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HEAVY METALS CONTENT IN THE SPROUTS OF *Glyceria maxima* (Hartm.) Holmb. AND IN RIVER SEDIMENTS (NORTHERN POLAND)

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Abstract

The aim of this study was to evaluate the content of Zn, Mn, Cu and Ni in the aboveground and underground shouts of *Glyceria maxima* and in the bottom sediments of the Słupia River. These studies allow for assessment of the existing and potential hazards resulting from toxic influence of heavy metals on water environment and human health. The concentration of research elements was determined by atomic absorption spectrometry (AAS). Results indicate that the concentration of heavy metals in the examined bottom sediments remained within the limits of the geochemical background for majority of the determined elements. The concentrations of Zn and Cu, sporadically exceeded the level of the geochemical background at the stations in the central part of the city, and in the case of Ni in all researched positions. Following the LAWA classification, the bottom sediments within the Słupsk area were classified in the first class, as slightly contaminated. It was found the *G. maxima* underground sprouts accumulated several times more of Zn, Mn, Cu and Ni than their aboveground sprouts. The indices of quality of the tested bottom sediments and the enrichment factors of the sprouts with heavy metals indicate that the Słupia River is the least contaminated along the segments of the river with a low or moderate transformation of the river bed and the largest load of Zn, Mn, Cu and Ni is found at the stations with a high transformation of the river bed. The strong positive correlations between the concentrations of Mn in bottom sediments and the level this element in aboveground and underground sprouts indicate that the sprouts of *Glyceria maxima* are potentially useful in biomonitoring environmental contamination with Mn.

Key words: bottom sediments, heavy metals, indicators of quality of sediments, macrophytes

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1. Introduction

Due to their common character of application in different branches of economy, heavy metals are hazardous to the natural environment (Baptista Neto et al., 2000; Tam and Wong, 2000; Tang et al., 2010). As natural components of ecosystems, they are necessary in minute quantities for correct functioning of organisms. However, their excessive concentration in the environment is harmful. At relatively high concentrations, they disturb functioning of ecosystems, being harmful for living organisms (Hlihor et al., 2009; Obolewski and Glińska-Lewczuk, 2006). Natural processes and industrial and agricultural activity constitute the source of heavy metals. At present, the intensity of use of river catchments as well as the inflow of sewage have substantial impact on the chemical composition of sediments (Salati and Moore, 2009). It leads to increase of heavy metal content in fluvial deposits which are important elements of the water environment. Their quantity often exceeds the concentration provided by the geochemical background and is a strong indicator of rivers pollution (Klavins et al., 2000; Kobus et al., 2016). Most heavy metals introduced to rivers are connected

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and transported with the suspended matter whose deposition leads to origination of bottom sediments in surface waters, both with fast and slower flow. A part of such chemical compounds is deposited at bottom sediments (Kruopiene, 2007).

Heavy metals are biologically transformed and can be maintained in bottom sediments for a long time in tens or hundreds of years (Bettinetti et al., 2003; Liu et al., 2009). When accumulated in bottom sediments, they can constitute secondary sources of pollution which are still harmful to water ecosystems (Yuan et al., 2004). The quality of sediments is a good indicator of pollution of water environment, as well as the quantity of emitted pollutants in the river catchment (Klavins et al., 2000; Vandecasteel et al., 2004; Wiśniowska-Kielian and Niemiec, 2005). Tests of benthos revealed that the polluted sediments can cause acute and chronic toxic effects water organisms, especially fish (Obolewski and Glińska-Lewczuk, 2006; Obolewski et al., 2016).

The pollution of bottom sediments has impacts on the reduction of many species of water fauna which are important from the point of view of exploitation and ecology, such as snails and fish. Heavy metals are biologically accumulated in plant and animal tissues, so the toxic hazard increases at subsequent levels of the trophic chain (Klink et al., 2013; Kurilenko and Osmolovskaya, 2006; Loska and Wiechuła, 2003). Plants react in various ways to increased concentration of heavy metals in the environment. Absorption and bioaccumulation of trace elements by plants is a part of the natural cycle. In biological identification of water ecosystems, the plants of coastal zone (macrophytes) are used, which, along with phytoplankton, macrozoobenthos and fish, constitute basic elements of ecological evaluation of the status of rivers (Klink et al., 2013, Obolewski and Glińska-Lewczuk, 2006; Skorbiłowicz, 2003; Skorbiłowicz and Skorbiłowicz, 2011). Macrophytes reflect the status of heavy metal pollution of water reservoirs very well (Samecka-Cymerman and Kempers, 1996, Miretzky et al., 2004, Aksoy et al., 2005).

The heavy metals content in aquatic plants may exceed many times their content in the surrounding water environment, the wide range of variability is caused by biology and ecology of particular species. Some aquatic plants are used in environmental research (Salt and Kramer 2000, Baldantoni et al., 2004, Mishra and Tripathi, 2008). *Glyceria maxima* plays the role of bioindicator of water pollution (Tanner 1996, Sriyaraj and Shutes 2001, Rabajczyk and Jóźwiak 2009, Teuchies et al., 2013). Control of the chemical composition of bottom sediments and aquatic plants in municipal areas is very important due to the harmfulness of heavy metals (Dauvalter and Rognerud, 2001; Xiangdong et al., 2000). These studies allow for specification of the existing and potential hazards resulting from toxic influence of heavy metals on water environment and human health.

The research aimed at (1) evaluation of the content of Zn, Mn, Cu and Ni in above-ground and underground sprouts of *Glyceria maxima* as well as in the bottom sediments of the Słupia River, (2) specification of accumulation coefficients of the above mentioned heavy metals in sprouts of *Glyceria maxima*, and (3) evaluation of the quantity of the bottom sediments within the area of the city of Słupsk from the point of view of the concentration of selected heavy metals in them.

2. Material and methods

2.1. Research area

The Słupia River is situated in the central part of Pomerania (Northern Poland). It is a lowland watercourse 138.6 km in length and with a catchment area of 1620 km^2. In the north the Słupia River catchment borders the Baltic Sea catchment; in the west, the Wieprza River catchment; in the South, the Brda River catchment, and from the east, Łeba and Łupawa. The Słupia River headwater is at the Kashubian Lake District close to Sierakowska Huta at the height of 178 m a.s.l.

The river flows to the Baltic Sea in Ustka. The width of the river bed varies from 7 m in the upper part of the river to 40 m at its mouth, where the average flow is 15.5 $m^3 \cdot s^{-1}$. The river stream is strongly meandered (Piechura et al., 1997). The area of the City of Słupsk covers a 8 km stretch of the Słupia River with various levels of transformation of the water bed (low, moderate or high) (Table 1) (Obolewski and Glińska-Lewczuk, 2006), whose banks are covered with numerous macrophytes.

2.2. Research methods

The research was done in July 2013 at the area of 10 stations situated within the city limits. Samples of bottom sediments and aboveground sprouts (leaves, stems) and underground ones (rootstock) of *Glyceria maxima*, (Fig. 1) were taken at the river bank zone of the Słupia River where the sedimentation of the suspended material takes place. The bottom sediments were collected with the use of the *Eckman* sampler from the depth of 0-15 cm.

After their transport to laboratory, the samples were dried at a temperature of 65ºC, they were sieved through a 1mm and ground in a mortar. Before analysis, the deposit samples were tested as to the content of $CaCO_3$ (with 0,1M HCl). In the bottom sediments, the granulometric composition was marked by means of the gradation test, as well as active acidity (pH, H_2O), exchange acidity (pH, KCl), and the organic matter content by the method of heat loss in a muffle furnace at the temperature 550ºC. The samples of *Glyceria maxima* at the area of each station were taken for testing from several sprouts creating mixed samples both from aboveground and underground sprouts. After their transport to laboratory, the plant material was cleaned of mineral parts of the soil and flushed in distilled water.

Table 1. Characteristic of sampling points

Stations	***The degree of transformation river bed***	***Type ground***	***The dominant of macrophytes***			
			Glyceria maxima	***Typha latifolia***	***Phragmites australis***	***Phalaris arundinacea***
1	low	silt	+	+	+	
2	low	silt	+		+	+
3	low	silt	+		+	
4	moderate	sand	+	+	+	+
5	high	stone	+	+		+
6	high	stone	+	+	+	+
7	high	stone	+	+	+	+
8	moderate	sand	+			+
9	moderate	stone	+		+	
10	low	silt	+			

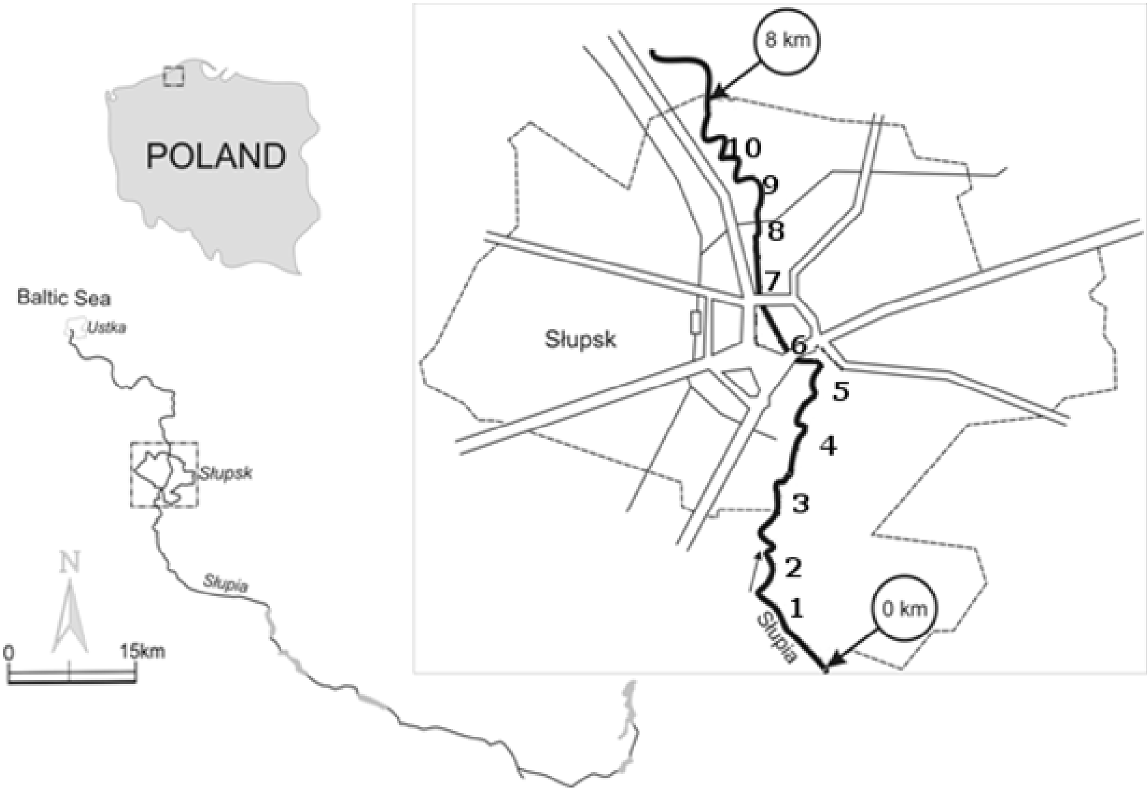

Fig. 1. Sediment sampling points

The aboveground sprouts (leaves, stems) were separated from the underground ones (rootstock), dried to stable mass at the temperature of 65ºC, and then homogenized in a laboratory grinder. The content of Zn, Mn Cu and Ni were determined by AAS method (Perkin Elmer, Aanalyst 300) in a solution after mineralization in a mixture of the concentrated HNO_3 and 30% H_2O_2. The analyses were performed in the oxy-acetylene flame according to Ostrowska et al. (1991). The tests were carried out following the original standards (Merck KGaA,1g/1000ml).

2.3. Elaboration of results

The results obtained were verified by means of statistic methods using Statistica software (7.1.). The values of minimum, maximum, mean, standard deviation, Spearman correlation coefficients and coefficients of variation (CV) are presented. Classification of bottom sediments was made in according with the classification of LAWA (1998), which divides the sediments on the purity class as the increasing content of heavy metals (Table 2). It is assumed that the metal content in the dry matter of bottom sediments for classes I and I-II at the level of the geochemical background, while class II to IV indicate to the increasing influence of anthropogenic pollution of bottom sediments of rivers, and thus of the whole aquatic ecosystem.

For evaluation of the level of contamination of sediments, classification of water sediments in Poland on a basis of geochemical criteria was used (Bojakowska and Sokołowska, 1998). The indexes calculated were pollution load index (*PLI*), Geoaccumulation index (I_{geo}) and enrichment factor (*EF*) according to Eqs. (1-4).

Table 2. Classification of LAWA

	Purity class						
	I	***I-II***	***II***	***II-III***	***III***	***III-IV***	***IV***
Zn	≤ 100	≤ 200	≤ 400	≤ 800	≤ 1600	≤ 3200	> 3200
Cu	≤ 20	≤ 40	≤ 80	≤ 160	≤ 320	≤ 640	> 640
Ni	≤ 30	≤ 60	≤ 120	≤ 240	≤ 480	≤ 960	≤ 960
Class I	Uncontaminated						
Class I-II	Uncontaminated / Moderately contaminated						
Class II	Moderately contaminated						
Class II-III	Moderately contaminated / Heavily contaminated						
Class III	Heavily contaminated						
Class III-IV	Heavily / Very heavily contaminated						
Class IV	Very heavily contaminated						

$$PLI = \sqrt[n]{CF_1 \times CF_2 \times CF_3 \times ... \times CF_n} \quad (1)$$

where:
n – number of analyzed positions;
CF – pollution factor, (Chakravarty and Patgiri, 2009)

$$CF = \frac{C_e}{(C_e)_{EC}} \quad (2)$$

$$I_{geo} = \frac{C_e}{1.5(C_e)_{EC}} \quad (3)$$

$$EF = \frac{\left(\frac{C_e}{C_{Al}}\right)_S}{\left(\frac{C_e}{C_{Al}}\right)_{EC}} \quad (4)$$

where:
$(C_e)_s$ - concentration of elements in the sample,
$(C_{Al})_s$ – concentration of aluminum in the sample,
$(C_e)_{EC}$ – geochemical background

3. Results and discussion

The bottom sediments in the Słupia River were characterized by diverse granulometric composition. Fine sand constituted the largest part (0.25-0.1 mm) – over 50%, and medium grained sand (0.5-0.25 mm) – over 23%. At the research stations 5, 6, 7 and 9 small quantities of gravel (7.9 %) and stone (0.5 %) were found. At all stations, the lowest contribution had a fraction of dust (<0.05 mm) – average 1.2 %, (Fig. 2).

The tested sediments did not contain $CaCO_3$. They were characterized by the a slightly alkaline reaction both in the case of pH (H_2O), and pH (KCl), (Table 3).

The average reaction was from 7.00 to 8.19, reflecting variability at the level of 4.6 % within the area of 10 research stations. The content of organic matter in the bottom sediments of the Słupia River was substantially diverse with the levels from 0.56 to 7.94 %, and variation coefficient was 117.0 % (Table 3).

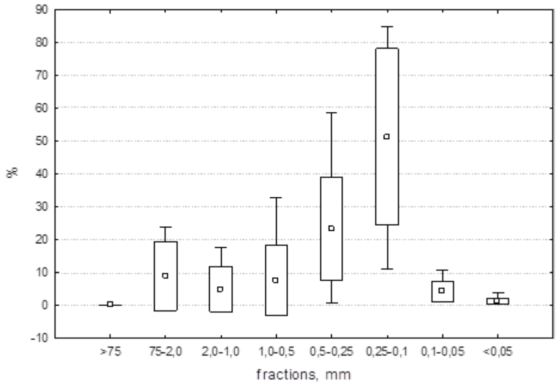

Fig. 2. Granulometric composition sediments of the River Słupia, point (mean), rectangle (standard deviation), whiskers (minimum-maximum)

The highest level of organic matter content was in the samples of sediments from stations 4 and 10, characterized by strong river meanders which welcomed substantial accumulation. The lowest quantities of accumulated organic matter (<1%) were found at the stations 2, 3, 5, 6 and 8, with a prevailing process of free transport of organic matter down the river stream.

Zinc content in the bottom sediments of the Słupia River varied substantially (CV= 82.2 %) with levels from 12.4 to 104.7 mg·kg^{-1}, average 34.1 mg·kg^{-1} (Table. 4). In 25 % of tested samples, the zinc content was between 20 and 25 mg·kg^{-1} (Fig. 3). The zinc concentration in the river sediments within the city limits of Słupsk in 2013 exceeded the value of geochemical background (>48 mg·kg^{-1}) only at stations 4 and 9.

Table 3. The organic matter content and pH of bottom sediments

	pH (H_2O)	***pH (KCl)***	***Organic matter***
Average ± SD	7.84 ± 0.36	7.66 ± 0.40	2.14 ± 2.51
Median	7.95	7.79	0.91
Minimum	7.00	6.68	0.56
Maximum	8.19	8.08	7.94
CV, %	4.6	5.2	117.0

The natural content of Zn in sediments of surface water (lakes and rivers) in Poland is about 74 mg·kg^{-1} (Lis and Pasieczna, 1995). As a geochemical background of zinc in the bottom sediments of the Vistula River and its tributaries, the value of 110 mg·kg^{-1} (Helios-Rybicka, 1991) was adopted.

A slightly different type of aquatic ecosystems of rivers and lakes are old river beds. This is particularly evident in the assessment of the concentration of individual metals in bottom sediments, which is usually more. Concentration of Zn in the bottom sediments of old river beds of the Słupia River was on average 142.6 mg·kg^{-1} and resulted from accumulation and the lack of water outflow (Obolewski and Glińska-Lewczuk, 2013). Zinc is a metal commonly introduced to surface waters along with municipal sewage and surface flow. Burning of coal is a source of zinc in the environment along with use of zinc covered water pipes. Zn concentration in bottom sediments of the Słupia River does not have negative impact on living organisms. According to the classification Lawa (1998) the Słupia River sediments should be classified to the 1st quality class as to the zinc content – uncontaminated sediments (Table 2).

Manganese content was between 58.1 and 376.7 mg·kg^{-1}, average 152.1 mg·kg^{-1}. The manganese concentration variability coefficient in the bottom deposits was 73.3 % (Table. 4). For 50 % of the examined stations Mn content was from 50 to 100 mg·kg^{-1}.

Table 4. Heavy metals (mg·kg^{-1}) contents in bottom sediments of the river Słupia

	Zn	***Mn***	***Cu***	***Ni***
Average ± SD	34.1 ± 28.0	152.1 ± 111.5	8.4 ± 4.4	11.9 ± 2.8
Median	22.8	119.0	7.5	11.7
Minimum	12.4	58.1	2.6	8.5
Maximum	104.7	376.7	15.1	16.8
CV, %	82.2	73.3	52.8	23.5

Only at two stations (4, 10) Mn content exceeding 300 mg·kg^{-1} was discovered (Fig. 3). Obtained manganese contents in bottom sediments of the Słupia River did not exceed the level of geochemical background (500 mg·kg^{-1}). Slightly higher manganese concentrations were found in the old river beds of the Słupia River – 645 mg·kg^{-1} (Obolewski and Glińska-Lewczuk, 2006), which could have been a result of accumulation connected with the lack of outflow of water.

The Oder River bottom sediments contained 770 mg·kg^{-1}, and the Rhine River deposits even 960 mg·kg^{-1}Mn (Kucharzewska et al., 1991). Manganese of the bottom sediments is characterized by high mobility (Kabata-Pendias and Pendias, 1999), which is especially stimulated by pH~8. The main source of manganese in environment is washing out of rocks and soils. Anthropogenic sources comprise mainly coal and gasoline.

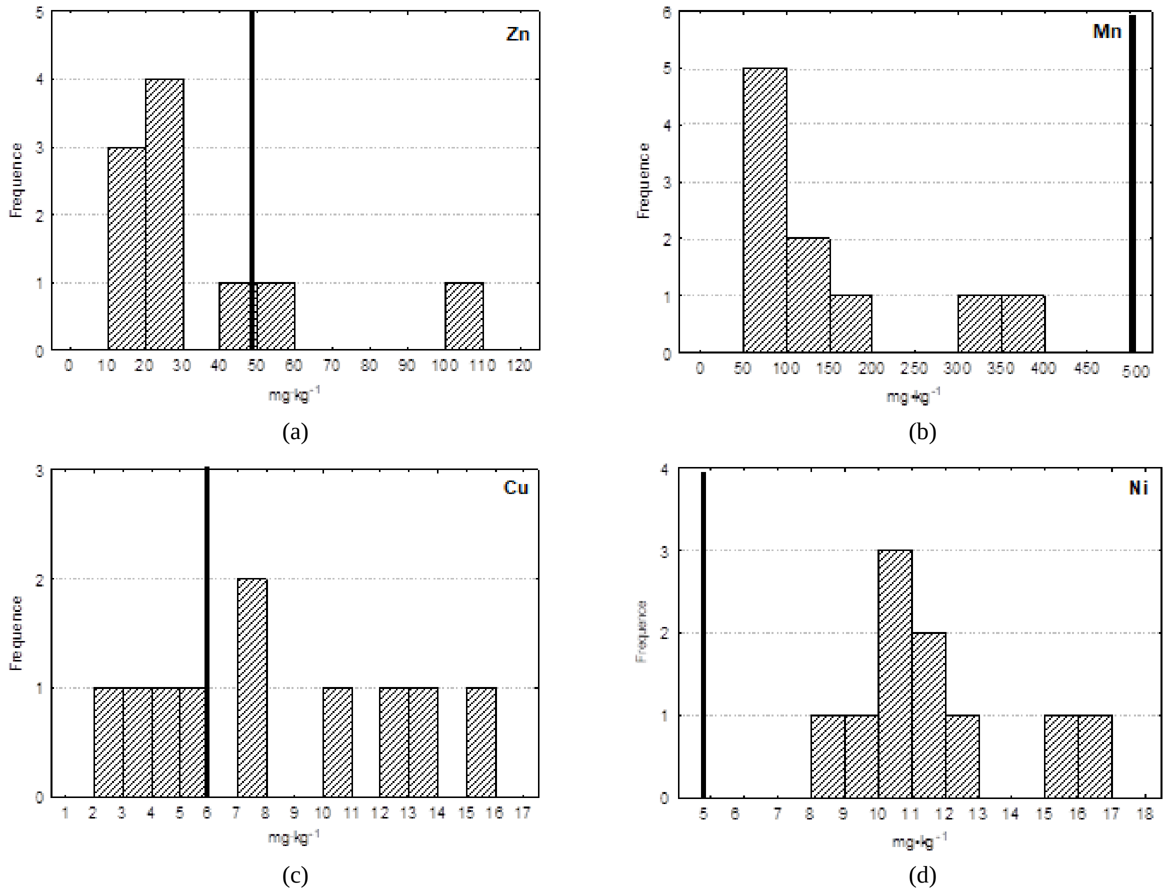

Fig. 3. Histograms of heavy metals contents in bottom sediments of River Słupia. Black line – values of geochemical background

Copper content in bottom sediments of the Słupia River was on average 8.4 $mg \cdot kg^{-1}$ with the values ranging from 2.6 to 15.1 $mg \cdot kg^{-1}$. Cu concentration showed variability at the level of 52,8% within the area of research stations (Table 4). The copper content in the sediments was low and was within the limits of the geochemical background (6 $mg \cdot kg^{-1}$) except the stations 4, 5, 6, 7, 9 and 10. The highest content of Cu (15.1 $mg \cdot kg^{-1}$) was found at station 5, where substantial transformation of the river bed took place (concrete covering), (Fig. 3). Slightly higher levels of Cu (34.9 $mg \cdot kg^{-1}$) were revealed in bottom sediments of the old river beds of the Słupia River by Obolewski and Glińska-Lewczuk (2006), which could have resulted from the increased accumulation of organic matter caused by the lack of water outflow (Bettinetti et al., 2003; Liu et al., 2009). The copper content in the water sediments is connected with the kind of the parent rock and usually is several $mg \cdot kg^{-1}$. According to Lis and Pasieczna (1995) the natural content of Cu in the river sediments usually does not exceed 20 $mg \cdot kg^{-1}$. Contamination of environment with copper, including river sediments, takes place mainly due to mining and processing of copper ore, but can also be a result of applied pesticides, additives to fodder in agriculture and a result of burning fossil fuels. Discharge of untreated sewage from galvanizing plants and their improper storage makes ions of copper penetrate the bottom waters and sediments (Bojakowska and Sokołowska, 1998). Due to its small content in tested sediments (Cu<36 $mg \cdot kg^{-1}$), copper has no negative impact on living organisms.

Nickel content in the bottom deposits of the Słupia River was from 8.5 to 16.8 $mg \cdot kg^{-1}$, average 11.9 $mg \cdot kg^{-1}$. The concentration variation coefficient of Ni was the lowest from among tested heavy metals and was 23,5 % (Table 4). The largest quantity of nickel (>15 $mg \cdot kg^{-1}$) was found at the stations 4 and 10, as well as in the case of manganese (Fig. 3). At all stations, the content of Ni exceeded the level of the geochemical background (>5 $mg \cdot kg^{-1}$), but according to classification Lawa (1998) it belonged to the class I of the clarity (<30 $mg \cdot kg^{-1}$), Table 2. Higher Ni content was found in the sediments of the old river beds of the Słupia River – 32.2 $mg \cdot kg^{-1}$ (Obolewski and Glińska-Lewczuk, 2013), and most probably, it was an effect of increased accumulation of organic matter and the lack of water outflow (Bettinetti et al., 2003; Liu et al., 2009). The natural nickel content in the bottom sediments of the Vistula River was 40 $mg \cdot kg^{-1}$ (Helios-Rybicka, 1991), and in the case of other rivers of Poland, about 10 $mg \cdot kg^{-1}$ (Lis and Pasieczna, 1995). Burning of coal and liquid fuels is a source of nickel in the natural environment. Effluents from the municipal and industrial dump sites constitute additional sources of nickel contamination of water sediments, as a result of dumping of accumulators and nickel-cadmium batteries and discharge of waste from galvanizing plants used catalysts. A series of statistically significant relationships were found among the tested parameters (Table 5).

Along with the increase of organic matter content in bottom sediments, decrease of pH was observed ($r=-0.78$ and $r=-0.81$, $p<0.05$, $n=30$) together with increase of concentration of Mn, Cu and Ni ($r=0.90$, $r=0.53$ and $r=0.91$, $p<0.05$, $n=30$). Active acidity and exchange acidity were also significantly related to one another. Increase of acidity had a significant impact on release of ion forms of Mn, Cu and Ni from bottom sediments. It was also found, that with the increase of concentration of Zn and Mn, an increase of Cu concentration was found. A positive and statistically vital correlation was also found between Mn and Ni and Cu and Ni (respectively $r=0.90$ and $r=0.47$, $p<0.05$, $n=30$), (Table 5).

The values of geo-accumulation indexes were between: $0<I_{geo}<1$, which according to a 7-grade classification of bottom sediments LAWA (1998), Eqs. 1, 3 and 4 shows moderate contamination of the bottom sediments of the Słupia River in relation to Zn, Mn, Cu and Ni. The values of enrichment factors *EF*, show the lack of contamination of bottom sediments of the Słupia River in case of Zn and Mn (*EF*<1) and a slight contamination with copper and nickel (Table 6). Enrichment factors (*EF*>1) in the case of Cu and Ni reveal anthropogenic contamination with these elements. Also the indexes of pollution load (*PLI*) show slight contamination of the Słupia River bottom sediments with Zn and Mn (*PLI*<1) and Cu and Ni (*PLI*<2.33), (Table 6).

Table 5. The correlation coefficient between the researched parameters ($n = 30$, $p <0.05$, $r_{crit.} = 0.30$) in the bottom sediments of Słupia

	Organic matter	***pH H_2O***	***pH KCl***	***Zn***	***Mn***	***Cu***	***Ni***
Organic matter	-						
pH (H_2O)	**-0.78**	-					
pH (KCl)	**-0.81**	**0.98**	-				
Zn	0.29	-0.28	-0.24	-			
Mn	**0.90**	**-0.65**	**-0.67**	0.21	-		
Cu	**0.53**	**-0.44**	**-0.40**	**0.41**	**0.43**	-	
Ni	**0.91**	**-0.76**	**-0.75**	0.10	**0.90**	**0.47**	-

$r_{crit.}$ - critical values of Spearman's correlation coefficient referred to Ramsey (1989), bold values are statistically significant

Table 6. Quality indicators of bottom sediments of the Słupia River

	Zn	*Mn*	*Cu*	*Ni*
PLI	0.57	0.25	1.21	2.33
I_{geo}	0.0099	0.0004	0.1548	0.3167
EF	0.71	0.30	1.39	2.38

The heavy metal content in the tissues of the water plants and in the bottom sediment of the rivers reflects the impact of anthropomorphic pressure on natural environment. The zinc content was from 17.9 to 53.0 mg·kg^{-1} in aboveground sprouts and from 15.8 to 119.5 mg·kg^{-1} in underground sprouts of *Glyceria maxima*, showing variability at the level of 43.3 % and 56.0 % (Table 7). To cover physiological needs of most plants, the concentration in leaves at the level of 15-30 mg·kg^{-1} is sufficient (Kabata-Pendias and Pendias, 1999). The plants absorb Zn in the quantities proportional to its concentration in soil (Kozanecka et al. 2002). An average zinc content in aboveground parts of the plants which are not under the influence of pollution is 10-70 mg·kg^{-1} (Kabata-Pendias and Pendias, 1999), which shows a permissible level of Zn in aboveground sprouts of *Glyceria maxima* covering the banks of the Słupia River**.**

Manganese content in *Glyceria maxima* was on average 261.7 mg·kg^{-1} in aboveground sprouts and 441.2 mg·kg^{-1} in underground ones. Variation in concentration at 10 stations, at 68.4% and 86.8%, was much higher than in the case of Zn. According to Kabata-Pendias and Pendias (1999), the demand of plants for manganese varies and in most cases 10-25 mg·kg^{-1} is sufficient. A concentration about 500 mg·kg^{-1} can be toxic for most of the plants. Increased Mn content in the sprouts of *Glyceria maxima* in relation to physiological demand can show a positive impact of that macrophyte on purification of water and bottom sediments of the Słupia River. The main factor deciding about the availability of heavy metals for plants is the reaction of bottom sediments.

Solubility of metals is low as to neutral and alkaline reactions (Table 3), and increases along with lowering of the value of pH (Smal and Salomons, 1995). Increase of mobility of Zn and Mn is most effective with pH=6, while Cu and Ni at pH=5.5. Manganese, however, is characterized by increased solubility also in alkaline environment (pH~8), (Alloway, 1995, Martinez and Motto, 2000).

Cu content in aboveground and underground sprouts of *Glyceria maxima* was 10.3 mg·kg^{-1} and 21.1 mg·kg^{-1} respectively and shows variability within the area of 10 stations of 21.9% and 55.7% respectively (Table 7). Copper in plants displays low mobility (Kabata-Pendias and Pendias, 1999). The physiological demand of most plants is below 4-5 mg·kg^{-1} and is quite variable depending on the part of the plant, its development stage, variety and species. Its average content in the aboveground parts of the plants is from 5-20 mg·kg^{-1} (Kabata-Pendias and Pendias, 1999). The average nickel content was 17.4 mg·kg^{-1} and 24.9 mg·kg^{-1} respectively in aboveground and underground sprouts of *Glyceria maxima*. Variability coefficients within the area of the research stations were 25.8% and 18.5% respectively (Table 7).

Physiological nickel content in plants at the area which was not under the impact of pollution was most often: 0.1-5.0 mg·kg^{-1} (Kabata-Pendias and Pendias, 1999), and in municipal agglomerations such values can be higher since nickel easily undergoes bio accumulation especially in water plants which are sensitive bio-indicators of waters (Sarosiek and Wożakowska-Natkaniec, 1993). The slightly higher Ni content than physiological demand in the sprouts of *Glyceria maxima* therefore indicates some pollution of bottom sediments with that element. Enrichment factors (*EF*) of determination of heavy metals in aboveground sprouts had the values lower than 1.9, and in the underground sprouts < 3.3 (Table 7). All of the determined heavy metals were accumulated much easily in underground sprouts than in the aboveground ones of *Glyceria maxima*.

Table 7. Heavy metals (mg·kg^{-1}) contents, coefficients of variation (%) and the enrichment factor (EF) in the aboveground and underground sprounts of *Glyceria maxima*

	Zn	*Mn*	*Cu*	*Ni*
	Glyceria maxima - aboveground sprouts			
Average ± SD	29.9±12.7	261.7±179.1	10.3±2.3	17.4±4.5
Median	23.4	200.9	10.1	17.2
Minimum	17.9	98.2	7.6	11.9
Maximum	53.0	622.7	13.7	24.3
CV, %	43.3	68.4	21.9	25.8
EF	1.2	1.9	1.7	1.5
	Glyceria maxima - underground sprouts			
Average ± SD	59.3±33.2	441.2±383.1	21.1±11.7	24.9±4.6
Median	57.3	242.7	19.3	25.8
Minimum	15.8	130.3	12.3	17.8
Maximum	119.5	1276.3	51.5	30.3
CV, %	56.0	86.8	55.7	18.5
EF	2.5	3.1	3.3	2.2

The values of enrichment factors (*EF*>1) indicate slight contamination with the tested metals. The relationships among the determined elements made up the following decreasing series: Mn>Zn>Ni>Cu.

Between the content of Zn, Mn, Cu and Ni in the bottom sediments of the Słupia River and the level of concentration of heavy metals in the sprouts of *Glyceria maxima*, a series of statistically significant relationships were determined. With the increase of concentration of manganese in underground sprouts, the Mn content increase in aboveground sprouts. A reverse dependency was revealed in the case of copper, which could have resulted from the low mobility of Cu in plant tissues (Kabata-Pendias and Pendias, 1999).

These relationships are consistent with the results obtained by Aksoy et at. (2005), which indicates a relatively low mobility of Cu in aquatic plants and accumulation it in large quantities in the rhizomes and roots. In the case of manganese concentration, a statistically significant relationship between Mn content in the sediments and its concentration in underground and aboveground sprouts of *Glyceria maxima* was revealed (Table 8). No similar dependencies were found between Zn and Cu content which can suggest a limited availability of those elements for the plants from of bottom sediments with pH~8, (Table 3).

According to Kabata-Pendias (2001) many factors influence intake of heavy metals by plants. pH of soil is one of them (Takač et al, 2009). In alkaline environment (Table 3) most heavy metals is non-available for plants. Increase of mobility of Zn is most effective with pH<6.2 (Martinez and Motto, 2000), and manganese in alkaline environment (pH~8), (Kabata-Pendias and Pendias, 1999). Along with the increase of concentration of tested metals in bottom sediments of the Słupia River, the values of *EF* factors decreased, which is manifested by negative values of correlation coefficients (Table 8).

Table 8. The correlation coefficients (r) of heavy metals contents in the relationship: aboveground prouts/underground sprouts, bottom sediment/aboveground sprouts, bottom sediment/ underground sprouts, bottom sediment/$EF_{\text{(aboveground sprouts)}}$, bottom sediment/$EF_{\text{(underground sprouts)}}$, (n=30, $p < 0.05$, $r_{crit.} = 0.30$)

r in relation:	***Zn***	***Mn***	***Cu***	***Ni***
aboveground sprouts/ underground sprouts	0.21	0.64	-0.45	0.20
bottom sediment/ aboveground sprouts	-0.02	0.87	-0.20	0.58
bottom sediment/ underground sprouts	0.19	0.75	0.06	-0.04
bottom sediment/ $EF_{\text{(aboveground sprouts)}}$	-0.72	-0.34	-0.81	-0.31
bottom sediment/ $EF_{\text{(underground sprouts)}}$	-0.50	-0.17	-0.62	-0.70

4. Conclusions

The bottom sediments of the Słupia River were classified as slightly polluted. The indexes of the bottom sediments quality and heavy metals enrichment factors of the sprouts indicate that the lowest pollution is found at the section of the Słupia River with low and moderate transformation of the river bed.

All of the determined heavy metals were accumulated much easily in underground sprouts than in the aboveground ones of *Glyceria maxima*. The values of enrichment factors (3.3>*EF*>1.2) indicate slight contamination with the tested metals. The research results indicate that the sprouts of *Glyceria maxima* are potentially useful in biomonitoring environmental contamination with Mn.

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