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EVALUATION OF THE HEAVY METAL CONTENT OF THE UPPER TISZA RIVER FLOODPLAIN SOILS OVER THE LAST DECADE

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In early 2000, two contamination events at Baia Mare first and Baia Borsa second involving large amounts of toxic elements impacted the Hungarian section of the River Tisza with disastrous ecological and economical impacts. We evaluated the sort- and long-term effects of this pollution by determining the total and bioavailable concentrations of potentially toxic metals from soil samples collected along the Tisza (Tivadar, Vásárosnamény, Rakamaz, and Tiszacsege) in 2000 and between 2011 and 2013. The current and previous results were compared in respect of copper and lead contents.

Keywords: River Tisza, floodplain soils, heavy metal pollution, Lakanen-Erviö extraction, nitric acid/peroxide extraction

1. Introduction

There were intensive Cu, Zn, Pb, Au, and Ag mining activities during early 2000 in the catchment area of the River Tisza [1]. In the last two decades of the previous century, the processing of tailings pond using cyanide was popular as a recovery technology. The resulting wastewaters contain fine-grained sediments with heavy metal contents [2].

In early 2000, two contamination events (at Baia Mare first and Baia Borsa second) involved the release of large amounts of toxic elements that impacted the Hungarian section of the River Tisza with disastrous ecological and economical consequences. The first one released 100,000 m^3 wastewater that contaminated with cyanide and heavy metals the river Tisza via its tributary Lápos-Szamos. The second disaster sent about 20,000 tons of mud containing heavy metals into the river Lápos-Tisza along with a simultaneous flood settling, forming a layer of approximately 5-10 cm in depth on the pre-existing soil [3-8]. Metals were primarily bound to floating material and deposited in floodplain areas.

The metal pollution of the floodplains was also observable [9, 10]. The environmental risk of this type of soil contamination is that the buffer capacity of new layer is smaller than the previously and the potential decreases in pH enhance metal bioavailability and toxicity. The mobility and phytoavailability of metals depend on their chemical forms [11]. The speciation justifies the use of sequential extraction method (SEP) for analyzing these soil samples.

Considering the above information, it is likely that the residual heavy metal load may entail economic effects that cannot be envisaged at the moment as the valley of River Tisza is under agricultural use (pastures, meadows, orchards, and arable land). This is the reason why intensive research has aimed at testing and monitoring the ecological systems of both water and floodplains. This paper presents only the vertical distribution and forms of heavy metals in polluted areas, although plant relations were also examined [6]. The aim of this study was to evaluate the effects of these sources of pollution on the total and bioavailable metal contents of soil samples collected in 2000 and between 2011 and 2013 from floodplains and pastures along the Tisza (Tivadar, Vásárosnamény, Rakamaz, and Tiszacsege) and compare these results to earlier ones.

2. Materials and Methods

Soil samples were collected in 2000 after the flood and in April 2011 and September 2013 by deep drilling using a Nordmeyer drill (Nordmeyer Holland, Overveen, The Netherlands). We sampled the 3 m-deep soil layer in triplicates. Sampling sites are represented in *Table 1*.

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Table 1. Summary of sampling sites.

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

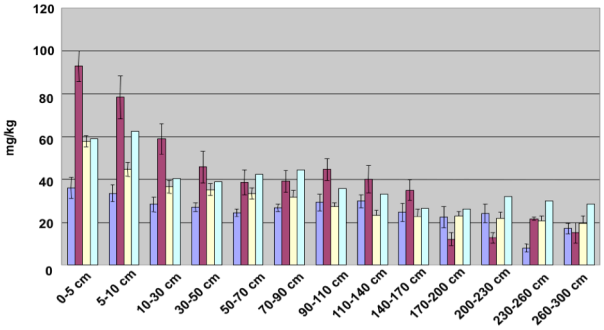

Figure 1. HNO_3-H_2O_2-extractable copper concentration of different layers of soils (blue: Tivadar; burgundy: Vásárosnamény; yellow: Rakamaz; and light green: Tiszacsege).

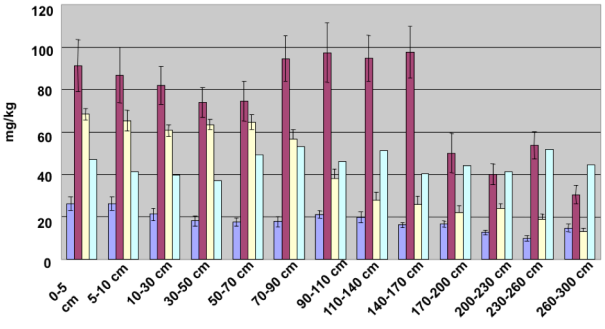

Figure 2. HNO_3-H_2O_2-extractable lead concentration of different layers of soils (blue: Tivadar; burgundy: Vásárosnamény; and yellow: Rakamaz; light green: Tiszacsege).

Soil samples were air dried and sieved (< 2 mm) for further analysis. The chemical analysis was carried out in accordance with a Hungarian Standard [12], using HNO_3-H_2O_2 digestion, which yields total elemental contents. The extraction of the easily available metal contents was conducted according to Lakanen and Erviö [13].

Sequential extractions were performed to determine the concentration of metals associated with different operationally defined soil fractions, in the course of which, stronger and stronger extractants are used to remove metals from the sample. In this case the McGrath method [14] was used, which uses 0.1 M $CaCl_2$ to determine water soluble and exchangeable metal fractions, 0.5 M NaOH to determine the fraction of metals bound to organic matter; 0.05 M Na_2EDTA to determine metals bound to carbon and finally, destruction using *aqua regia* determines the residual fraction. In order to obtain the standard data we used a Merck-made (E. Merck, Darmstadt, Germany) analytical grade HNO_3 (65%) solution. Merck and BDH standard solutions were used to prepare the stock solutions, and REANAL (Budapest, Hungary) solid chemicals were used. Ultrapure water was used to prepare the solutions (Millipore, Paris, France).

Samples were analysed using an Inductively Coupled Plasma - Optical Emission Spectrometer (ICP-OES) to determine Cu content (Perkin-Elmer Optima 3300 DV; Perkin-Elmer Ltd., Shelton, USA). The Pb content was measured by a QZ 939 GF-AAS (Unicam) in 2000 and by an X7 ICP-MS (Thermo Fischer Scientific) between 2011 and 2013.

Target analytics were Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, La, Li, Mg, Mn, Mo, Na, Ni, P, Pb, S, and Zn. In this study, we focused on Cu and Pb, because these elements were connected to the contamination on the floodplain. Certified standard materials used in QA/QC were BCR CRM 141R: calcareous loam soil [15]; BCR CRM 142R: light sandy soil [16], and BCR CRM 143R: sewage sludge amended soil [17]. We assumed that the investigation of the upper 30 cm soil layer every five years using sequential extraction could give accurate information about the changes in the bioavailability of heavy metals and the rearrangement among fractions. All statistical analyses were performed using SPSS (version 22.0).

3. Results and Discussion

Figs.1 and *2* show the total elemental composition for the four sampling sites. Although replicate cores and sampling locations differ, they show an overall trend. The Cu content of the topsoil was higher than that of the lower layers formed earlier. Data indicates that the Cu and Pb contents of the topsoil are greater in Vásárosnamény compared to in Tivadar, possibly due to the combined effects of the two contamination incidents convening at the confluence of the rivers Tisza and Szamos. The 70 to 170 cm soil layers at Vásárosnamény show high lead content.

The Lakanen-Erviö soluble element content is shown in *Figs.3* and *4*. Data indicate that the heavy metal content of the floodplain soils is greater in Vásárosnamény compared to in Tivadar. From this point downstream, the level of contamination appears to decrease with distance, with the lowest value (data not shown) in the topsoil of the arboretum at Tiszakürt (275 river km) where atmospheric deposition may be the

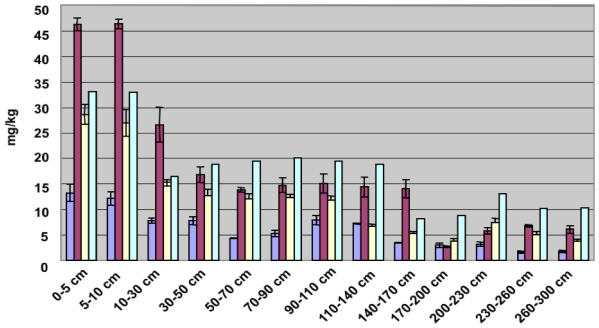

Figure 3. Ammonium-acetate-EDTA (Lakanen-Erviö)-extractable Cu concentration of different layers of soils (blue: Tivadar; burgundy: Vásárosnamény; yellow: Rakamaz; and light green: Tiszacsege).

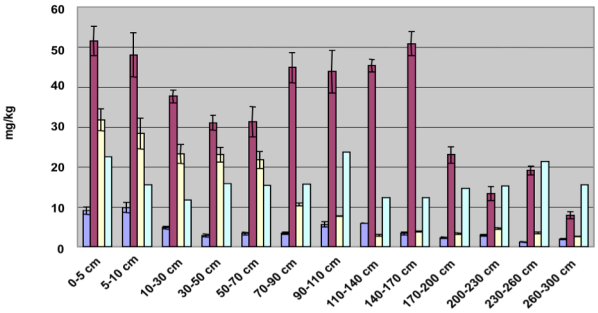

Figure 4. Ammonium-acetate-EDTA (Lakanen-Erviö)-extractable Pb concentration of different layers of soils (blue: Tivadar; burgundy: Vásárosnamény; yellow: Rakamaz; and light green: Tiszacsege).

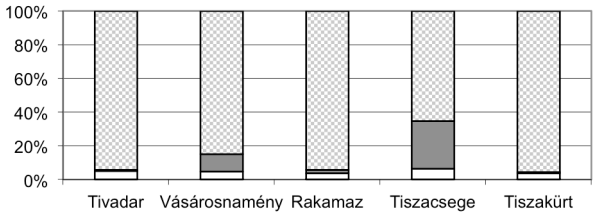

Figure 5. Proportions of the different Cu fractions in the topsoil (solid: $CaCl_2$ soluble, hollow: NaOH soluble, small dotted: Na_2EDTA soluble, checked:aqua regia soluble).

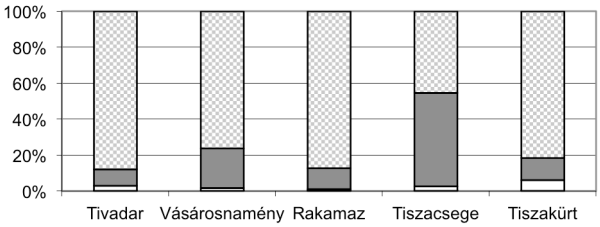

Figure 6. Proportions of the different Pb fractions in the topsoil (solid: $CaCl_2$ soluble, hollow: NaOH soluble, small dotted: Na_2EDTA soluble, checked:aqua regia soluble).

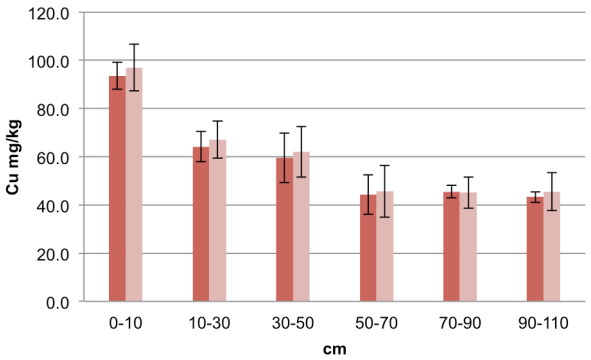

Figure 7. Total Cu concentration (HNO_3/H_2O_2 soluble) at Vásárosnamény (dark: 2002, light: 2013).

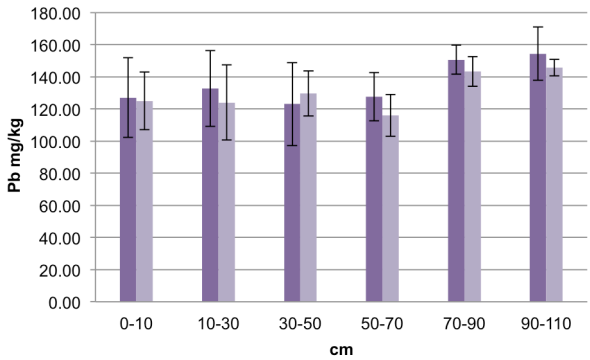

Figure 8. Total Pb concentration (HNO_3/H_2O_2 soluble) at Vásárosnamény (dark: 2002, light: 2013).

source of pollution. The Cu content of the upper 10 cm soil layer is nearly twice as high as levels measured in the other layers. The bioavailable Cu and Pb contents at Vásárosnamény exceeded the temporary limit values of Lakanen-Erviö extractable metal contents for soil contamination [18], while the upper soil layer of the Tivadar floodplain appeared to be uncontaminated.

The McGrath method of sequential extraction can be used for assessing the contents of toxic and potentially toxic elements in soil, and their biological effects, i.e. for the determination of the amounts bound to various forms of compounds in soils. The proportion of the water soluble and exchangeable fractions ($CaCl_2$ extraction fraction) is negligible as regards Cu and Pb. The ratio of metals bound to organic matter (NaOH extraction) is low, according to the expectations, as metals bound to carbonates (Na_2EDTA extraction) is higher in the Vásárosnamény and Tiszacsege soils, but lower at the other sites. The residual fraction of metals (*aqua regia* extraction) is the largest amongst the samples (*Figs.5* and *6*).

We determined the Cu and Pd content of the floodplain soils after ten years of the previous waves of contamination. *Figs.7* and *8* illustrate the vertical distribution of HNO_3/H_2O_2 extractable Cu and Pb contents. There is no statistically proven difference between the results of the samples taken at two different times.

Figs.9–12 show the Lakanen-Erviö soluble element contents of the same core. There is no statistically significant difference between the results of the samples taken at the two different times. The effect of the second source of 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. [19].

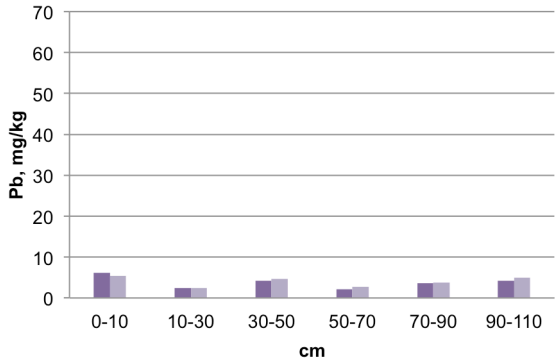

Figure 9. Soluble Pb contents of the 110 cm deep soil profile at Tivadar (dark: 2002, light: 2013).

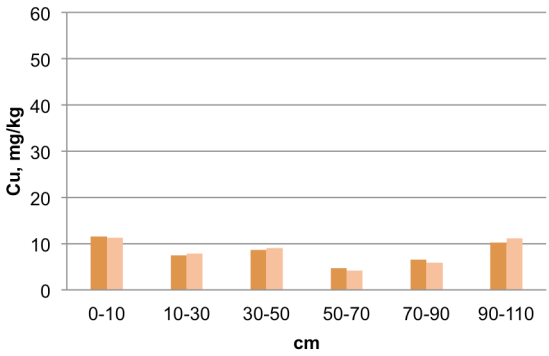

Figure 10. Soluble Cu contents of the 110 cm deep soil profile at Tivadar (dark: 2002, light: 2013).

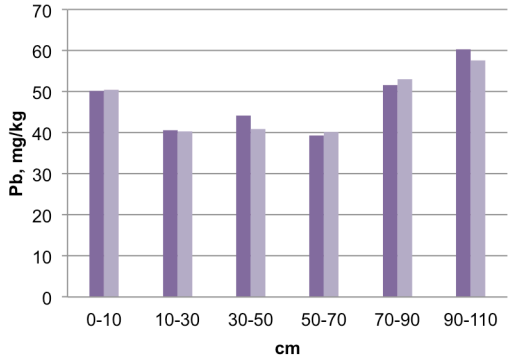

Figure 11. Soluble Pb contents of the 110 cm deep soil profile at Vásárosnamény (dark: 2002, light: 2013).

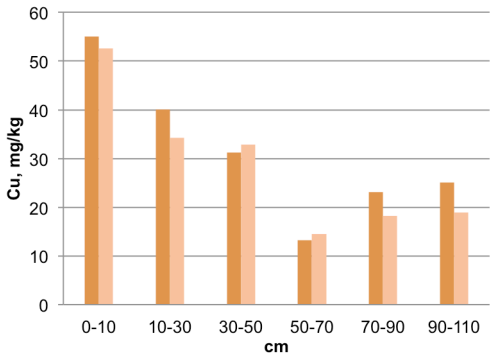

Figure 12. Soluble Cu contents of the 110 cm deep soil profile at Vásárosnamény (dark: 2002, light: 2013).

4. Conclusion

The Cu and Pb contents of the topsoil were found to be the highest in the upper 10 cm layer as a result of the latest sources of contamination. The degree of this effect varies according to the sampling sites. The lowest element content was measured at Tivadar, while samples from Vásárosnamény showed a maximum for many elements because of the first coincidence of the two pollution waves. According to the core samples, higher element contents could be found in some of the deeper layers as marks of former sources of pollution. The investigation of the upper 30 cm soil layer in the coming years using sequential extraction could give accurate information about the changes in the bioavailability of heavy metals and the rearrangement among fractions in addition to laboratory experiments of the effects on soil acidity.

Acknowledgement

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