

Effects of Anthropogenic Activities on the Elemental Concentration in Surface Sediment of Oxbows

Zsuzsanna Balogh · Sándor Harangi ·
János Tamás Kunderát · István Gyulai ·
Béla Tóthmérész · Edina Simon

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Abstract The Upper Tisza floodplain region provides a mosaic of aquatic habitats including a series of oxbows. Inorganic contaminants can accumulate in the sediment; thus, the sediment is good indicator of the contamination of these oxbows. Our aim was to explore the effects of anthropogenic activities on the concentration of elements and also to study the influence of vegetation types on the element in surface sediment of oxbows. We studied eight oxbows: two of them were protected, four of them were used for fishing and two of them were contaminated with domestic sewage. The following elements were measured with MP-AES in surface sediment: Al, Cr, Cu, Fe, Mn, Pb and Zn. The elemental concentration was compared to the toxicity classes of Environmental Protection Agency (EPA), and the assessment of the level of toxicity was based on this comparison. We found that studied oxbows were different from each other based on the elemental concentrations of sediment using canonical discriminant analysis and analysis of variance. Based on the elemental concentration in surface sediment of oxbows, separation

was also found among vegetation types. But significant difference was not found in the concentrations of elements based on vegetation types. Our results demonstrated that the anthropogenic activities had remarkable effects on the elemental concentration of surface sediment in oxbows. Our findings suggest that the sediment is useful to assess the effects of anthropogenic activities on elemental concentrations of oxbows.

Keywords Heavy metals · Aquatic vegetation · MP-AES · Abiotic indicator

1 Introduction

Floodplain ecosystems are one of the most productive ecosystems on the Earth (Tockner and Stanford 2002). Floodplains provide high diversity of aquatic habitats and many vertebrate uses these habitats as nursery, nesting and feeding places (Ward et al. 1999; Robinson et al. 2002; Sandu et al. 2004). The natural habitats are threatened in the floodplains; thus, floodplains have endangered status (Varga et al. 2013). The region of the Upper Tisza (North-Hungary, Central Europe) is rich in oxbows: more than 160 oxbows are along the river Tisza (Pálfi 2001; Lukács et al. 2009). These oxbows were formed by natural cut off meander or by river control. The river control produced drastic changes in the ecosystem which are related to increased anthropogenic activities in the floodplain area (Varga et al. 2013). These anthropogenic activities include changes in traditional land use, farming intensification,

Z. Balogh · S. Harangi · J. T. Kunderát · E. Simon (✉)
Department of Ecology, University of Debrecen, Debrecen P. O.
Box 71, H-4010, Hungary
e-mail: edina.simon@gmail.com

I. Gyulai
Department of Hydrobiology, University of Debrecen, Debrecen
P. O. Box 71, H-4010, Hungary

B. Tóthmérész
MTA-DE Biodiversity and Ecosystem Services Research Group,
Debrecen P. O. Box 71, H-4010, Hungary

irrigation and pesticides fertilizers machinery, which played important role in the floodplain area (Varga et al. 2013).

Anthropogenic activities cause higher metal concentrations in aquatic environments (Sarmani et al. 1992; Virkanen 1998). These activities influence sediments through increased load and leads to an increased metal transport to the biosphere (Lindström 2001). Recently, water-influenced natural systems have suffered the most through anthropogenic influences (Varga et al. 2013). The sources of heavy metals are various: natural like weathering of soil and bedrock, and anthropogenic, such as industry and agriculture (Lindström 2001). In 2000, there were two large mining disasters in Romania, which contaminated the whole Tisza river basin by means of the flood of the Tisza River (Szabó et al. 2010). Moreover, there are regular contamination events in the catchment area of Tisza River from the Romanian mining area (Gosztonyi et al. 2011). The suspended particulate material was settled and buried in the sediment so the oxbows are functioning as sediment trap (Papp et al. 2007). The sediment is a good indicator of the contamination of oxbows because many organic and inorganic contaminants, especially heavy metals, can accumulate in the sediment (Bentivegna et al. 2004).

Aquatic macrophytes, both living and dead, are heavy metal accumulators (Keskinen et al. 2003). Earlier studies reported that aquatic plants were used for the removal of heavy metals from sediments (Wang et al. 1996; Schneider et al. 1999; Keskinen et al. 2003). Sawidis et al. (1995) concluded that the accumulation from sediment was dependent on the metals properties. Aquatic roots can accumulate heavy metals in higher concentration than leaves, while stem and flowers can accumulate metals in the lowest concentrations (Sawidis et al. 1995). Many studies demonstrated that aquatic flora and particularly the sediments reflect the metal content of their environment and the aquatic macrophytes have effect on the lake's physical and chemical environment (Harding and Whitton 1978; Sawidis et al. 1995; Lukács et al. 2011).

The aim of the paper is to study the effects of anthropogenic activities and vegetation types on elemental concentrations of surface sediment. Our hypothesis was that elemental concentration is higher in the fishing oxbows and sewage-contaminated oxbows than in the protected oxbows. Submerged macrophytes may or may not be rooted to the sediment (Greenway 1993; Thomas et al. 1995) so they can accumulate metals both from the

water and from the sediment (Denny 1980; Aulio 1986). Several studies have demonstrated that submerged macrophytes accumulate heavy metals directly from the water (Dunbabin and Bowmer 1992; Cardwell et al. 2002). This explains that the uptake of metals by submerged macrophytes was higher than the uptake by emergent aquatic macrophytes (Dunbabin and Bowmer 1992; Albers and Camardese 1993; Cardwell et al. 2002). The emergent macrophytes' element uptake by roots is the primary source of metal from the sediment (Crowder 1991). The uptake of metals in leaves is lower from the ambient water than in roots (Crowder 1991). Our hypothesis was that lower elemental concentration is found near the submerged and emergent aquatic macrophytes than near the open water surface sediment.

2 Materials and Methods

2.1 Study Area

The study area is in the Upper Tisza region (North-Eastern Hungary, Central Europe) in the catchment area of the Tisza River. One part of this active floodplain area has conservation priority and another part is a Natura 2000 site within the Hortobágy National Park (Varga et al. 2015). The oxbows were located near the Hungarian-Ukrainian border. The following eight oxbows were studied in the Upper Tisza region: Boroszlókerti-Holt-Tisza, Foltos-kerti-Holt-Tisza, Gyürei-Holt-Tisza, Vargaszegi-Holt-Tisza, Lónyai-morotva, Tuzséri-Holt-Tisza, Szabolcsi-Holt-Tisza and Tímári Morotva-tó. The Boroszlókerti- and Foltos-kerti-Holt-Tisza are under Hortobágy National Park's authority so these oxbows are protected, while the water of Gyürei-, Vargaszegi-Holt-Tisza, Tuzséri Holt-Tisza and Szabolcsi-Holt-Tisza oxbows are under different anglers association's authority. Therefore, the monitoring of these oxbows is important from human point of view because heavy metals can getting into the food chain and accumulate in the living beings (Gosztonyi et al. 2011). Water of other two oxbows (Lónyai-morotva and Tímári Morotva-tó) were contaminated with domestic sewage. These oxbows are under self-governing's authority so this oxbow is negligent and presumably it is contaminated with domestic sewage (Table 1).

Oxbows were located in the floodplain area; thus, they are connected to the Tisza River during floodplain

Table 1 Characteristics of the studied oxbows

Name of the oxbow	Utilization	GPS coordinates	Depth of the oxbows (cm, mean±SD)
Boroszló-kerti-Holt-Tisza	Protected oxbow	48°05'10"N, 22°24'41"E	191±113
Foltos-kerti-Holt-Tisza	Protected oxbow	48°06'01"N, 22°23'02"E	119±73
Gyürei-Holt-Tisza	Fishing oxbow	48°11'03"N, 22°15'58"E	197±257
Vargaszegi-Holt-Tisza	Fishing oxbow	48°06'15"N, 22°33'57"E	131±111
Tuzséri-Holt-Tisza	Fishing oxbow	48°19'24"N, 22°05'58"E	103±54
Szabolcsi-Holt-Tisza	Fishing oxbow	48°10'20"N, 21°30'18"E	57±36
Tímári Morotva-tó	Sewage-contaminated oxbow	48°08'36"N, 21°27'03"E	129±62
Lónyai morotva	Sewage-contaminated oxbow	48°18'48"N, 22°15'46"E	159±57

events. The oxbows average depth varies between 1 and 2 m, except the Szabolcsi-Holt-Tisza which was very shallow. During our research, 62 sediment samples were collected from the eight oxbows. Surface sediment samples (0–2 cm) were taken from 7 locations from Tímári Morotva-tó, Tuzséri-, Szabolcsi-, Vargaszegi-, Gyürei- and Foltos-kerti-Holt-Tisza; 9 locations from Lónyai-morotva and 11 locations from Boroszló-kerti-Holt-Tisza. The aquatic vegetation of the oxbows was extremely diverse. The sediment sampling points were determined by the vegetation types. We identified there were three vegetation types to study the effect of vegetation types on the elemental concentration in the studied oxbows sediment. The first vegetation type was floating leaves aquatic plants; the following species were frequent: *Trapa natans*, *Nymphaea alba*, *Nuphar lutea*, *Polygonum amphibium*. The second vegetation type was submerged aquatic plants where *Myriophyllum verticillatum*, *Potamogeton lucens*, *Ceratophyllum demersum* and *Utricularia vulgaris* species were typical. The third vegetation type was emergent aquatic plants which were characterized with the *Phragmites australis*, *Typha angustifolia* and *Typha latifolia*. The control was the open water without vegetation.

2.2 Sample Collection and Preparation

The surface sediment samples were collected with a core sampling in June and July 2013. Plexiglas (46 mm ID) gravity corer was used to take the surface samples. The surface sediment samples were stored at 4 °C until sample preparation to protect them against microbial saprophytic activity. The top 2 cm thick wet surface sediment samples were air-dry during 1 week. Then samples were homogenised with agate mortar. From

air dried sediment 0.2 g samples were measured on an analytical balance (Analytical Balance Sartorius 1702–004) and samples dried (WTB Binder ED 53) at 105 °C for 4 h.

2.3 Elemental Analysis

For elemental analysis, 0.2 g of sediment samples was digested in glass beakers with 5 ml 65 % (m/m) nitric acid at 80 °C in three replicates. After 1 ml of 30 % (m/m) hydrogen peroxide and 5 ml of double deionized water were added to the samples, they were dried again. The digested samples were diluted to 10 ml using 1 % (m/m) nitric acid and ultrasonic mixer. The elemental concentrations were measured with Microwave Plasma-Atomic Emission Spectrometer (MP-AES) (Agilent MP-AES 4100). The following elements were determined: Al, Cr, Cu, Fe, Mn, Pb and Zn. Certified reference material BCR 700 was included in each batch of samples during the measurement. The analytical error was less than ±10 % of the certified values for the metals.

2.4 Determination of Organic Matter Content

After drying, three repeated samples (0.2 g) were cremated at 550 °C for 4 h in a muffle furnace (Nabertherm L5/C6, Germany). To determine the organic matter content of surface sediment, the loss on ignition method was used. The loss on ignition was calculated with the following equation: $LOI_{550} = 100 (DW_{105} - DW_{550}) / WS$, where LOI_{550} was the percentage of loss on ignition at 550 °C, DW_{105} was the dry weight of samples at 550 °C and DW_{550} was the weight of the sample at 550 °C (Bengtsson and Enell 1986; Heiri et al. 2001).

2.5 Statistical Analysis

SPSS/PC+ and Canoco packages were used during the calculations. The elemental concentrations of sediment in the oxbows and vegetation types were analysed by canonical discriminant analysis (CDA). Homogeneity of variance was tested by Levene test. The normal distribution was tested with a Shapiro-Wilk test. The differences among oxbows and vegetation types on elemental concentrations and organic matter contents of surface sediment were tested by two-way ANOVA. The factors were the oxbows and the vegetation types. In the case of significant differences, Tukey's Multiple Comparison test was used. The correlation between organic matter content and elemental concentrations was studied with Pearson Rank correlation.

3 Results

3.1 Effects of Anthropogenic Activities on the Elemental Concentrations in Surface Sediment

Table 2 contains the elemental concentrations of surface sediments. The concentrations of elements in the surface sediment of the oxbows were evaluated by CDA. The total variance of the first two axes was 100 %. The first axis's variance distribution was 87.4 %, while the second axis's variance distribution was 12.6 %. The elemental concentrations of surface sediment were separated from each other, but there was overlap between the fishing oxbows and the sewage-contaminated oxbows (Fig. 1). Significant positive correlation were found between the first

discriminant function and the concentration of aluminium ($r=0.12$), chromium ($r=0.28$) and copper ($r=0.31$). Significant negative correlation was found between the first discriminant function and the concentration of zinc ($r=-0.31$). Significant positive correlation were found between the second discriminant function and the concentration of manganese ($r=0.69$), iron ($r=0.35$) and lead ($r=0.16$).

Using variance analysis (ANOVA), the concentration of chromium ($F=3.536$; $p=0.035$), copper ($F=4.17$; $p=0.020$), zinc ($F=4.6$; $p=0.014$), manganese ($F=3.75$; $p=0.002$) and iron ($F=5.31$; $p=0.008$) differed significantly between the oxbows. The chromium and the copper concentration were the highest in the protected oxbows and significant differences were not found between protected oxbows and fishing oxbows. Significant differences were found between protected oxbows and sewage-contaminated oxbows. The manganese concentration was similar in protected oxbows and sewage-contaminated oxbows, and significant differences were not found between protected oxbows and fishing oxbows. Zinc concentration was the highest in the protected oxbows, and significant differences were found between protected oxbows and fishing oxbows and sewage-contaminated oxbows. The Fe concentration was the highest in the protected oxbows and significant differences were not found between protected oxbows and fishing oxbows, but significant differences were found between protected oxbows and sewage-contaminated oxbows (Table 2).

Table 2 Trace element concentration of sediment (mean \pm SD) according to use of water

Elements	Protected oxbows	Fishing oxbows	Sewage-contaminated oxbows
Al, g/kg	278 \pm 22a	263 \pm 62a	262 \pm 42a
Cr, mg/kg	77 \pm 4.6ab	67 \pm 17ac	71 \pm 14bc
Cu, mg/kg	67 \pm 12ab	55 \pm 14ac	58 \pm 15bc
Fe, g/kg	720 \pm 75ab	589 \pm 136ac	664 \pm 180bc
Mn, g/kg	21 \pm 6.2ab	12 \pm 5.1ab	21 \pm 17bd
Pb, mg/kg	78 \pm 19ac	87 \pm 23ac	89 \pm 25ac
Zn, mg/kg	157 \pm 22bd	211 \pm 85bc	216 \pm 60bc

Different letters indicate significant differences ($p>0.05$)

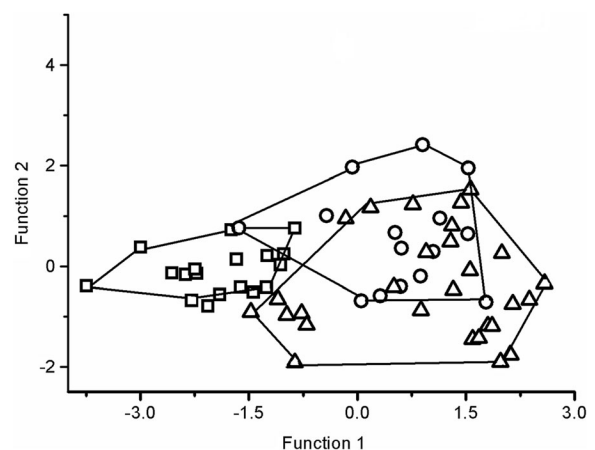


Fig. 1 Canonical discriminant analysis of the oxbows based on the elemental concentrations in surface sediment (mg/kg). Notations: square—protected oxbows, circle—fishing oxbows, triangle—sewage-contaminated oxbows

3.2 Elemental Concentrations in Surface Sediment Based on Vegetation Types

The total variances of the first two axes were 90.3 % using canonical discriminant analysis. The variance of the first axis was 65.8 %, while the variance of the second axis was 24.5 %. The elemental concentration of the sediment of oxbows was not separated from each other based on aquatic vegetation types (Fig. 2). Significant positive correlation was found between the second discriminant function and the concentration of aluminium ($r=0.737$), iron ($r=0.90$), chromium ($r=0.8$), manganese ($r=0.82$), copper ($r=0.66$) and lead ($r=0.44$). Significant negative correlation was found between the third discriminant function and the concentration of zinc ($r=-0.41$). The effect of the first discriminant function was not significant.

Significant difference was found in the concentrations of iron ($F=3.69$; $p=0.018$) among aquatic vegetation types. In the case of iron concentration, significant differences were found between open water sampling sites and emergent aquatic vegetation types and open water sampling sites and floating leaves plants sampling sites (Table 3).

4 Discussion

The aim of this paper was to explore the differences between protected, fishing and sewage-contaminated

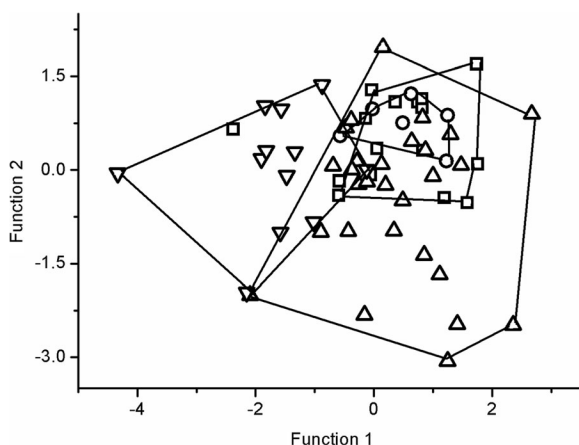


Fig. 2 Canonical discriminant analysis of floating leaves, submerged, emergent vegetation types and open water based on the elemental concentrations of surface sediment (mg/kg). Notations: *square*—floating leaves, *circle*—submerged, *triangle*—emergent aquatic plants, *inverted triangle*—open water

oxbows in the elemental concentrations of surface sediment, and to study the correlation between elemental concentrations of surface sediments and aquatic vegetation types in oxbows of the Upper Tisza region. Our results demonstrated that there are differences among the elemental concentrations of surface sediment of oxbows based on anthropogenic activities. But, our results did not show correlation between elemental concentrations of surface sediments and the aquatic vegetation types, except in the case of iron.

The elemental concentrations of surface sediments were compared to the Environmental Protection Agency values (Baudo and Muntau 1990). Our results showed that all studied oxbows were heavily contaminated for Cu, Mn and Fe (Table 2). The protected oxbows were heavily contaminated for Cr and the fishing oxbows and sewage-contaminated oxbows were moderately polluted for Cr. Fishing oxbows and sewage-contaminated oxbows were heavily contaminated for Zn and protected oxbows were moderately polluted for Zn.

In Hungary the mean geochemical concentration in the upper level (0–10 cm) of floodplain sediments is 25 mg kg⁻¹ for Cr, 25 mg kg⁻¹ for Cu, 21 mg kg⁻¹ for Pb, 95 mg kg⁻¹ for Zn, 25,000 mg kg⁻¹ for Al₂O₃, 35,000 mg kg⁻¹ for Fe₂O₃ and 1000 mg kg⁻¹ for MnO (Ódor et al. 1997). Based on this report, all of studied elements exceed the geochemical concentration. The high Mn and Fe concentration in all oxbows originate from the geochemical background of Upper Tisza region. Heavy metals adsorption plays a significant role of organic matter, iron and manganese oxides (Jain and Ram 1997). The particle size of the sediments is in inverse ratio to the manganese and iron adsorption in

Table 3 Trace element concentration of sediment (mean±SD) based on vegetation of oxbows

Elements	Floating leaves	Submerged	Emergent	Open water
Al, g/kg	263±36a	264±16a	257±59a	298±341a
Cr, mg/kg	74±8.3a	77±3.5a	66±17a	76±9.1a
Cu, mg/kg	61±16a	62±8.7a	56±16a	63±8.4a
Fe, g/kg	615±107a	645±79ac	616±160a	762±127bc
Mn, g/kg	14±4.5a	19±8.9a	17±14a	20±6.6a
Pb, mg/kg	89±12a	96±29a	80±28a	83±15a
Zn, mg/kg	194±60a	175±25a	191±70a	224±92a

Different letters indicate significant differences ($p>0.05$)

the various fractions (Jain and Ram 1997). Therefore, there is a link between high concentration of iron, manganese and oxbows fine-grained clayey silt sediments (Papp et al. 2007).

Compared to our results with earlier studies about elemental concentration in different river surface sediment, our study indicated the moderate level of pollution in the Upper Tisza region. Bird et al. (2003) studied two rivers surface sediment in Romania which was Lapus River and Somes River. The concentration value of Cu (Lapus River, 240 mg kg^{-1} ; Somes River, 220 mg kg^{-1}), Pb (Lapus River, 200 mg kg^{-1} ; Somes River, 97 mg kg^{-1}) and Zn (Lapus River, 770 mg kg^{-1} ; Somes River, 1200 mg kg^{-1}) was higher in the surface sediment than our findings (Bird et al. 2003). Vystavna et al. (2012) studied the metal concentration in the sediment of Udy River and Lopan River in Ukraine. They found lower Cu (Udy River, $33 \pm 39 \text{ mg kg}^{-1}$; Lopan River, $42 \pm 32 \text{ mg kg}^{-1}$), Pb (Udy River, $15 \pm 7 \text{ mg kg}^{-1}$; Lopan River, $30 \pm 17 \text{ mg kg}^{-1}$) and Zn (Udy River, $59 \pm 35 \text{ mg kg}^{-1}$; Lopan River, $111 \pm 95 \text{ mg kg}^{-1}$) concentration in sediment than in the Upper Tisza region. Hiller et al. (2010) studied two water reservoirs sediment in Slovakia. In the case of Cu (Ruzin, $382 \pm 191 \text{ mg kg}^{-1}$; Velke Kozmalovce, $78 \pm 22 \text{ mg kg}^{-1}$) and Zn (Ruzin, $517 \pm 209 \text{ mg kg}^{-1}$; Velke Kozmalovce, $469 \pm 69 \text{ mg kg}^{-1}$) higher concentration was found than in our case. The Pb concentration in Ruzin surface sediment was similar to our findings ($79 \pm 22 \text{ mg kg}^{-1}$), and in the case of Velke Kozmalovce, the Pb concentration was lower $66 \pm 8 \text{ mg kg}^{-1}$ compared to our results.

The metal accumulation is known to vary significantly between aquatic macrophytes species (Albers and Camardese 1993; Cardwell et al. 2002). Some studies demonstrated that aquatic macrophytes as emergent plants are an integral part of all wetland functions (Dunbabin and Bowmer 1992). Our results showed that there were no significant differences between aquatic vegetation types in the elemental concentration of sediment. Submerged aquatic macrophytes mostly can uptake higher quantity of metals than emergent aquatic macrophytes (Albers and Camardese 1993; Cardwell et al. 2002). Earlier studies demonstrated metal uptake correlation between aquatic macrophytes and sediment concentrations. These studies found poor correlation between aquatic macrophytes and sediment concentrations (Jackson and Kalff 1993; Cardwell et al. 2002). Mishra et al. (2008) concluded that significant

correlation was not found between metal concentrations of sediment and metal concentrations of aquatic macrophytes root.

5 Conclusions

In this study, the effects of anthropogenic activities and vegetation types were analysed to the elemental concentration of the sediment of oxbows. Earlier studies demonstrated that the agricultural runoff (zinc phosphate chemical fertilizer), domestic wastes (Sawidis et al. 1995), particle size (Jain and Ram 1997) and vegetation structure (Szabó et al. 2009; Szalai 1998) have effect on the elemental concentrations of oxbows. Therefore, the anthropogenic activities and vegetation have remarkable effect on the elemental concentration of sediment. Our results demonstrated that the protected and fishing oxbows were heavily contaminated with Cr. For Zn, our results demonstrated that the fishing oxbows and sewage-contaminated oxbows were heavily contaminated. In the case of Cu, Mn and Fe, all oxbows were contaminated heavily. In the case of sewage-contaminated oxbows, our results indicated that remarkable differences were not found similar to the fishing oxbows. In Hungary, especially the industrial wastewater contains heavy metals in high concentration (Gulyás et al. 2015). At the same time, the ammonium, phosphorus and organic material contents of commercial wastewater are high (Kalló 1995; Domokos et al. 2005; Szabó et al. 2008). In summary, our results show that the anthropogenic activities and geochemical background were the main factors which play important role in the contaminant level of the oxbows. However, the sediment is useful to assess differences between fishing, sewage-contaminated-, and protected oxbows on elemental concentrations of surface sediment.

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