



# HEAVY METAL DISTRIBUTION OF FLOODPLAIN SOILS AND PASTURES OF THE TISZA RIVER

Zoltán Gyóri<sup>[a,b]</sup>, Norbert Boros<sup>[c]</sup>, Emese Bertáné Szabó<sup>[a]\*</sup>, Péter Sipos<sup>[a]</sup>

Paper was presented at the 4th International Symposium on Trace Elements in the Food Chain, Friends or Foes, 15-17 November, 2012, Visegrád, Hungary

**Keywords:** Tisza River, heavy metal pollution, Lakanen-Erviö extraction

In January and March 2000 two tailings dam failed in Baia Mare (Nagybánya) and Baia Borsa (Borsabánya) which resulted cyanide and metal pollution in the Lápos - Szamos - Tisza and metal pollution in the Visó - Tisza rivers, respectively. The main aim of this study was to evaluate the long term effects of pollution on environment. Samples of easily available metal contents were collected in year 2011 from these floodplains and pastures along the Tisza (Tivadar, Vásárosnamény, Rakamaz, Tiszacsege) and were investigated and compared with our earlier results. It was noticed that during an 11 year span the easily available Cd, Cu, Zn and Pb contents of the floodplain soils have increased. This may be due to the periodical floods and the mobilization of the pollutants. Furthermore, high concentration of Zn and Pb contents – crossing the natural background values of available metal content – were also observed in the soils studied.

\* Corresponding Authors

Tel.: +(36).(52).417572

Fax: +(36).(52).417572

E-mail address: [szaboemese@agr.unideb.hu](mailto:szaboemese@agr.unideb.hu) (E. Bertáné Szabó).

[a] Institute of Food Science, Quality Assurance and Microbiology, University of Debrecen, Debrecen, H-4032, Hungary

[b] Institute of Regional Economics and Rural Development, Szent István University, Gödöllő, H-2100, Hungary

[c] Department of Chemical Engineering, University of Debrecen, Debrecen, H-4032, Hungary

In January and March 2000 two tailings dam failed in Baia Mare (Nagybánya) and Baia Borsa (Borsabánya) and resulted cyanide and metal pollution in the Lápos - Szamos - Tisza and metal pollution in the Visó - Tisza river systems, respectively.<sup>3</sup>

The short term effects of the pollution events were studied by many of researchers, and the Lápos-Szamos-Tisza and Visó-Tisza river systems were found to be contaminated by Cu, Zn, Pb and Cd.<sup>2,4-8</sup>

## Introduction

The Hungarian part of the Tisza River is highly contaminated by metals from mining activities in Romania. Mining in Maramures County (former Máramaros) traditionally exploits host ores of base metals (Cu, Zn and Pb) and precious metals (Au and Ag). Besides mining, metal pollution in upper Tisza catchment has also a long history.<sup>1</sup> Nowadays the processing of old tailings pond material by using cyanide in the recovery of Ag and Au is spread over this region. Mining activities use dangerous and toxic chemicals like cyanide which is prime source of contamination. Besides this, wastewater may contain some other heavy metals associated with fine-grained sediments. However, metal concentration of river water is not remarkable 30 km downstream from the point sources,<sup>2</sup> sediment-associated metals are dispersed at much greater distances.

The mining accidents were followed by floods; therefore the metal pollution of the floodplains were also observed.<sup>9,10</sup> Deposition of contaminated sediment on floodplains during flood events and the mobilization of the pollutants may increase the plant available metal content of the upper soil layer.

The mobility and phyto- availability of metals depend on their chemical compositions.<sup>11</sup> Hence, the floodplain soils and river sediment were measured by sequential extraction procedures (SEP)<sup>4,10</sup> and Lakanen-Erviö extraction.<sup>6</sup> A remarkable rate of Cd and Zn contents of polluted sediments (Lápos, Szamos and Tisza Rivers) were in exchangeable form.<sup>4</sup> Besides this, the Cd and Zn contents of the floodplain soils (Szamos and upper Tisza ) could be found in an easily available form.<sup>10</sup>

**Table 1.** Sampling sites

Sampling sites	Geographical coordinates	River km	Type of samples	Additional information
Tivadar	N 48° 04' 00.6" E 22° 31' 04.8"	709	active floodplain	affected by the 2 <sup>nd</sup> pollution event
Vásárosnamény	N 48° 07' 46.5" E 22° 19' 39.5"	683	pasture	affected by the 1 <sup>st</sup> and 2 <sup>nd</sup> pollution events
Rakamaz	N 48° 07' 43.8" E 21° 26' 28.7"	543	pasture	affected by the 1 <sup>st</sup> and 2 <sup>nd</sup> pollution events
Tiszacsege	N 47° 42' 59.9" E 20° 57' 08.7"	455	active floodplain	affected by the 1 <sup>st</sup> and 2 <sup>nd</sup> pollution events 8 years ago the area was refilled with soil

The aim of this study was to evaluate the phyto-available metal content of soils by Lakanen-Erviö extraction, and comparing these results to our earlier results.

## Experimental

Soil samples were collected in April 2011 by deep drilling with a Nordmeyer drill (Nordmeyer Holland, Overveen, The Netherlands). We collected samples from the 300 cm deep soil layer in three replications. Sampling sites are represented in Table 1.

The control area was an arboretum in Tiszakürt. The metal content of the soils originated from Tiszakürt could be considered as natural background levels, because the only source of pollution was atmospheric deposition in this site.

Soil samples were air dried, grinded and sieved (<2mm) for further analysis. The extraction of the easily available metal content was conducted according to Lakanen and Erviö.<sup>14</sup> Cu, Zn contents were determined by an Optima 3300 DV ICP-OES (Perkin-Elmer). The measurement of Pb and Cd was conducted by a QZ 939 GF-AAS (Unicam) in 2000 and by an X7 ICP-MS (Thermo Fisher) in 2011.

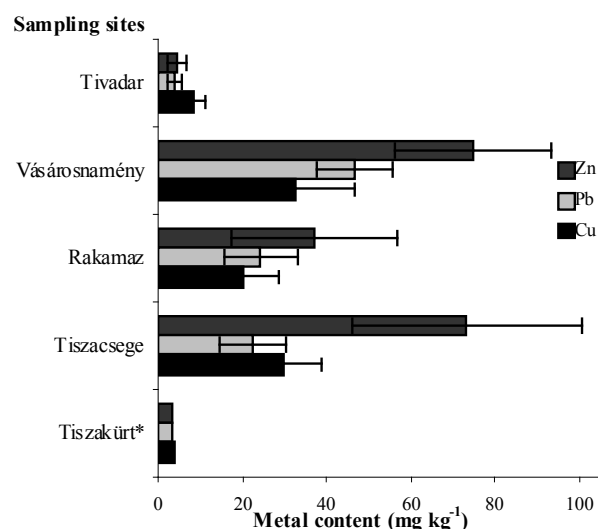
All statistical analyses were performed with SPSS (version 13). Significant differences between the metal contents of the soils in the year 2000 and 2011 were examined by nonparametric, two related samples test (Wilcoxon test).

## Results and discussion

Lakanen-Erviö extractable Zn, Pb and Cu contents of the studied soils (average element content of the 100 cm deep soil profile) and the background values are presented in Figure 1. Tivadar floodplain is considered to be unpolluted, because its metal content did not exceed background values. Our finding is in accordance with the results of other researches.<sup>12</sup> The easily available metal contents of Vásárosnamény, Rakamaz and Tiszacsege were remarkable compared to the background levels.

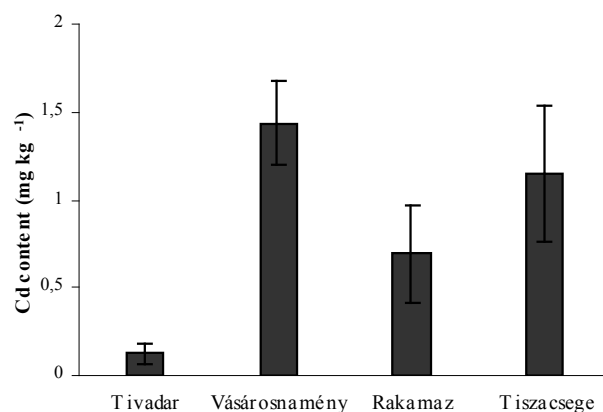
Cadmium contents of Vásárosnamény, Rakamaz and Tiszacsege (Figure 2) were found in remarkable amount comparing them to the average Cd content of the unpolluted reference soil. The Cd content of Vásárosnamény was higher by two orders of magnitude than that of unpolluted soil.

Sharma et al.<sup>15</sup> studied the easily mobilizable (Lakanen-Erviö extraction) Cd, Cu, Pb and Zn contents of high, medium and low contamination areas (due to mining activities). Comparing our observations to these results it is concluded that the Cd, Cu and Zn contents of the studied soils in Vásárosnamény, Rakamaz and Tiszacsege exceed the average Cd, Cu and Zn contents (0.87, 12 and 26 mg kg<sup>-1</sup>, respectively) of the low contamination area.



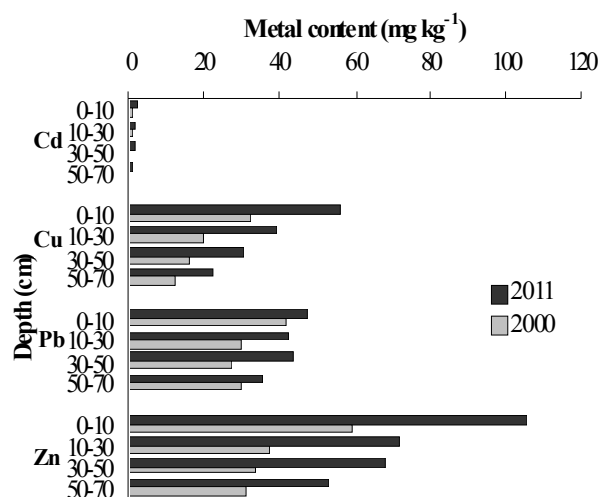
**Figure 1.** Available Zn, Pb and Cu contents (mg kg<sup>-1</sup>) of the 1 m deep soil profile (2011) (\*Natural background value for the measured river section; Remark: Error bars represent the 95% confidence interval)

Farsang et al.<sup>13</sup> studied the health risk of metals in the topsoil of a Fluvisol soil (pH<sub>H2O</sub> 7.7, loamy texture) located near the River Tisza. They found moderate risk (if the proportion of vegetables grown in the studied soil is extremely increased in the consumption) when the Lakanen-Erviö extractable Cd, Cu and Zn contents were 0.41, 27.1 and 53.1, respectively. Cadmium contents in Vásárosnamény, Rakamaz and Tiszacsege, and Zn contents in Vásárosnamény and Tiszacsege exceed these values, which refers to the hazard of the agricultural use of these soils.



**Figure 2.** Cadmium contents (mg kg<sup>-1</sup>) of the 1 m deep soil profile. Cadmium level of the unpolluted reference soil (Tiszakürt) was <0.02 mg kg<sup>-1</sup>; Remark: Error bars represent the 95% confidence interval).

We compared the metal contents of the 300 cm deep soil profile with our earlier results [9]. Significant increases were observable ( $P \leq 0.05$ ) in the case of Zn, Cd and Pb contents (data not shown). The increase was remarkable in the upper soil layers of the pasture near Vásárosnamény (Figure 3).



**Figure 3.** The Lakanen-Erviö extractable metal content of the 0-70 cm deep soil layer of a pasture near Vásárosnamény in 2000 and 2011

## Conclusion

Our results proved that the sampling sites affected by the first pollution event (Baia Mare, January 2000) are significantly contaminated. Zinc, Pb and Cd contents of Vásárosnamény, Rakamaz and Tiszacsege were remarkably high. The effect of the second pollution (Baia Borsa, March 2000) on the available metal contents of the Tivadar floodplain was not detectable.

We found that during the 11 year period the easily available Cd, Zn and Pb contents of Vásárosnamény floodplain increased significantly. This may be due to the periodical flood events and the mobilization of the pollutants.

## Acknowledgements

The work is supported by the TÁMOP 4.2.1/B-09/1/KONV-2010-0007 project. The project is implemented through the New Hungary Development Plan, co-financed by the European Social Fund and the European Regional Development Fund.

This research was supported by the Environmental Remediation Sciences Division of the Office of Biological and Environmental Research, U.S. Department of Energy, through Financial Assistance Award No. DE-FC09-96-SR18546 to the University of Georgia Research Foundation.

## References

- <sup>1</sup>Nguyen, H. L., Braun, M., Szaloki, I., Baeyens, W., Grieken, R., Van Leermakers, M., *Water Air Soil Pollut.* **2009**, *200*, 119-132.
- <sup>2</sup>Macklin, M. G., Brewer, P. A., Balteanu, D., Coulthard, T. J., Driga, B., Howard, A. J., Zaharia, S., *Appl. Geochem.* **2003**, *18*, 241-257.
- <sup>3</sup>UNEP/OCHA. *Assessment Mission Report*, **2000**, Geneva.
- <sup>4</sup>Bird, G., Brewer, P. A., Macklin, M. G., Balteanu, D., Driga, B., Serban, M., Zaharia, S. *Appl. Geochem.* **2003**, *18*, 1583-1595.
- <sup>5</sup>Brewer, P. A., Macklin, M. G., Balteanu, D., Coulthard, T. J., Driga, B., Howard, A. J., Bird, G., Zaharia, S., Serban, M. *NATO Science Series: IV: Earth and Environmental Sciences*, **2003**, *20*, 73-83.
- <sup>6</sup>Györi, Z., Alapi, K., Sipos, P., Zubor, Á. In: *Natural Attenuation of Metals Along the Tisza River-Floodplain-Wetlands Continuum*, Debreceni Egyetem, **2003**, Debrecen, pp. 161-163.
- <sup>7</sup>Osán, J., Kurunczi, S., Török, S., Van Grieken, R., *Spectrochim. Acta* **2002**, *57*, 413-422.
- <sup>8</sup>Wehland, F., Panaiotu, C., Appel, E., Hoffmann, V., Jordanova, D., Jordanova, N., Denut, I. *Phys. Chem. Earth*, **2002**, *27*, 1371-1376.
- <sup>9</sup>Györi, Z., Alapi, K., Szilágyi, Sz. In: *Natural Attenuation of Metals Along the Tisza River-Floodplain-Wetlands Continuum*, Debreceni Egyetem, **2003**, Debrecen, pp. 146-160.
- <sup>10</sup>Kraft, C., von Tümpling J. W., Zachmann, D. W. *Acta Hydrochim. Hydrobiol.*, **2006**, *34*(3), 257-264.
- <sup>11</sup>Kabata-Pendias, A.; Pendias, H. *Trace Elements in Soils and Plants*, CRC Press, Ltd. Boca Raton, **2001** (3<sup>rd</sup> ed.), Florida.
- <sup>12</sup>Szabó, Sz., Posta, J., Gosztonyi, Gy., Mészáros, I., Prokisch, J. *AGD Landscape & Environ.*, **2008**, *2*(2), 120-131.
- <sup>13</sup>Farsang A.,; Puskás I., Szolnoki Zs., *AGD Landscape and Environ.*, **2009**, *3*(1), 11-27.
- <sup>14</sup>Lakanen, E., Erviö, R., *Acta Agr. Fenn.* **1971**, *123*, 223-232.
- <sup>15</sup>Sharma, P., Steckel, H., Koschinsky, A., Schnug E. *Landbauforschung – VTI Agricult. Forestry Res.*, **2009**, *59*/1, 11-18.

Received: 24.10.2012.

Accepted: 07.11.2012