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HEAVY METAL CONCENTRATIONS IN SEVERAL WETLANDS SITUATED ON THREE BULGARIAN DANUBE TRIBUTARIES

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Abstract: The heavy metal contents of different aquatic ecosystem components were studied in several wetlands along the Danube River. The sampling stations included three oxbows and downstream parts of two Danube tributaries. Concentrations of the elements Cu, Pb, Zn and Cd were determined in water, sediment and plant samples. The study was carried out in April and August 2016. As expected, sediments contained the highest amounts of heavy metals. Water samples contained the lowest concentrations of the investigated elements. Notably, the plant samples from the main macrophyte species were the richest in zinc, followed by copper, lead, and cadmium.

INTRODUCTION

Danube wetlands play an important role in maintaining and enriching the biodiversity in the Danube River Basin. The Danube tributaries and adjacent oxbow lakes are significant for the preservation of specific rare and endangered plant species and communities. Aquatic contaminations by heavy metals are very harmful since these elements are not degradable and may accumulate in living organisms. Furthermore, the ability of aquatic plants to accumulate metals has been documented (Balogh et al., 2015; Outridge and Noller, 1991; Pajević et. al., 2008). Heavy metals are an important environmental pollutant with high toxicity to plants (Ederly et al., 2004; Prasad et al., 2004). Danube tributaries and their oxbows are affected by human activities (factories, power plants, fertilizers from agriculture, transport infrastructure, etc.) resulting in contamination of the water, sediments and living organisms in the wetland ecosystems. So far, there are only several studies on heavy metal concentrations in Danube wetlands in Bulgaria (Yurukova, 2000; Yurukova, 2004; Yurukova and Kochev, 1996; Yurukova and Kochev, 2000; Hiebaum et al., 2012; Ihtimanska et al., 2014) and very scarce data on freshwater aquatic plants heavy metal concentrations (Gecheva et al., 2006; Gecheva et al., 2011; Yurukova, 2000; Yurukova, 2004; Yurukova and Gecheva, 2004; Yurukova and Kochev, 1994; Yurukova and Kochev, 1996; Yurukova and Kochev, 2000). There is a lack of permanent monitoring of the chemical composition of water and sediments in many of the tributaries, as well as in tributaries' oxbows. This study is the first one designed to determine the concentration of heavy metals in several wetlands situated near the Danube River. The surveyed wetlands are rich in biodiversity and some of them are part of the Natura 2000 network of nature protected areas. Consequently, in order to preserve these important habitats profound surveys are required. Such studies provide information on the concentration of heavy metals in different components of aquatic ecosystems.

The aim of the study is to determine the concentration of copper, lead, zinc and cadmium in water, sediments and dominant aquatic plant species in several wetlands situated near the Danube River.

MATERIALS AND METHODS

The heavy metal concentration is studied in five wetlands situated along the lowest stretches of Yantra and Vit Rivers (Fig. 1.).

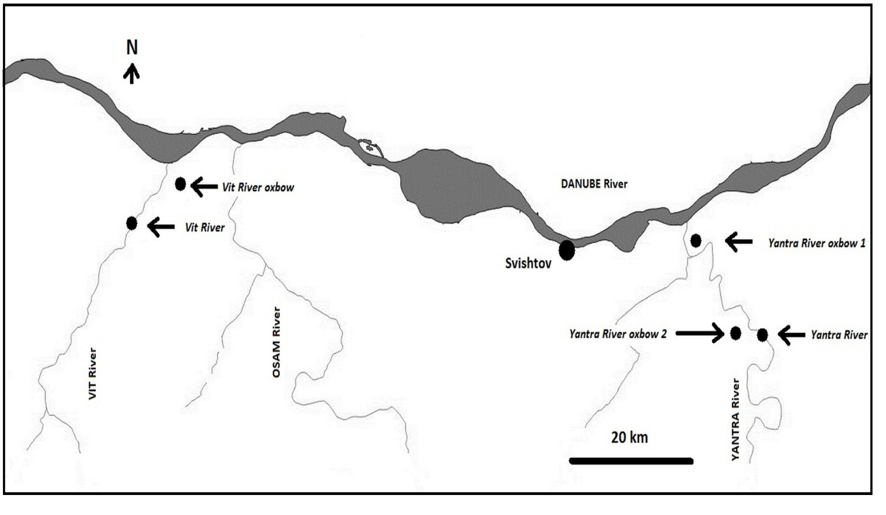

Fig.1. Map of the study area

Two of the wetlands are oxbows, situated on Yantra River, one is an embayment of Yantra River, one is a Vit River oxbow and one is the Vit River near the town of Gulyantsi. The studied oxbows are part of the Ecological network Natura 2000. They belong to sites BG0000610 Reka Yantra and BG0000181 Reka Vit. The sampling stations were eight, divided in two categories - rivers and oxbows. Six of them were located on oxbows and two on rivers. The fieldwork was carried out in April and August 2016.

Samples were taken from surface sediments (0-0.3 m), water and aquatic plants. The examined aquatic plants were found widely in the studied wetlands and were easily accessible for sampling. Heavy metal concentration was measured in *Phragmites australis* roots. The other sampled plants were *Myriophyllum spicatum* and *Ceratophyllum demersum* (whole vegetative parts).

The analytical methods used were as follows: concentrations of Cu, Zn, Pb and Cd (mg/l-water; mg/kg- sediment) - ISO 11047 were determined by employing atomic emission spectroscopy with inductively coupled plasma (ICP-AES); potential of hydrogen (pH) in sediments - BDS ISO 10390. Water and sediment samples were collected and preserved according to BDS 16777 and to BDS ISO 11466 respectively, plant samples-according to BDS ISO 12506.

The concentrations of the four studied elements in oxbows were pooled together, separately for substrate and water samples. The same was performed for river samples. The comparisons were performed for mean values of the pools.

RESULTS AND DISCUSSION

Elemental concentration in surface sediments

The average values of the measured pH in oxbows and rivers sediments are the same (8.15).

Mean concentrations of heavy metals in the sediments of the two types of studied water bodies (oxbows and rivers) were compared (Fig. 2). There is no significant difference in the concentrations of zinc, cadmium and lead between oxbow and river sediments ($p>0.05$). However, the quantity of copper in the oxbow sediments is higher than in river sediments (21.65±3.68 vs 28.98±2.88, Kruskal-Wallis test, $p <0.05$). This is probably due to the fact that oxbows are functioning as sediment trap (Balogh et al., 2016). The sediment is a good indicator of oxbows contamination because many organic and inorganic contaminants, especially heavy metals, can accumulate in the sediment (Bentivegna et al., 2004).

Our results show that the zinc concentration in sediments is the highest, followed by lead, copper and cadmium. This is comparable to Yurukova and Kochev's (1996) results for Srebarna Lake. However, there is a distinct difference in zinc levels: in our survey, they are ten times higher than those reported by Yurukova and Kochev.

Hibaum et al (2006) also confirmed that Srebarna Lake sediments are the richest in zinc, followed by lead, copper and cadmium. Compared to that study, our results again show much higher heavy metal concentrations in the sediments:

the zinc concentration is 30 times higher than in Srebarna Lake, the copper concentration is two times higher, and the cadmium concentration is 8 times higher.

Due to a lack of legislation in Bulgaria concerning surface sediment quality, the quality of the sediments was compared to the Environmental Protection Agency values (Baudo and Muntau, 1990). Our results showed that all studied oxbow sites and both river sampling stations were heavily contaminated with Zn. Both river stations and Yantra River oxbow 1 station are moderately polluted with Cu.

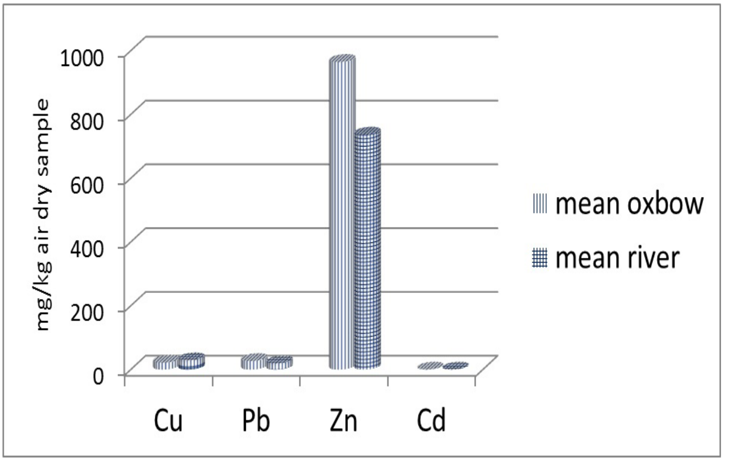

Fig. 2. Mean concentrations of heavy metals in the sediments of the two types of studied water bodies.

Elemental concentrations in water

Comparison between heavy metal concentrations in water samples of rivers and oxbows shows that the mean quantities of studied elements in water samples are similar (Fig. 3). However, the concentrations of the studied elements in river water samples are relatively higher, although the difference in copper and zinc concentrations is not significant ($p>0.05$). Notably, the quantity of lead in river waters is higher than in oxbow waters (0.031 ± 0.003 vs 0.022 ± 0.002; Kruskal-Wallis test $p<0.05$). Similar relation was found for cadmium concentration in rivers (0.03 ± 0.00) and oxbows (0.02 ± 0.00), with significant difference (Kruskal-Wallis test $p<0.05$).

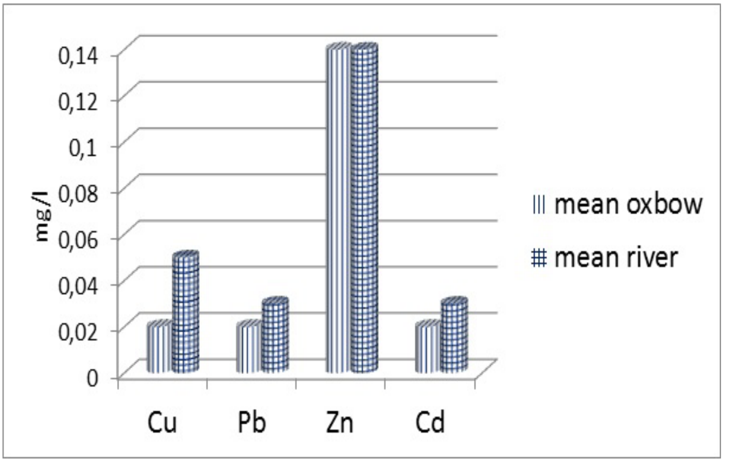

Fig. 3. Mean water concentrations of heavy metals from the two types of water bodies.

In the present study zinc has the highest values in water samples, followed by copper, lead and cadmium. This order of heavy metal distribution was also demonstrated by Yurukova and Kochev (1996), but the cadmium concentration measured in water samples in our study is 20 times higher than theirs, lead is 3 times higher and zinc is 1.5 times higher

In the present survey the heavy metal concentrations in water and sediments follows an order determined for natural waters (Yurukova and Kochev, 1996): Zn>Pb>Cu>Cd.

Elemental concentrations in aquatic plants

Results on heavy metal concentrations in aquatic plant samples show that *Ceratophyllum demersum* accumulates the highest quantities of the examined elements (Fig. 4). Lower concentrations of heavy metals are detected in *Myriophyllum spicatum,* and the lowest - in *Phragmites australis* (roots). Moreover, the amount of zinc in *Ceratophyllum demersum* is quite higher compared to the other two species, especially compared to *Phragmites australis*. Similar results on the accumulation capacity of the species *Ceratophyllum demersum* and *Myriophyllum spicatum* are published by Yurukova (2004).

Yurukova (2000, 2002) noted that *Ceratophyllum demersum* is a good bioaccumulator of Cu, Pb, Zn and Cd. In addition, in our study, the sequence of accumulation of heavy metals (Zn> Cu> Pb> Cd) in *Ceratophyllum demersum* is the same as that established by Yurukova (2000).

Our study confirms the ability of *Ceratophyllum demersum* to accumulate heavy metals in larger amounts than the other tested plant species. In the present study *Ceratophyllum demersum* accumulates two times more copper, zinc and lead compared to *Myriophyllum spicatum*, which confirms Yurukova's data (Yurukova, 2004) (Fig. 4). Accumulation of cadmium in *Ceratophyllum demersum* is also higher related to *Myriophyllum spicatum* concentrations.

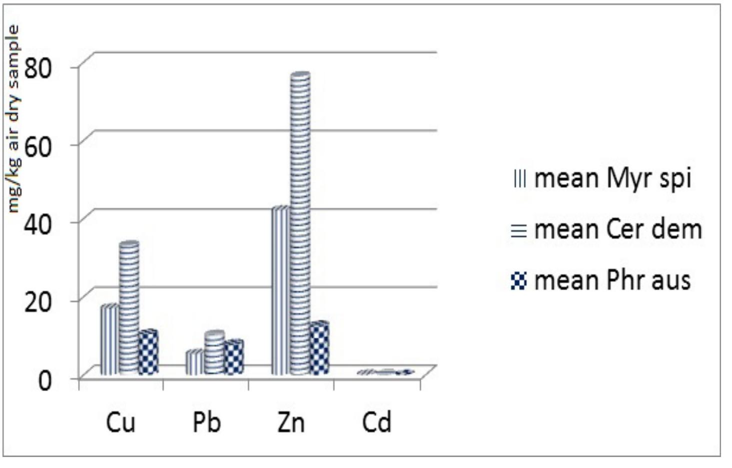

Fig. 4. Mean concentrations of studied heavy metals in plant samples from all studied sites.

The results for the heavy metal concentration in *Phragmites australis* roots in our survey and Yurukova and Kochev's survey for Srebarna Lake (1996) are very similar. In both studies, the zinc values are highest, followed by copper, lead and cadmium. However, in some of our study points (Yantra River oxbow 1) the roots of *Phragmites australis* accumulate five times more lead than *Phragmites australis* roots from Srebarna Lake.

The values of copper in *Ceratophyllum demersum* and in *Myriophyllum spicatum* plants from all the studied wetlands are higher compared to values for uncontaminated water environment (Outridge and Noller, 1991). Zinc concentrations are also higher in *Ceratophyllum demersum* from both rivers and in *Myriophyllum spicatum* from Yantra oxbow 2 station. Lead values determined in *Ceratophyllum demersum* samples from Vit River station are also greater. There is higher lead concentration in *Phragmites australis* from Yantra River oxbow 1 and Vit River oxbow and higher copper concentration in *Phragmites australis* from Yantra River oxbow 1.

The comparison between the data obtained for the four studied heavy metals from all samples (sediments, water, plants) from all investigated wetlands shows that the zinc content is the highest in all samples. This is most pronounced in samples of sediments (907.68 mg/kg) compared to the other samples where values are about 9 to 10 times lower (Fig 5).

The quantity of copper is the highest in *Ceratophyllum demersum* samples.

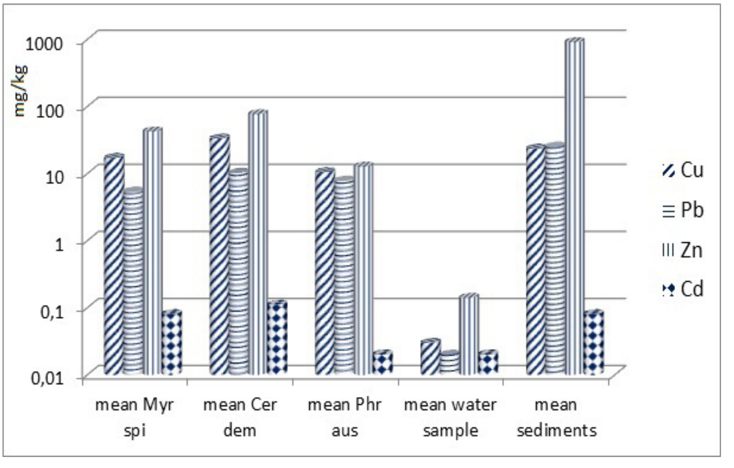

Fig. 5. Mean concentration of heavy metals in all of the studied components (water, sediment and plant samples). The y axis was log 10 transformed to improve legibility due to the large range of the values.

The intermediate concentrations of heavy metals found in the studied plants confirm that they are good accumulators of these pollutants. This is evident especially from the *Ceratophyllum demersum* data. This plant could be used to detect heavy metal pollution in wetlands, because it is relatively common and easily accessible

CONCLUSIONS

As in previous studies, we confirm that the lowest heavy metal concentrations are detected in the water samples, while the highest are found in the sediments.

The surface sediments of all the studied wetlands are heavily contaminated with zinc. Yantra and Vit Rivers stations and one of the sampling points from Yantra River oxbow 1 are moderately contaminated with copper. This contamination could be the result of the existence of several sources of sewage waters and the extensive agriculture in the region of the studied oxbows and rivers.

The studied plants were found to accumulate intermediate quantities of the surveyed heavy metals, with *Ceratophyllum demersum* having the highest accumulation capacity. Therefore, *Ceratophyllum demersum* is suitable for detection of heavy metal pollution in wetlands.

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