depth, but according to our  $^{137}\text{Cs}$ -examination this is not possible (Dezső et al., 2009). The sediment of the Chernobyl accident is in 26 cm deep in the profile 1 and in the 8 cm depth in the profile 2. Thus, zone 'B' with low concentration is rather situated in the 35-50 cm layer. The explanation is that the first profile is

situated in the active floodplain, approximately 20 m from the summer dyke, and the second profile was created in a river bed section of the Boroszló-kert Holt-Tisza which is recently going dry soon after the floods. Due to the relief and the vegetation coverage the rate of the sedimentation is different in the two areas. The second profile was created farther from the main river bed, its situation is deeper and the vegetation coverage is also denser here than in the case of the first profile. Due to the farther situation the sediments are more clayey (since most of the coarser sediments is deposited earlier, on the other hand the deposited sediments are richer in colloids). The first profile is more often flooded owing to its situation so the deposition of the sediments contaminated with metals is also more probable. According to this, the layer of the profile 2 with low metal concentration (85-100 cm) derives from a period that can be found deeper in the profile 1 due to the more intense sedimentation. It does not appear in a 1-meter-deep profile.

## CONCLUSIONS

It is evident that the database can be an important element of the environmental researches. Its real value is that we can store every data in one place, in one environment; the technique of the sampling and the measurements are the same in every case (most of the metal analyses were carried out in an accredited laboratory). With the continuation of the data collecting and the development of the geoinformation environment we can make the system more versatile and useful. The work is intended to continue in the framework of the further tenders.

## ACKNOWLEDGEMENTS

The research was supported by the Nr. 68566 Hungarian Scientific Research Fund.

## REFERENCES

- Alapi, K., Györi, Z. 2003. Sediment examinations in the active floodplain of the River Tisza, loaded by heavy metals. (in Hungarian) *Acta Agraria Debreceniensis* 6 p.
- Black, M., William, P. 2001. Preliminary assessment of metal toxicity in the Middle Tisza River (Hungary) flood plain. *Journal of Soils and Sediments* 1 (4): pp. 213-216.
- Braun M., Szalóki I., Posta J., Dezső Z. 2003. Estimation of the sediment deposition rate in the active floodplain of the River Tisza (in Hungarian). MHT XXI. Vándorgyűlés 2003. július 2-4. CD-Proceedings
- Ciszewski, D. 2003. Heavy metals in vertical profiles of the middle Odra river overbank sediments: evidence for pollution changes. *Water, Air and Soil Pollution* 143 (1-4): 81-98.
- Cser, V., Farsang, A., Barta, K. 2008. Field Experiments of Induced Phytoextraction. Case study in Hungary. In: W.E.H. Blum, M.H. Gerzabek, M. Vodrazka (eds.) *European Confederation of Soil Science Societies (ECSSS), Eurosoil 2008.: Soil-society-environment*. Bécs, Ausztria, 2008.08.25-2008.08.29. p. 211.
- Dezső, Z., Szabó Sz., Bihari Á. 2009. The sedimentation of the active floodplain of the River Tisza based on <sup>137</sup>Cs isotope gamma spectrometric analysis. In: Mócsy I. – Szacsvai K. – Urák I. – Zsigmond A R. szerk: *Proc. V. Kárpát-medencei Környezettudományi Konferencia, Sapientia-Erdélyi Magyar Tudományegyetem, Kolozsvár* pp. 443-438. (in Hungarian)
- Government Joint Decree No. 6/2009. (IV. 14.) KvVM-EüM-FVM on limit values established for the protection of groundwater and the geological medium, 2009.
- Farsang, A., Cser, V., Barta, K., Mezősi, G., Erdei, L., Bartha, B., Fekete, I., Pozsonyi, E. 2007. Application of phytoremediation on extremely contaminated soils. *Agrokémia és Talajtan* 56 (2): 317-332. (in Hungarian with English abstract)
- Hum, L. 2005. Dirty gold. The floodwaves of 2000 contaminated with cyanide and heavy metals, and the heavy metal content of the sediments (in Hungarian). A környezettudomány elmélete és gyakorlata c. konferencia, Szeged, *Proceedings on CD* 10 p.
- Hum, L., Matschullat, J. 2002. Heavy metal and arsenic content of the sediments of the River Tisza and its tributaries. Autumn-winter condition of 1999/2000 (in Hungarian). *Hidrológiai Közöny* 82 (1): 23-30.
- Juggins, S. 2003. C2 Software for ecological and palaeoecological data analysis and visualisation. Tutorial Version 1.3 School of Geography, Politics and Sociology, Newcastle University <http://www.staff.ncl.ac.uk/stephen.juggins>
- Lakanen, E., Erviö, R. 1971. A comparison of eight extractants for the determination of plant available micronutrients in soils. *Acta Agr. Fenn.* 123: 223-232.
- Sándor, A., Kiss, T. 2008. Floodplain aggradation caused by the high magnitude flood of 2006 in the Lower Tisza Region, Hungary. *Journal of Environmental Geography* 1 (1-2): 31-39.
- Sándor A., Kiss T. 2009. Land use challenges and their effect on floodplain aggradation along the Middle-Tisza River, Hungary. *Acta Geographica Debrecina Landscape & Environment* 3 (1): 1-10.
- Szalai, Z. 1998. Trace metal pollution and microtopography in a floodplain. *Geografia Fisica e Dinamica Quaternaria* (21): 75-78.
- Szalai, Z., Baloghné Di Gléria, M., Jakab, G., Csuták, M., Bádonyi, K., Tóth, A. 2005. Physical speciation of sediment associated heavy metals in active floodplains of the Danube and Tisza

- rivers, Hungary. Földrajzi Értesítő 54 (1-2) pp. 61-84. (in Hungarian)
- Szalai, Z. 2007. Effects of channelization on natural levee development, *Geografia Fisica e Dinamica Quaternaria*. 30 (2) pp. 249-254.
- Hungarian Standard *MSZ-08-1722/1989*. Soil analysis. Determination of soluble toxic element and heavy metal content of the soils (In Hungarian). Magyar Köztársaság Mezőgazdasági és Élelmezésügyi Ágazati Szabvány, 11 p.
- Hungarian Standard *MSZ-08-0206/2-1978*. Analysis of the chemical properties of the soils. Laboratory investigations (pH, alkalinity, water soluble total salt content, hydrolitic and exchangeable acidity) (In Hungarian), Mezőgazdasági és Élelmezésügyi Ágazati Szabvány, 12 p.
- Hungarian Standard *MSZ-08-0210-1977*. Determination of the organic carbon content of the soil (In Hungarian). Mezőgazdasági és Élelmezésügyi Ágazati Szabvány, 6 p.