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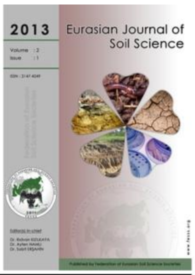

Long term effect of metal pollution in the catchment area of Tisza River

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Abstract

In January and March 2000 two tailings dam failures occurred in the upper Tisza catchment area near Baia Mare and Baia Borsa (Romania). These accidents focused attention on the metal pollution of the Tisza catchment area, and the short term effects of them were studied by many researchers. The aim of this study was to evaluate the long term effects of these pollutions by determining the Lakanen-Erviö extractable easily available metal contents of samples collected in 2011 from floodplains and pastures along the Tisza (Tivadar, Vásárosnamény, Rakamaz, Tiszacsege), and comparing them to our earlier results. Cu and Zn contents were measured by Optima 3300 DV ICP-OES (Perkin-Elmer). The measurement of Pb and Cd was conducted by QZ 939 GF-AAS (Unicam) in 2000 and by an X7 ICP-MS (Thermo Fisher) in 2011.
We found that the Cd, Zn and Pb contents of the pasture near Vásárosnamény exceed limit values and natural background values. In addition, during a 11 year period the easily available Cd, Zn and Pb contents increased significantly, suggesting that the hazard of this pollution should not be neglected.

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

Introduction

The Hungarian section of the Tisza River is highly influenced by metal pollution sourced from mining activity 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, metal pollution has also a long history in the upper Tisza catchment (Nguyen et al., 2009). Nowadays the processing of old tailings pond material by using cyanide to recover Ag and Au is spreading in this region. Mining activities that use dangerous and toxic chemicals such as cyanide can be serious sources of contamination. Besides, wastewater may contain heavy metals associated with fine-grained sediments. However, metal concentration of river water is not remarkable 30 km downstream from the point sources (Macklin et al., 2003), sediment-associated metals are dispersed much greater distances.
In January and March 2000 two tailings dam failures occurred 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 (UNEP, 2000). The short term effects of the pollution events were studied by many researchers, and water and sediment of the Lápos-Szamos-Tisza and Visó-Tisza river

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systems were found to be contaminated by Cu, Zn, Pb and Cd (Bird et al., 2003; Brewer et al. 2003; Győri et al., 2003a, Macklin et al. 2003; Osán et al., 2002; Wehland et al., 2002).

The mining accidents were followed by floods; therefore the metal pollution of the floodplains were also observable (Kraft et al., 2006; Győri et al., 2003b). 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 phytoavailability of metals depend on their chemical forms (Kabata-Pendias and Pendias, 2001). Hence, the river sediment was measured by sequential extraction procedures (SEP). Bird et al. (2003) by the BCR (Community Bureau of Reference) SEP found that a remarkable rate of Cd and Zn contents of polluted sediments (Lápos, Szamos and Tisza Rivers) were in exchangeable form. Sulfide fraction of Cu and Zn were significant in the Lápos River but this phase decreased by the increasing distance from the source of pollutants. Non-destructive speciation of metals showed that high amounts of Zn and Cu contents of sediment particles and suspended particles from the main bed of the Tisza near to Tivadar exist in sulfide form (Osán et al., 2002). Kraft et al. (2006) found that by SEP in the floodplains of the Szamos and upper Tisza, Cd and Zn could be found in an easily available form.

The aim of this study was to evaluate the long term effects of these pollutions on the phytoavailable metal content of soils by Lakanen-Erviö extraction of samples collected in 2011 from floodplains and pastures along the Tisza (Tivadar, Vásárosnamény, Rakamaz, Tiszacsege), and comparing these results to our earlier ones.

Materials and Method

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

Table 1. Sampling sites

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

Soil samples were air dried and sieved (<2mm) for further analysis. The extraction of the easily available metal content was conducted according to Lakanen and Erviö (1871). Cu, Zn contents were measured 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 2000 and 2011 were examined by nonparametric, two related samples test (Wilcoxon test).

Results

Lakanen-Erviö extractable Zn, Pb and Cu contents of the studied soils (100 cm deep soil profile) and the limit values (Kádár, 1998) are presented in Figure 1. According to the easily mobilizable metal contents the Tivadar floodplain considered to be unpolluted. The Zn contents of Vásárosnamény, Rakamaz and Tiszacsege and the Pb content of Vásárosnamény exceed the limit values. Cd contents of the sampling sites (Figure 2) were remarkable in Vásárosnamény, Rakamaz and Tiszacsege. The average Cd content of unpolluted reference soils (Meers et al., 2007) is also presented in Figure 2. The Cd content of Vásárosnamény was nearly 6 times higher than that of unpolluted soils.

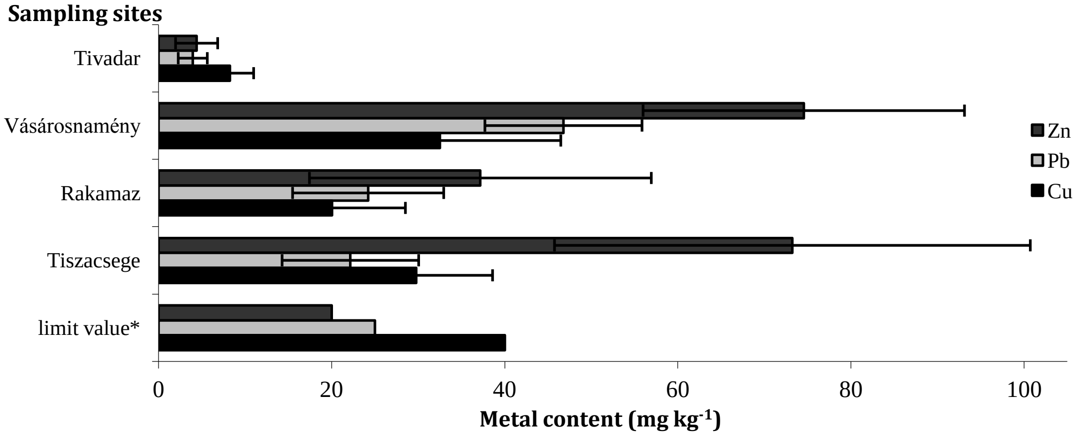

Figure 1. Available Zn, Pb and Cu contents (mg kg^{-1}) of the 1 m deep soil profile (2011)
*Proposed temporary limit value of available metal content for soil (Kádár, 1998)

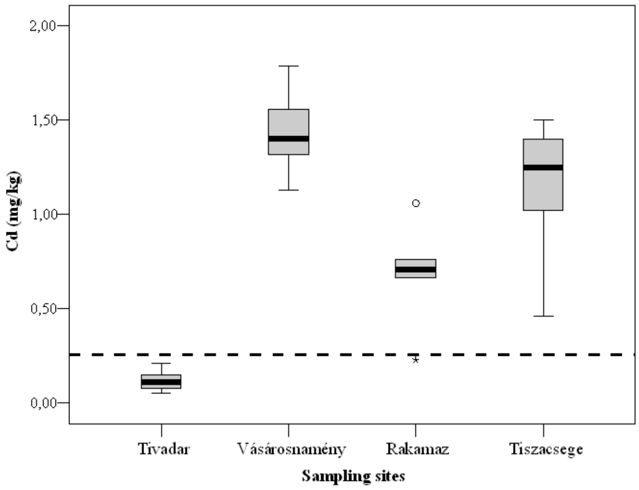

Figure 2. Box-plot of Cd contents (mg kg^{-1}) of the 1 m deep soil profile. Cd level (mg kg^{-1}) in unpolluted reference soils is indicated according to Meers et al. (2007) (0.26 ± 0.04 in soils with pH≤7 and 0.25 ± 0.10 in soils with pH≥7)
* extreme outlier ° outlier

Our results proved that the pasture near Vásárosnamény is significantly polluted with Zn, Cd and Pb. Hence, we compared the metal contents of the 300 cm deep soil profile to our earlier results (Győri et al., 2003b) (Table 2).

Table 2. Changing of the Lakanen-Erviö extractable metal content of the 300 cm deep soil layer of a pasture near Vásárosnamény (2000 and 2011)

Year	2000			2011		
Depth (cm)	Zn	Cd	Pb	Zn	Cd	Pb
0-10	60	0.75	42	106	1.79	47
10-30	37	0.58	30	72	1.56	42
30-50	34	0.48	28	68	1.38	44
50-70	31	0.45	30	53	1.13	36
70-90	41	0.59	41	68	1.32	51
90-110	40	0.53	38	80	1.42	61
110-140	34	0.39	26	71	1.31	48
140-170	26	0.22	15	43	0.66	12
170-200	19	0.04	7	35	0.48	10
200-230	26	0.20	15	42	0.53	11
230-260	28	0.25	18	80	1.36	38
260-300	17	0.08	11	30	0.56	14

Significant increases were observable ($P \leq 0.05$) in the case of Zn, Cd and Pb contents. The increase is remarkable in the upper 150 cm. A second peak is observable in the curves in 250 cm depth that may refer to a previous major pollution event.

Discussion

Our results proved that the sampling sites affected by the first pollution event (Baia Mare, January 2000) are significantly polluted. Zn, Pb and Cd contents of Vásárosnamény, Rakamaz and Tiszacsege were remarkable. Farsang et al. (2009) studied the health risk of metals in the topsoil of a Fluvisol soil (pH_{H2O} 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. Cd and Zn contents of the studied soils in Vásárosnamény and Tiszacsege exceed these values, which refers to the significant hazard of the pollution. Sharma et al. (2009) 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 measurements to these results it can be 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^{-1}, respectively) of the low contamination area. The effect of the second pollution (Baia Borsa, March 2000) on the available metal contents of the Tivadar floodplain was not detectable, which is in accordance with the results of Szabó et al. (2008).

We found that during the 11 year period the easily available Cd, Zn and Pb contents of Vásárosnamény floodplain increased significantly. This may caused by the periodical flood events and the mobilization of the pollutants. Further investigations (solid state partitioning of metals by sequential extraction) are required to find an explanation of this increase.

Acknowledgements

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