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DISTRIBUTION OF HEAVY METALS IN BOTTOM SEDIMENTS OF FLOODPLAIN LAKES AND THEIR PARENT RIVER – A CASE STUDY OF THE SŁUPIA*

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Abstract

Concentration of trace elements in bottom sediments can be a result of natural accumulation or caused by anthropogenic factors. The content of heavy metals (Cd, Cr, Cu, Ni, Mn, Pb and Zn) in bottom sediments of oxbow lakes and river-bed of the Słupia River at Słupsk was determined. Sediment samples were taken from two oxbow lakes: naturally disconnected and artificially re-connected with the river. The research showed variation in the content of the elements in sediments in relation to the accumulative and erosive activity of the river. At the water inflow into the re-connected oxbow lake, the transporting strength of the river decreased, which favoured the accumulation of heavy metals. The content of heavy metals in bottom sediments taken from the re-connected floodplain lake at the outlet was several-fold lower than at the inlet, for example there was 11-fold less Mn, 9-fold less Cu 9-fold, 3-fold less As and half the amount of Cd, Cr and Ni. The content of heavy metals at the outlet was similar to the one found in sediments of the oxbow lake separated from the river.

Key words: floodplain lake, Słupia river, bottom sediments, heavy metals.

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ROZMIESZCZENIE METALI CIĘŻKICH W OSADACH DENNYCH STARORZECZY I ICH MACIERZYSTEJ RZEKI (NA PRZYKŁADZIE DOLINY SŁUPI)

Abstrakt

Koncentracja pierwiastków śladowych w osadach dennych może być wynikiem naturalnej akumulacji lub jest zdeterminowana czynnikami antropogenicznymi. Badania terenowe wykonano w dolinie rzeki Słupi, na przedmieściach miasta Słupska. Próbki osadów pobrano na 4 stanowiskach zlokalizowanych w dwóch starorzeczach (w ich ramionach) oraz w rzece Slupi między zbiornikami. Zawartość Cd, Cr, Cu, Ni, Mn, Pb i Zn oznaczono po mineralizacji próbek na mokro w stężonym kwasie azotowym metodą ASA. Wykazano różnice w zawartości pierwiastków w osadach w zależności od poziomu akumulacji i erozyjnej działalności rzeki. W wyniku napływu wody do udrożnionego starorzecza i spadku siły transportowej rzeki zaobserwowano spadek poziomu akumulacji metali ciężkich. Ich zawartość w osadach dennych pobranych na wyjściu (ramię dolne) z OLS-4 była kilkakrotnie niższa niż na wlocie (ramię górne). Zawartość Mn zmalała 11-krotnie, Cu 9-krotnie, As 3-krotnie, Cd, Cr i Ni 2-krotnie. Zawartość metali ciężkich w miejscu wypływu (ramię dolne) była podobna do ich zawartości w osadach starorzecza oddzielonego od rzeki (OLS-5).

Słowa kluczowe: tereny zalewowe, rzeka Słupia, osady denne, metale ciężkie.

INTRODUCTION

Bottom sediments are an important element of a river valley, which are conducive to the absorption of chemical particles, whose content in the riverbed exceeds by several-fold the respective concentrations in the overlying water column (LINNIK, ZUBENKO 2000). In relation to the riverbed morphology and hydrological conditions, dissolved or suspended matter may undergo accumulation along the watercourse, often many kilometers below the source of pollution (CHOI et al. 2006, ANICIC et al. 2009). The source of heavy metals in bottom sediments, excluding natural processes of parent rock leaching, are municipal and industrial wastes, aerial runoff supplied by dry and wet atmospheric depositions, fertilizers and crop protection products (pesticides) (ZHAO et al. 1999, SKORBIŁOWICZ, SKORBIŁOWICZ 2010, BENCHEA et al. 2011, GLINA, BOGACZ 2013).

Some meandering river sections are more likely to be exposed to the deposition of the matter transported by the river. In the middle course, the transportation strength of the river weakens and bigger fractions are deposited as sandbanks. The accumulative and erosive activity of the Słupia River appears more profoundly along the meandering section of the river channel, where numerous oxbow lakes mark a former watercourse. Topographic depressions forming single loops along both sides of the river channel are permanently filled with water. Artificial oxbow lakes were created in the 20th century during hydro-engineering works on the river floodplain. The river regulation works composed of the reinforcement of the channel and the cutting-off of some river curves aimed at accelerating the water outflow by raising the slope of the riverbed. Beside some obvious changes in the habitat conditions for phyto- and zoocenoses, the water potential for self-purification decreased significantly (GALLARDO et al. 2008, LIGĘZA, WILK-WOŹNIAK 2011). A solution was found by redirecting the river water flow through oxbow lakes previously separated from the river, which would therefore be re-connected (OBOLEWSKI, GLIŃSKA-LEWCZUK 2011). The re-connection of oxbow lakes to the river may enhance the resuspension of bottom sediments and thus release previously accumulated heavy metals into the water. These are the underlying consideration for an attempt that has been made towards determination of effects of the unblocking of ox-bow lakes and the water inflow of the Słupia on the content of heavy metals in bottom sediments. The problem was discussed against the background of sediments in an ox-bow lake disconnected from the river as well as the river itself.

MATERIAL AND METHODS

Study area

The studied area covered the middle part of the Słupia River, rich in numerous floodplain lakes (Figure 1). This river is one of the biggest water-courses on the East European platform in Poland, which flows into the Baltic Sea (water catchment basin covers 1,620 km^2; the river is 138.6 km long, the average annual flow equals 15.5 $m^3 s^{-1}$, floods and a flow rate higher than 100 $m^3 s^{-1}$ usually appear between October and March). Most wetlands are agriculturally used and constitute 5.6% of the total studied area. In the early 20^{th} century, a number of river regulation works were performed, mainly cutting off the river meanders. As a result, almost 50 oxbow lakes appeared. The oxbow lakes are located on the right-hand side of the river. The one re-connected to the river (OLS-4) is a water body covering 0.13 ha and its maximal depth reaching 2 m. The re-connection was performed in 2000 using two PCV pipes (inlet and outlet ones) 0.3 m in diameter (OBOLEWSKI, GLIŃSKA-LEWCZUK 2011). The other lake (OLS-5) is separated from the river. Its area is to 0.7 ha and the maximal depth reaches 1.65 m (Table 1).

Samples

The investigation on the content of heavy metals in bottom sediments was conducted on the floodplain of the Słupia River above the town of Słupsk. In the autumn of 2007-2008, low stages of the river water facilitated the collection of sampling material. Sediment samples were taken from the river bank zone and 2 arms of both oxbow lakes. In the case of the re-connected oxbow lake (OLS-4) samples were taken from the zones of water inlet and outlet (Figure 1).

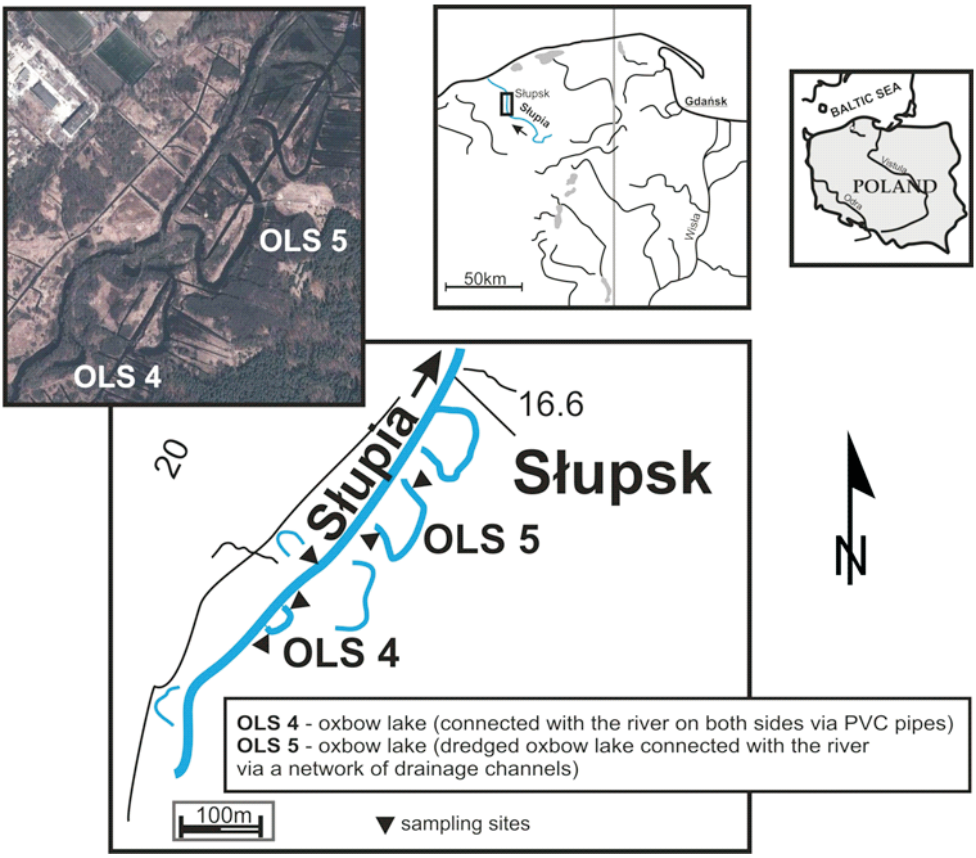

Fig.1. Location of sampling sites along the Słupia floodplain near the city of Słupsk, N Poland

At each sampling site, soil samples were taken at depths of 0 to 10, 10-20 and 20 to 30 cm. Representative samples (*ca* 1000 g) consisting of mixed sediment material were transported in linen bags to a laboratory and air-died. In the laboratory, before chemical analyses, the soil samples were dried at 40°C for 48 h and then passed through a 0.2-mm nylon sieve to obtain an optimal fraction for the assessment of pollution. A sediment fraction with the grain size below 0.125 mm was used for determination of the total content of contaminants. Portions of about 0.5 g from mixed samples were weighed out accurately and placed in 100 ml Teflon digestion tubes, where they were mixed with 8 ml of concentrated HNO_3 and 2 ml of 30% H_2O_2 (SALMINEN et al. 2005). Afterwards, the samples were digested for two hours in a microwave digester CEM MARS 5 (Microwave Accelerated Reaction System, USA).

Table 1

Morphological characteristics of the studied oxbow-lakes

Oxbow-lake			OLS-4		OLS-5	
Geographical coordinates			N 54º26'45.21"	E 17º01'38.70"	N 54º26'52.99"	E 17º01'58.41"
Type of connection with river			LOTIC (pipe PVC)		LOTIC (melioration ditches)	
Length	D (m)		116		468	
Width	S (m)		13.7		20.0	
Area	A (ha)		0.13		0.71	
Sinuosity	S=D/a-c (-)		1.5		2.5	
Distance between arms	a-c (m)		75		188	
Distance from river	upper arm (m)		23		37	
	lower arm (m)		21		22	
	max.(m)		46		160	
Width	river	S_{rz}(m)	15.2		14.5	
	river valley WWW	S_{dol} (m)	374		308	
Depth	$h_{śr}$ (m)		0.88		0.79	
	h_{max}(m)		1.82		1.65	
Volume	$V_{śr}$ (thou m^3)		1.14		5.51	

The following trace metals: Cd, Cr, Cu, Ni, Mn, Pb, Zn and As were determined in bottom sediments in an atomic absorption spectrometer Spectra AA100 (Varian, Australia). The accuracy of determinations of the total content of heavy metals was verified against certified reference material, which was analyzed at the beginning and the end of the sampling series. The observed error was less than 5% of the certified value.

The non-parametric Kruskal-Wallis and Dunns (p<0.05) tests were applied in order to indicate statistical significance of differences in environmental conditions between the sampling sites.

RESULTS AND DISCUSSION

The Słupia River belongs to young glacial watercourses, which are characterized by numerous channel bends, meanders and oxbow lakes (OBOLEWSKI, GLIŃSKA-LEWCZUK 2011). The character of the river are conducive to the deposition of material transported by the river. Near the town of Słupsk, the slope of the riverbed diminishes, which results in more intensive formation of sandbanks. These are potential sites for the accumulation of many chemical elements. Bottom sediments in the re-connected oxbow lake are also the result of intensive accumulation of matter originating from the river. The decreased velocity of water inflowing into the oxbow lake enables the deposition of substances just behind the inlet pipe.

The quality of bottom sediments depends on amounts of pollutants introduced to the river above the study site, the chemical composition of water as well as the parent rock on which the river valley lies (GLIŃSKA-LEWCZUK 2005). Heavy metals are mainly derived from agriculture in the catchment basin of the Słupia River and from the wastewater, whose handling and treatment remain unregulated. Another source of pollution is municipal sludge discharged into the river or its tributaries.

Despite the low pollution of the sediments with heavy metals, the results demonstrated significant differences between the sampling sites (Table 2). The river, which acts as a direct recipient of pollutants generated by people in the catchment area, showed the highest content of such heavy metals as Cd, Cr, Cu, Ni and Zn in bottom sediments relative to the other sampling sites, except Mn, Pb and As, which were found in higher concentrations in samples from OLS-4, a lake permanently connected with the Słupia River. The highest concentrations of the above metals were determined in sediments at the in-flow zone of the river water to the oxbow lake.

The analyses showed that bottom sediments in the river channel and the site of the oxbow lake connected to the river contain significantly higher amounts of heavy metals than the geochemical background defined by BOJAKOWSKA and SOKOŁOWSKA (1998) or LIS and PASIECZNA (2001). Comparing the lead contents in bottom sediments in the Słupia riverbed to the background value computed for flowing water sediments *i.e.* 10-15 mg Pb kg^{-1} d.m., it needs to be pointed out that the content of Pb (54.80 mg kg^{-1}) was four-fold higher than the natural level. Similarly, the Cd content (0.79 mg kg^{-1}) was found to exceed the background value (0.5 mg Cd kg^{-1}). The content of chromium in the investigated bottom sediments ranged from 3.9 to 33.7 mg Cr kg^{-1}, being also higher than the geochemical background for aquatic sediments in Poland: 5 mg Cr kg^{-1} according to BOJAKOWSKA and SOKOŁOWSKA (1998), or 10 mg Cr kg^{-1} according to LIS and PASIECZNA (2001). Sediments in the river and in the re-connected oxbow lake contained copper at amounts five-fold higher than the background, *i.e.* 6 mg Cu kg^{-1} (Table 2). Nickel varied from 11 to 32 mg kg^{-1}, and was 2- to 6-times as much as the natural

Table 2

Content of heavy metals (mg kg^{-1}±s.d.) in bottom sediments at the study sites in the Słupia River valley

	Oxbow lake				the Słupia River (*N*=4)	Average
	OLS-4 N=4		OLS-5 N=4			
	in-flow	out-flow	upper arm	lower arm		
	1	2	3	4	5	
Cd	0.44±0.32	0.23±0.14	0.10±0.08	0.12±0.06	0.79±0.29	0.34±0.21
Cr	7.9±0.2	3.9±2.2	6.2±1.9	6.1±2.0	33.7±11.5	11.6±3.2
Cu*	30.9±13.72	3.4±0.71	3.7±1.1	2.8±0.9	34.9±14.7	15.1±6.8
Ni	10.6±3.7	4.8±1.0	6.5±1.6	4.7±1.6	32.2±10.6	11.8±4.8
Mn	1190±112	111±33	193±76	130±54	645±289	454±89
Pb*	164.9±78.92	12.3±2.71	8.4±1.85	8.0±2.25	54.8±23.63,4	49.7±8.9
Zn*	67.4±28.92,5	18.8±4.11,5	22.0±11.05	19.4±5.75	142.6±35.21,2,3,4	54.0±15.9
As	2.66±0.88	0.96±0.12	0.50±0.20	0.60±0.33	2.03±0.90	1.4±0.53

*statistically significant differences between the studied sites; non parametric Kruskal-Wallis test, $P<0.05$
1-5 statistically significant differences between the studied sites; non parametric Dunns test, $P<0.05$
N – number of samples

level, *i.e.* 5 mg Ni kg^{-1}. The cadmium content in sediments was similar to the geochemical background level (0.5 mg Cd kg^{-1}). The geochemical background level was not exceeded by arsenium versus the normal level in aquatic sediments in Poland (5 mg As kg^{-1}).

The results showed that the direct connection of OLS-4 with the river channel did not influence the quality of all bottom sediments in the water body. The comparison of heavy metals in its sediments showed significant differences between the inlet (OLS4- in-flow) and outlet (OLS-4) sites. At the outlet site, the Pb concentration was 13-fold lower than at the inlet ($P < 0.05$). The highest decrease was observed for manganese, copper, zinc and arsenium (Table 2). The smallest differences in the content of metals between the inlet and outlet zones in the sediments of OLS-4 were found for cadmium, chromium and nickel.

The sediments from OLS-5, an oxbow lake separated from the river, were characterized by the content of the heavy metals similar to that at the outlet from the re-connected oxbow lake. In comparison to the amounts of heavy metals found in bottom sediments of the river channel, the content of the elements was several-fold lower: Cu 12-fold, Cd, Ni, Pb and Zn by 7-fold, Cr by 6-fold, Mn by 5-fold and As by 3-fold. Samples taken from both arms of OLS-5 (upper and lower arm) showed similarly low levels of all the investigated heavy metals.

Any motion of river water in the re-connected oxbow lake (in-flow) may cause the resuspension of bottom sediments and secondary water pollution. Although oxbow lakes are thought to serve as a biogeochemical filter (water - bottom sediments - plants - animals) in the riverine landscape, it is worth noticing that most natural aquatic sediments commonly have a living and active biological component and inorganic and non-living bio-logical particles (WALLING, OWENS 2003, SCHROEDER et al. 2005). Presumably, elements which have not been leached out with the river water are partly accumulated in plants overgrowing intensely the oxbow lake and absorbed into a trophic network. This is confirmed by non-significant amounts of heavy metals in the surface water of the re-connected lake (OBOLEWSKI, GLIŃSKA-LEWCZUK 2011).

In any evaluation of the mobility of heavy metals in sediments, the composition of the uppermost layer appears to be very important. Following the river regulation works, the newly formed oxbow lakes are characterized by an amorphic layer composed mostly of organic matter, which corresponds to the sediments stored for about 30 years, and demonstrates the up-to-date environmental pollution in the region. This layer holds the maximal (direct) accumulation of pollutants that normally reside within the upper 30 cm of a profile (ZHAO et al. 1999, IBRAGIMOW et al. 2010). Beneath surface deposits, the parent material is built mostly of the clay, which – owing to its absorptive properties – is supposed to accumulate particles of heavy metals. Thus, the parent material should indicate the background (uncontaminated) levels of heavy metals in aquatic deposits. It can be useful in further studies on sediment pollution by trace elements.

CONCLUSIONS

1. Bottom sediments of the Słupia River and oxbow lakes are characterized by a low level of heavy metal contamination, close to the natural content determined for sediments of aquatic systems in Poland.

2. The maximal content, exceeding the background levels, of the metals under investigation was determined in the sediments taken both from the river channel and the inlet of river water to the re-connected oxbow lake.

3. The results showed that concentrations of heavy metals in sediments of oxbow lakes generally decrease after they have been reconnected to a river. Unblocked oxbow lakes may play a role of filters for heavy metal pollution transported down the river. Although significant accumulation of heavy metals was found at the inlet to the oxbow lake, the content of heavy metals found at the outlet was several-fold lower. The manganese content at the outlet site decreased by 11-fold, copper by 9-fold, zinc by 4-fold, arsenic by 3-fold and cadmium, chromium and nickel by two-fold.

4. Most of the investigated heavy metals in sediments of the oxbow lake separated from the river represented values similar to those found in sediments at the outlet from the re-connected oxbow lake. The lack of direct connection to the river allowed maintaining relatively low contents of heavy metals in the oxbow lake sediments in comparison to river sediments: Cu by 12-fold, Cd, Ni, Pb and Zn by 7-fold, Cr by 6-fold, Mn by 5-fold, whereas As by 3-fold lower than in the riverbed sediments.

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