The Content of Heavy Metals in Bottom Sediments of Selected City Rivers of the Podlasie Province

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ABSTRACT

The purpose of the work was to determine the relationship between the state of the water environment quality of selected rivers (Zn, Cr, Pb, Cd and Cu tests in bottom sediments), and the sources of pollution resulting from the close proximity to the cities, through which they flow. The following rivers were selected for the study: the Biała river flowing through the city of Białystok, the Narew river flowing through the city of Tykocin and the village of Złotoria, the Supraśl river flowing through the village of Michałowo and Gródek as well as the Biała river flowing through the city of Bielsk Podlaski. The sediments were collected four times from the same points in 2016 in the period from July to October. The sediment samples were collected from the points located on rivers before and beyond towns and villages. The contents of the following metals were tested in the bottom sediment samples: Zn, Cr, Pb, Cd and Cu. The analyses were carried out applying the flame absorption spectrometry method. The statistical multivariate CA and FA analyzes were used. The highest contents of Zn, Pb and Cr were recorded in the bottom sediments from the following rivers: Biała (Białystok) and Biała inflow of Orlanka (Bielsk Podlaski), which resulted from the anthropogenic activity. The research also showed the impact of the agricultural activity due to the slightly elevated Cd level.

Keywords: heavy metals, river, bottom sediments

INTRODUCTION

The urban land use pattern and the urbanization degree have significant impacts on the heavy metal (HM) contamination, which have been extensively detected in soil, water, sediment, air, organisms, as well as city road dust [Giordano et al. 2005; Mohiuddin et al. 2010; Shi et al. 2008]. The deterioration of river water quality due to the indiscriminate discharge of untreated sewage, industrial waste and other anthropogenic activities like urbanization, population growths and land development along the river basin is one of the major concerns throughout the world [Kumar and Maiti 2015]. The rivers in the urban areas passing through the industrial zones are associated with the water quality problems because of the unregulated discharge of the domestic and industrial waste water into the water bodies that lead to the increased levels of heavy metal in the rivers [Lin

et al. 2013; Silva et al. 2014]. The heavy metal contamination in the sediment is a significant environmental problem because of their toxicity, non-degradability and high bioaccumulation potential in biota and food chain [Sundaray et al. 2014)]. The sediments act as a sink of contaminants, receive and absorb the pollutants resulting from these sources [Liu et al. 2003], and have been recognized as an important indicator of water pollution. Heavy metals are among the most common environmental pollutants, and their occurrence in waters and biota indicate the presence of natural or anthropogenic sources. Their accumulation and distribution in soil, water and environment are increasing at an alarming rate causing deposition and sedimentation in water reservoirs and affecting the aquatic organisms as well [Cataldo et al. 2001; Hobbelen et al. 2004; Koukal et al. 2004; Okafor and Opuene 2007; Mohiuddin et al. 2010]. Heavy metals like Cr, Pb, Cd, etc. exhibit

extreme toxicity [Miller et al. 2003; Harikumar et al. 2009]; heavy metals have become significant pollutants of many riverine systems [Dassenakis et al. 1998]. Heavy metals have a potential to contaminate soil and water, which can be dispersed and accumulated in plants and animals, and taken in by humans through consumption [Wcislo et al. 2002; Li et al. 2008]. The heavy metal contamination of sediments can critically degrade the aquatic systems [Charkhabi et al. 2005]. Their release from the sediment can make them enter the aquatic ecosystems and bring about severe problems [Mohammed and Markert 2006]. Despite the differences in the toxic effects of the metals with different metals as well as their concentrations and the time of exposure, their concentrations are reliable indicators of the ecosystem health [Singh et al. 2005]. The organic matter and fine grain content have often been considered two major apparent sediment properties associated with heavy metal enrichment in sediments [Laing et al. 2007]. Land use may also play crucial roles in the distribution of heavy metals in sediments. Land use is commonly classified as agriculture, forestry, industrial development, and urbanization. However, the types of land use resulting in heavy metal enrichment of sediments are not necessarily the same for different geographical locations. For example, Heikkila [1991] reported that high concentrations of organic matter and heavy metals in sediments were closely related to the increased intensity of agriculture, forestry, and peat harvesting in drainage basins. In contrast, Abrahim and Parker [2002] and Horowitz and Stephens [2008] demonstrated that the heavy metal concentrations in sediments tend to increase with the degree of industrial development and urbanization in the catchments. A successful evaluation for mixed accumulation of heavy metals from natural and anthropogenic sources typically requires normalizing methods for distinguishing the two different sources [Idris 2008]. The geochemical normalization approaches such as the enrichment factor (EF) and geo-accumulation index (Igeo) methods have been commonly used for the purpose.

The multivariate statistical techniques including the principal component analysis (PCA) and cluster analysis (CA) can be used as complementary tools for explaining the distribution of heavy metals in sediments. They statistically reduce the heterogeneity associated with the relationships among the sediment properties, metals, and other environmental factors. In particular, the PCA approach has been typically applied to identify the sources of heavy metals in sediments [Wang et al. 2011; Chabukdhara and Nema 2012]

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METHODS

As a research area, four rivers were selected in the Podlasie province: Biała (inflow of Supraśl), Narew, Supraśl and Biała (inflow of Orlanka), in which the dependence of the water quality (bottom sediment study) and close neighborhood of selected urbanized areas, through which they flow, were analyzed. In order to determine the extent of the negative impact on the river environment of anthropogenic activities resulting from the nature of development and infrastructure, agricultural and non-agricultural activities, the following towns were selected: Białystok for Biała river, Tykocin and Złotoria for Narew river, Michałowo and Gródek for Supraśl river as well as Bielsk Podlaski for Biała river (Orlanka tributary). The list includes both Białystok – aprovincial city with the largest number of inhabitants (296,000) and the most developed non-agricultural economic activity, as well as, to some extent, the direct opposite, i.e. Złotoria – a village without the sewage treatment plant, but with developed agricultural economy (Table 1).

The sediment samples were collected four times (from July to October 2016) from twelve measuring points located (in pairs) near each of the selected towns. The total number of samples was 48. It was assumed that the research material would be collected at a distance of 100 meters before and beyond the village, taking into account the course of the river. The bottom sediment collection points located on the rivers are marked as follows: before the village – A, while beyond the village – B (Figure 1).

The bottom sediments were collected in the littoral zone, in the top layer, where the deposition of the suspended material and accumulation of heavy metals occur [Bojakowska 2001]. Ten individual samples of bottom sediments from a depth of up to 5 cm below the surface of the water were collected at each designated measurement point.

Table 1. Basic characteristics of watercourses and urban areas

River/length [km]/average annual flowrate through urbanized area [$m^3 \cdot s^{-1}$]	Urbanized area	Number of residents	Industrial facilities	Sewage treatment plant [RLM]/average daily sewage amount [$m^3 \cdot d^{-1}$]
Biała/33/1,20	Białystok	296000	present	200000/100000
Górna Narew/199/17,56	Tykocin	2000	no	6000/500
Górna Narew/199/16,67	Złotoria	767	no	no
Supraśl/94 /1,22	Gródek	2900	no	3000/258
Supraśl/ 94/1,88	Michałowo	3107	no	2410/263
Biała/33 /0,14	Bielsk Podlaski	26000	present	45000/6000
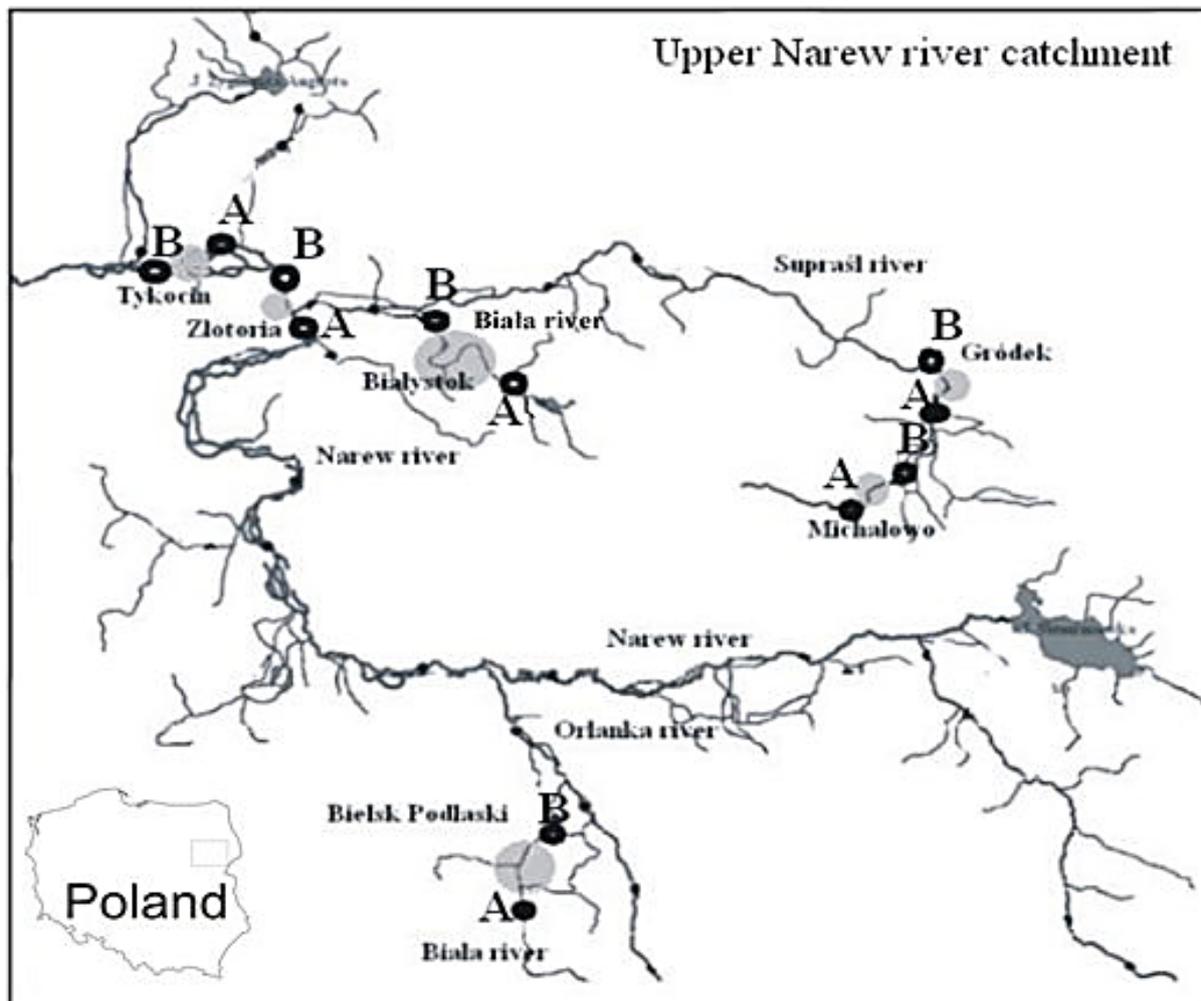
Figure 1. Location of measurement and control points on the examined rivers

After mixing the test material, a representative sample of approximately 1000 g was obtained. The samples were dried to an "air-dry" state and stored until assayed [Lis and Pasieczna 1995].

Before proceeding with the chemical analyses, the bottom sediment samples were dried at 40°C and sieved through a 0.2 mm sieve. The bottom sediments were mineralized in the MT1205-B2Magma Therm microwave system. Weighed samples (1 g) were poured in Teflon vessels with a mixture of concentrated HNO_3 (8 ml) and 30% H_2O_2 (2 ml) [Salminen et al. 2005]. The samples after filtration were quantitatively transferred to 50 ml graduated flasks. The following Zn, Cr, Pb, Cd and Cu metals were tested in mineralized solutions. The tests were carried out using flame absorption spectrometry method by means of the AAS ICE 3500 Thermo Scientific spectrometer.

The results of the sediment analyses were verified using a certified reference material for sediments NCS DC 73317a. The limit of quantification of the method [mg·dm⁻³] was: Cd – 0.01, Cr – 0.05, Cu – 0.035, Pb – 0.1 and Zn – 0.01. The obtained results of metals content were given in relation to air dry sediments and compared with the literature data. The content of organic substance was determined using the annealing method. The reaction of sediments in distilled water was examined with a potentiometric method.

In order to assess the degree of sediments contamination with heavy metals, the proposal to classify water sediments in Poland was used (Table 2).

In order to assess the quality of bottom sediments, the degree of sediment pollution was also employed, using a geochemical index (I_{geo}) and contamination factor (CF).

The geochemical index (I_{geo}) is defined using the formula [Müller 1979]:

$$I_{geo} = \log_2 \left(\frac{C_m}{1{,}5GM} \right) \qquad (1)$$

where: C_m – content of the analyzed metal (mg·kg⁻¹),
GM – geochemical background (mg·kg⁻¹).

As the geochemical background, the average contents in shales of the Earth's crust were assumed in mg·kg⁻¹: Zn – 95, Cr – 90, Pb – 20, Cd – 0.3, Cu – 45 [Turekian and Wedepohl, 1961].

The bottom sediments were classified on the basis of the obtained geochemical index values (I_{geo}) according to the following ranges: $I_{geo} < 0$ – class 0 (non-contaminated sediments), $0 < I_{geo} < 1$ – class 1 (uncontaminated moderately (weakly) contaminated sediments), $1 < I_{geo} < 2$ – class 2 (moderately contaminated sediments), $2 < I_{geo} < 3$ – class 3 (moderately strongly contaminated sediments), $3 < I_{geo} < 4$ – class 4 (strongly contaminated sediments), $4 < I_{geo}$

< 5 – class 5 (extremely strongly contaminated sediments), $5 < I_{geo} < 6$ – class 6 (extremely contaminated sediments).

Before performing the multidimensional analyses, the basic relationships in the prepared data set were checked. The calculations of Spearman's rank order correlation were made due to the number of some variables taken into analysis and the lack of normal distribution of numerical data. The statistic multivariate analysis (FA) and Ward cluster analysis (CA) were used for the analyses. In order to interpret the results of the factor analysis, it was assumed that the compounds of the variable (metal content) with the factor are strong when the absolute values of its charges are greater than 0.70. A similar value was used, among others, by Pucket, Bricker [1992] and Evans et al. [1996].

The cluster analysis was used to isolate the objects with similar contents of investigated metals in bottom sediments. This is a method that allows to isolate (classify) specific subsets of objects with mutually similar elements in a multidimensional space [Igras 2004]. Statistica software was used for the statistical calculations.

RESULTS AND DISCUSSION

The pH of bottom sediments ranged from 6.22 to 8.71 pH. The process of metals adsorption/desorption by various minerals and organic substance to a great extent depends on the reaction. Metals can be adsorbed under various pH conditions. For example, Cd and Zn have adsorption limits at higher pH than Cu, which makes these metals more mobile in the fluvial environment [Ciszewski and Aleksander-Kwaterczak 2015]. It should be emphasized that the solubility of micronutrients increases with decreasing the pH value [Small and Salomons, 1995]. The occurrence and rate of organic matter degrada-

Table 2. Classification of bottom sediments based on the geochemical criteria [Bojakowska and Sokołowska 1998, Bojakowska 2001].

Element	Geochemical background	Class I non-contaminated sediments	Class II moderately uncontaminated sediments	Class III contaminated sediments	Class IV strongly contaminated sediments
Zn	73	200	500	1000	>1000
Cr	6	50	100	400	>400
Pb	15	30	100	400	>400
Cd	<0,5	1,0	3,5	6,0	>6
Cu	7	40	100	200	>200

tion is also important for the binding of metals in sediments [Rubio et al. 2010]. In the tests carried out, the content of organic matter (OM) in the sediments of the examined rivers ranged from 1.14% to 16.70%. The largest variation in the average organic substance content (from four sampling dates) in the examined sediments occurred in the Biała river in Białystok city (A – 1.14%, B – 14.24%) and in Supraśl river in the city of Michałowo (A –5.87%, B – 11.52%). Figures 2 and 3 present the average contents of the investigated metals in the bottom sediments of the analyzed rivers. The obtained results of metal content analyses in particular samples showed the greatest variation in the case of the metals in the bottom sediments of the Biała river flowing through the city of Białystok, mainly for Zn, Cr, Pb (Zn A – 35.54 mg·kg⁻¹, B – 184.82 mg·kg⁻¹, Cr: A – 9.81 mg·kg⁻¹, B – 27.78 mg·kg⁻¹, Pb: A – 6.26 mg·kg⁻¹, B – 153.26 mg·kg⁻¹). Similar relations occurred for the Biała river (inflow of the Orlanka river), which was visible especially for Zn and Pb (Zn: A – 29.97 mg·kg⁻¹, B – 88.54 mg·kg⁻¹, Pb: A – 11.20 mg·kg⁻¹, B – 16.70 mg·kg⁻¹). However, in the bottom sediments from the Supraśl river near Michałowo, a considerable variation of Zn results was also obtained before (21.74 mg·kg⁻¹) and beyond (48.44 mg·kg⁻¹) the city.

First of all, the increased Zn and Pb contents in the bottom sediments of the Biała and Biała (tributary of Orlanka) rivers located in the research points beyond Białystok and Bielsk Podlaski are related to the city's infrastructure. Białystok and Bielsk Podlaski have the largest number of residents of about 296,000 and 26,000, respectively (Table 1), relative to other cities, which is also related to, among others, the largest number of motor vehicles. According to Dmochowski et al. [2011], toxic gases, dusts and aerosols containing heavy metals originate from communication routes. The greatest contamination of soils with automotive pollution is noticeable in the urban agglomerations where a large number of cars move in relatively small areas, and a high volume of traffic is conducive to high emissions. The research conducted by Plak et al. [2010] showed that the transport and the surface runoff from the roads with high traffic are the mainly source of
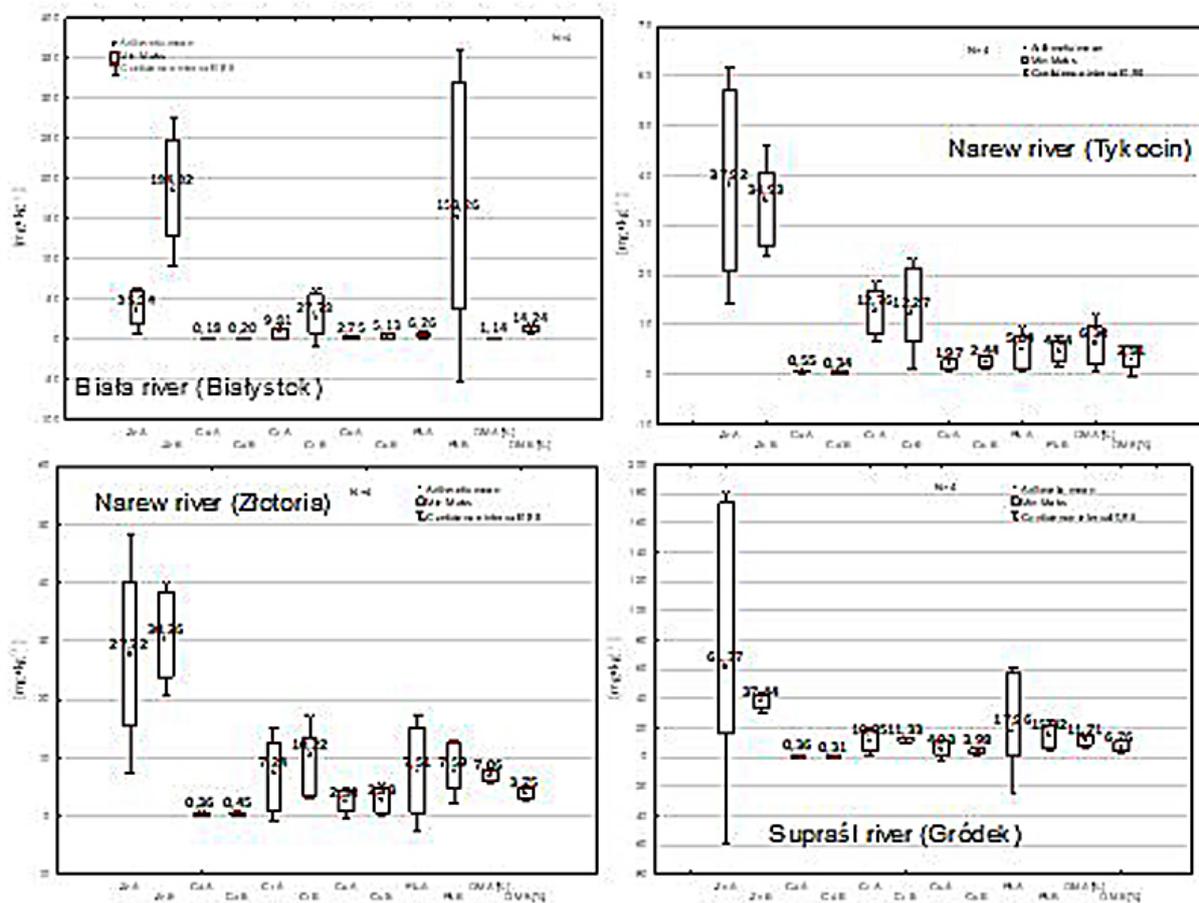
Figure 2. Contents of heavy metals and organic matter in the examined bottom sediments
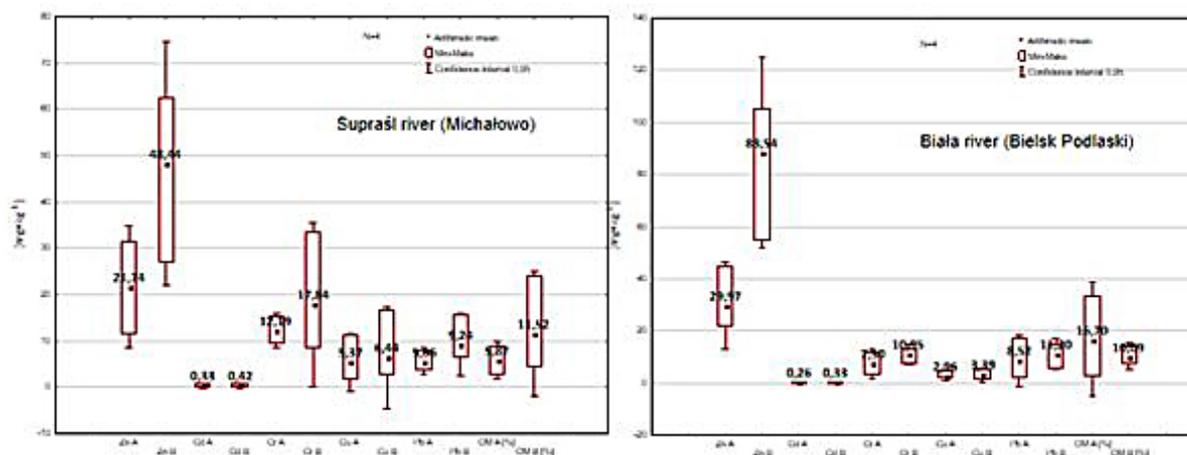
Figure 3. Contents of heavy metals and organic matter in the examined bottom sediments

lead, and – in smaller quantities – also zinc, copper, cadmium or nickel. The above-mentioned analyses are also confirmed by the Badyda's studies [2010], who states that the operation of the transport network causes pollution of soils in the immediate vicinity of busy roads. Another source of metals in urban agglomerations includes the pollution in the atmosphere. Rogula-Kozłowska et al. [2008], in their studies, proved that the highest concentrations of heavy metals are introduced into the atmosphere together with the so-called suspended dust, the largest emitter of which is the energy industry. In Białystok, there are also industrial facilities and a high capacity municipal sewage treatment plant. Bielsk Podlaski also has an industry and sewage treatment plant, but on a smaller scale. In other towns (Gródek, Tykocin, Złotoria and Michałowo), agriculture is the dominant branch of economy. A noticeable source of trace metals in the vicinity of Gródek and Michałowo may be the subsurface runoff from the fields fertilized with minerals and organics (slurry and manure). The possible reason for the presence of high Zn content in the sediment samples from rivers may be due to the huge discharge of the industrial waste and mixing of the runoff with fertilizers residue [Guo and He 2013; Mathivanan and Rajaram 2014; Benhaddya et al. 2014]. Michałowo does not have a developed industry and intense routes of car communication, which could explain the increase in the content of some metals in the Supraśl river sediments at point B, but it has a municipal sewage treatment plant, which can sometimes show certain irregularities in its operation. In the area of Michałowo, agricultural activity is conducted, which may be one of the reasons for the increased content of

some metals in the Supraśl river sediments. For instance, the increased level of Cd in the Supraśl river sediments in the vicinity of Michałowo may indicate the transport of pollutants from the subsurface runoff and mineral fertilization from the agricultural land near almost all of the studied areas.

According to the Bojakowska and Sokołowska [1998] and Bojakowska [2001] classification, most of the sediments tested were considered uncontaminated. The enrichment of sediments in Cr, Pb and Zn occurred in the Biała river at the measurement point beyond the city of Białystok.

The accumulation indices for individual metals are presented in Table 3 and they are differentiated depending on a given heavy metal. The indices calculated for copper ranged from -6.76 to -2.01, for chromium from -7.34 to -1.27, which indicates the lack of contamination with these metals (class 0)in the examined rivers. The examined sediments in the analyzed rivers can also be regarded as uncontaminated with zinc due to the negative values of the indices, only four samples took positive values (0.29, 0.62, 0.80, 0.01), while the I_{geo} analysis for Pb showed 91.7% of samples in class 0, four samples of the bottom sediments from the Biała river beyond Białystok accepted the following values: 0.41 (class I), 1.06 (class II), 2.67 (class III), and 3.42 (class IV).

The material tested in the form of the numerical content of indices was subjected to a statistical analysis. No Spearman correlation was detected in most cases between the organic matter (OM) and metal contents in the sediments studied. Only in the samples taken beyond the villages, there was the correlation between organic substance (MO) and Zn content (r = 0.69) and Pb (r = 0.49). There

Table 3. Range of the accumulation index (I_{geo}) for metals in river sediments

River (City)	Stat.	I geo									
		Zn A	Zn B	Cd A	Cd B	Cr A	Cr B	Cu A	Cu B	Pb A	Pb A
Biała (Białystok)	min	-2.79	-0.15	-5.49	-3.14	-6.69	-4.03	-5.97	-4.74	-3.20	0.41
	max	-1.22	0.80	-0.01	-0.68	-3.15	-1.27	-3.88	-3.31	-1.72	3.42
Narew (Tykocin)	min	-2.77	-2.46	-0.06	-2.66	-4.06	-4.33	-5.95	-5.58	-4.98	-3.58
	max	-1.32	-1.81	0.71	0.33	-2.99	-2.66	-4.49	-4.23	-1.92	-2.17
Narew (Złotoria)	min	-3.21	-2.58	-3.35	-1.24	-7.34	-5.22	-6.52	-6.76	-5.84	-2.62
	max	-1.83	-1.89	0.40	0.39	-3.45	-3.35	-3.95	-3.82	-0.97	-1.25
Supraśl (Gródek)	min	-3.12	-2.09	-3.86	-2.35	-4.95	-3.71	-5.57	-4.85	-6.33	-2.26
	max	0.29	-1.73	0.23	0.31	-2.95	-3.34	-2.67	-3.53	0.96	-0.51
Supraśl (Michałowo)	min	-3.64	-2.39	-5.49	-5.35	-3.82	-3.97	-5.14	-4.62	-3.02	-2.21
	max	-2.17	-1.19	0.92	0.68	-3.15	-2.00	-2.61	-2.01	-1.96	-0.95
Biała dopływ Orlanki (Bielsk Podlaski)	min	-2.68	-1.37	-2.09	-3.91	-5.22	-4.17	-5.12	-5.41	-3.65	-2.33
	max	-1.68	-0.43	-0.30	0.20	-3.49	-3.37	-3.80	-3.64	-0.81	-1.02

was no association between the metals investigated and organic matter (OM), indicating that OM cannot be a major factor for the distribution of heavy metals in sediments. As a result of the statistical analysis of Ward aggregates (CA) and the content of heavy metals in the bottom sediments, the dendrogram shown in Figure 4 could be prepared. There are 5 clusters (groups of rivers) on the dendrogram. The first group contains only one object, i.e. the Biała river (tributary of Supraśl), which flows through Białystok. Sometimes, only one object in a cluster from Ward cluster analysis is referred to as an isolated object [Skorbiłowicz 2010]. The isolated object often has special properties in comparison with those forming other groups (aggregates). The other group included the remaining rivers. The city of Białystok is an urbanized area with a high degree of exposure of the Biała river to the anthropogenic impact, which increased the content of metals in its river sediments. The second group included other rivers, the bottom sediments of which are less susceptible to pollution from other urban areas. Nevertheless, two additional groups (III and IV) can be separated within group II. In group III, there is the Biała river (inflow of Orlanka), which is located in the zone of Bielsk Podlaski influence. Group III, like I, also includes an isolated object that has special properties. The bottom sediments of Biała (inflow of the Orlanka) are exposed to the pollution from Bielsk Podlaski, where industry and sewage treatment plant is present (Table 1). In group IV, there are two rivers: Narew and Supraśl, which flow through Złotoria, Tykocin, Michałowo and
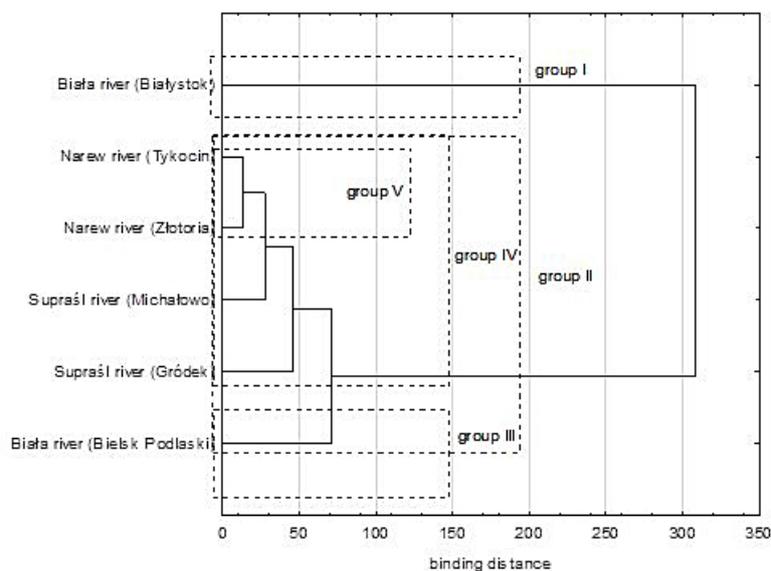
Figure 4. Ward agglomeration analysis of heavy metals in bottom sediments

Gródek, respectively. An interesting fact is group V, which includes the Narew river with two towns: Tykocin and Złotoria. The degree of impact of Złotoria and Tykocin on the Narew river sediments is smaller, as compared to the object from Group III and the objects from Group IV. The arrangement of objects in group V may be a consequence of a fairly close distance between the two towns along the Narew river. In the case of the Supraśl river, which flows through Gródek and Michałowo, the cluster analysis did not show similar results. Gródek and Michałowo located on the Supraśl river did not find themselves in one cluster (group) of cluster analysis. It has a supposed connection with the agricultural character of the areas adjacent to both towns, the intensity of impact of which is greater in the case of Michałowo. The impacts of agricultural activity may overlap the impact of urbanized areas, although the metal content in the Supraśl river sediments is not a threat to this ecosystem. Six-year studies performed by Skorbiłowicz [2012] upon the upper Narew river and its tributaries showed that the sediments of Supraśl and Narew river catchments are characterized by low contents of trace metals.

The work also looked for a compliance and confirmation of CA cluster analysis with the multifactor FA analysis. Two factors F1 and F2 were found on the basis of the FA analysis (Table 4). Factor F1 is the most dominant as it explains as much as 45% of the variability, as opposed to F2 explaining 20% of variability. The factor F1 correlates positively with Zn, Cr, Cu, Pb and OM in the bottom sediments located at points beyond the towns (designation B). The positive correlation of F1 with Zn, Cr, Cu, Pb and OM indicates the significant sources of these metals and organic matter. The FA analysis showed which metals leak from the analyzed and previously identified areas to the bottom sediments of rivers. It also indicated which metals migrate from other areas. The negative correlation between F1 and Cd in the sediments in both points before and beyond the cities is interesting, which excludes similar interpretation as in the case of other metals. Probably, there are other factors shaping the Cd content in the bottom sediments associated, for example, with the geochemical nature of sediments or unexplained processes connected with quite high mobility of this element. Large mobility of Cd can contribute to its easy mobilization from the bottom sediments and transport with river waters over further distances. Additionally, simultaneous processes of enriching and activating Cd from the bottom sediments may explain the negative correlation with the factor F1. The analyses showed a lower pH value in the river sediments at the points marked with the letter B, which may be one of the reasons for Cd mobilization. This issue certainly requires further research and analysis. The F2 factor has much less explanatory power (20%) and is associated with the sources of the bottom sediments enrichment in Zn, Cu and Pb of the studied rivers, but at the points marked with the letter A. This can be explained, for example, by the transport of metals in question from the upper sections of the examined rivers. Metals can migrate most often as bound to suspended matter, colloids or in a dissolved form, not only with the river water but also with the run-off from the surrounding areas.

The cluster analysis (CA) allowed to identify the urban areas, which contribute to the migration of metals to river ecosystems to the greatest degree. On the other hand, due to the multivariate analysis (FA), it was proven which metals migrate from the analyzed areas to the river ecosystems.

Table 4. Results of multivariate analysis (FA)

Variable	Factor 1	Factor 2
Zn A		0.75
Zn B	0.91	
Cd A	-0.79	
Cd B	-0.74	
Cr A		
Cr B	0.94	
Cu A		0.73
Cu B	0.70	
Pb A		0.92
Pb B	0.91	
OM A [%]		
OM B [%]	0.92	
Explained variance [%]	45	20

CONCLUSIONS

1. The highest contents of Zn, Pb and Cr were recorded in the bottom sediments from the rivers: Biała – inflow of Supraśl (Białystok) and Biała – inflow of Orlanka (Bielsk Podlaski). The influence of urbanization and anthropogenic activity such as: discharges of unpurified or insufficiently treated municipal and industrial sewage, surface runoff, emissions from communication routes, has been demonstrated. The changes pertaining to the content of metals in sediments were related to the nature of urbanized areas.

2. The research also showed the impact of agricultural activity (slightly elevated Cd level). The areas adjacent to the examined objects are in most cases the areas, on which agricultural activities related to mineral and organic fertilization are conducted.

3. Assessment of the bottom sediments contamination using the geo-accumulation index and classification of sediments in Poland according to Bojakowska and Sokołowska (1998) and Bojakowska (2001) showed that they are in most cases uncontaminated. The exceedances occurred in several samples of the bottom sediments from the Biała river beyond Białystok for Pb, Zn and Cr.

4. The statistic multivariate analyses allowed for the identification of the urban areas shaping the heavy metals content in the sediments of the examined rivers to varying degrees. It also turned out that they enabled to answer the question which metals migrate from the analyzed areas to the river ecosystems. The results of the conducted analyses complemented one another in explaining the origin of elements.

Acknowledgements

REFERENCES

1. Badyda A.J. 2010. Zagrożenia środowiskowe ze strony transportu. Nauka 4, Polska Akademia Nauk, Warszawa, 115–125.

2. Benhaddya M.L, Hadjel M. 2014. Spatial distribution and contamination assessment of heavy metals in surface soils of Hassi Messaoud, Algeria. Environ Earth Sci 71, 1473–1486.

3. Bojakowska I. 2001. Kryteria oceny zanieczyszczenia osadów wodnych. Przegl. Geolog. 49(3), 213–218.

4. Cataldo D. Colombo J.C., Boltovskoy D. Bilos C. Landoni P. 2001. Environmental toxicity assessment in the Parana river delta (Argentina): simultaneous evaluation of selected pollutants and mortality rates of Corbicula Fluminea (Bivalvia) early juveniles. Environ. Poll., 112 (3), 379–389.

5. Chabukdhara M., Nema A.K. 2012. Assessment of heavy metal contamination in Hindon River sediments: A chemometric and geochemical approach. Chemosphere, 87(8), 945–953.

6. Charkhabi A.H., Sakizadeh M., Rafiee G. 2005. Seasonal fluctuation in heavy metal pollution in Iran's Siahroud River. Environ Sci Pollut Res 12, 264–270.

7. Ciszewski D., Aleksander-Kwaterczak U. 2015. Zanieczyszczenie osadów metalami. Transport, akumulacja, remobilizacja, remdiacja, AGH, Wydawca AGH, Kraków, 2015, pp. 165.

8. Dassenakis M., Scoullos M., Foufa E., Krasakopoulou E., Pavlidou A., Kloukiniotou M. 1998. Effects of multiple source pollution on a small Mediterranean river. Appl. Geochem., 13 (2), 197–211.

9. Dmochowski D., Prędecka A., Mazurek M., Pawlak A. 2011. Ocena zagrożeń związanych z emisją metali ciężkich w aspekcie bezpieczeństwa ekologicznego na przykładzie ogródków działkowych w aglomeracji miejskiej, Polski przegląd medycyny i psychologii lotniczej, 3 (17), 257–265.

10. Evans C.D., Davies T.D., Wigington JRP.J., Tranter M., Kretschier W.A. 1996. Use od factor analysis to investigate processes controlling the chemical composition of four streams in Adirindack Mountaions. „J. Hydrol." 185, 297–316.

11. Giordano S., Adamo P., Sorbo S., Vingiani S. 2005. Atmospheric trace metal pollution in the Naples urban area based on results from moss and lichen bags. Environ. Pollut. 136, 431–442.

12. Guo R, He X. 2013. Spatial variations and ecological risk assessment of heavy metals in surface sediments on the upper reaches of Hun river, Northeast China. Environ Earth Sci 70, 1083–1090.

13. Harikumar P.S., Nasir U.P., Mujeebu Rahman M.P. 2009. Distribution of heavy metals in the core sediments of a tropical wetland system. Int. J. Environ. Sci. Tech., 6 (2), 225–232.

14. Hobbelen P.H.F., Koolhaas J.E., van Gestel C.A.M. 2004. Risk assessment of heavy metal pollution for detritivores in floodplain soils in the Biesbosch, The Netherlands, taking bioavailability into account. Environ. Poll., 129 (3), 409–419.

15. Idris A.M. 2008. Combining multivariate analysis and geochemical approaches for assessing heavy metal level in sediments from Sudanese harbors along the Red Sea coast. Microchemical Journal, 90(2), 159–163.

16. Igras J. 2004. Zawartość składnikow mineralnych w wodach drenarskich z użytków rolnych w Polsce. Monografie i Roprawy Naukowe. z. 13. Puławy.

17. Koukal B., Dominik J., Vignati D., Arpagaus P., Santiago S., Ouddane B., Benaabidate L. 2004. Assessment of water quality and toxicity of polluted rivers Fez and Sebou in the region of Fez (Morocco). Environ. Poll., 131 (1), 163–172.

18. Kumar A., Maiti SK. 2015. Assessment of potentially toxic heavy metal contamination in agricultural fields, sediment, and water from an abandoned chromite-asbestos mine waste of Roro hill, Chai-

basa, India. Environ Earth Sci 74(3), 2617–2633.

19. Li Y.L., Liu Y.G., Liu J.L., Zeng G.M., Li X. 2008. Effects of EDTA on lead uptake by Typha oreentalis Presl: a new lead-accumulating species in southern China. Bull Environ Contam Toxicol 81(1), 36–41.

20. Lin C., He M., Liu X., Guo W., Liu S. 2013. Distribution and contamination assessment of toxic trace elements in sediment of the Daliao river system, China. Environ Earth Sci 70(3), 163–3173.

21. Lis J., Pasieczna A. 1995. Atlas geochemiczny Polski 1:2 500 000. PIG, Warszawa.

22. Liu W.X., Li X.D., Shen Z.G., Wang D.C., Wai O.W.H., Li Y.S. 2003. Multivariate statistical study of heavy metal enrichment in sediments of the Pearl river Estuary. Environ Pollut 121, 377–388.

23. Mathivanan K., Rajaram R. 2014. Anthropogenic influences on toxic metals in water and sediment samples collected from industrially polluted Cuddalore coast, Southeast coast of India. Environ Earth Sci 72, 997–1010.

24. Miller C.V., Foster, G.D., Majedi B.F. 2003. Baseflow and stormflow metal fluxes from two small agricultural catchments in the coastal plain of Chesapeake Bay Basin, United States. Appl. Geochem., 18 (4), 483–501.

25. Mohammed MH., Markert B. 2006. Toxicity of heavy metals on Scenedesmus quadricauda (Turp.) de Brebisson in batch cultures. Environ Sci Pollut Res 13, 98–104.

26. Mohiuddin K.M., Zakir H.M., Otomo K., Sharmin S., Shikazono N. 2010. Geochemical distribution of trace metal pollutants in water and sediments of downstream of an urban river. Int. J. Environ. Sci. Tech., 7 (1), 17–28.

27. Müller G. 1981. Die Schwermettallbelastung der Sedimente des Neckars und seiner Nebenflusse: Eine Bestandsaufnahme. Chemiker Zeitung, "Chem., Techn. Chem., Chemiewirtschaft", 105, 6, 157–164.

28. Okafor E.C., Opuene K. 2007. Preliminary assessment of trace metals and polycyclic aromatic hydrocarbons in the sediments. Int. J. Environ. Sci. Tech., 4 (2) 233 – 240 pollutants and mortality rates of Corbicula Fluminea (Bivalvia) early juveniles. Environ. Poll., 112 (3), 379–389.

29. Plak A., Bartmiński P., Dębicki R. 2010. Wpływ transportu publicznego na zawartość wybranych metali ciężkich w glebach sąsiadujących z ulicami Lublina, Proceedings of ECOpole, Vol. 4, No. 1.

30. Puckett L.J., Bricker O.P. 1992. Factors controlling the major ion chemistry of streams in the Blue Rifge and Valley and Ridge physiographic provinces of Virginia and Maryland. Hydrol. Proc. 6, 79–98.

31. Rogula-Kozłowska W., Klejnowski K, Szopa S. 2008. Concentrations of 42 elements in atmospheric fine particles in Zabrze, Poland, Environment

32. Rubio B., Àlvarez-Iglasias P., Vilias F. 2010. Diagenesis and anthropogenesis of metals in the recent Holocene sedimetary record of the Ria de Vigo (NW Spania) Marine Pollution bulletin 60, 1122–1129.

33. Salminen R., Batista M.J., Bidovec M., Demetriades A., De Vivo B., Devos W., Duris M., Gilucis A., Gregorauskiene V., Halamic J., Heitzmann P., Lima A., Jordan G., Klaver G., Klein P., Lis J., Locutura J., Marsina K., Mazreku A., O'connor P.J., Olsson S.Å., Ottesen R.-T., Petersell V., Plant J.A., Reeder S., Salpeteur I., Sandström H., Siewers U., Steenfel T A., Tarvainen T. 2005. Geochemical atlas of Europe. Part 1 – Background Information, Methodology and Maps.

34. Shi G., Chen Z., Xu S., Zhang J., Wang L., Bi C., Teng J. 2008. Potentially toxic metal contamination of urban soils and roadside dust in Shanghai, China. Environ. Pollut. 156, 251.

35. Silva J.D., Srinivasalu S., Roy P.D., Jonathan M.P. 2014. Environmental conditions inferred from multi-element concentrations in sediments off Cauvery delta, Southeast India. Environ Earth Sci 71, 2043–2058.

36. Singh K.P., Malik A., Sinha S., Singh V.K., Murthy R. 2005. Estimation of source of heavy metal contamination in sediments of Gomti river (India) using principal component analysis. Water, Air and Soil Pollution, 166, 321–341.

37. Skorbiłowicz E. 2012. Studia nad rozmieszczeniem niektórych metali w środowisku wodnym zlewni górnej Narwi. Rozp nauk nr 222. Białystok: Oficyna Wydawnicza Politechniki Białostockiej, pp. 212.

38. Skorbiłowicz M. 2010. Czynniki i procesy kształtujące obieg składników mineralnych w wodach rzecznych zlewni górnej Narwi. Oficyna Wydawcza Politechniki Białostockiej, Białystok, pp. 150.

39. Smal H., Salomons W. 1995. Acidification and its long-term impact on metal mobility. In: Salomons W., Stigliani W. (Eds), Biogeodynamics of pollutants in soils and sediments, Springer-Verlag, Berlin, 193–212.

40. Sundaray S.K., Nayak B.B., Lee B.G., Bhatta D. 2014 Spatio-temporal dynamics of heavymetals in sediments of the river estuarine system: Mahanadi basin (India). Environ Earth Sci 71(4), 1893–1909.

41. Wang Y., Yang Z.F., Shen Z.Y., Tang Z.W., Niu J.F., & Gao F. 2011. Assessment of heavy metals in sediments from a typical catchment of the Yangtze River, China. Environmental Monitoring and Assessment, 172(1–4), 407–417.

42. Wcislo E, Ioven D, Kucharski R, Szdzuj J. 2002. Human health risk assessment case study: an abandoned metal smelter site in Poland. Chemosphere 47(5), 507–515.

Protection Engineering, 34(4), 5–15.