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Assessment of metals content in river bottom sediments near sewage treatment plants

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ABSTRACT

The study attempts to determine the degree of discharged treated wastewater impact on the Biebrza ecosystem and its tributaries. The content of metals: Cu, Cr, Zn, Mn, and Fe was analyzed in bottom sediments (HCl and HNO_3 decomposition and HCl extraction) located above and below the cross-section of the discharge of treated wastewater. Wastewater treatment plants were located in the following towns: Lipsk, Szczuczyn, Dolistowo, Sztabin, Goniądz, Rajgród, and Trzcianne – Poland. A higher content of both forms of metals was found in places after the discharge of wastewater compared to places before the discharge, which indicates the influence of the treatment plant on the bottom sediments of the tested receivers in the absence of other metal sources. The average content of metals in bottom sediments (decomposition in HCl and HNO_3) from the points before the sewage discharge was: Cu – 11.3, Zn – 51.1, Cr – 11.7, Mn – 141.8, Fe – 1,029.8 mg kg^{-1} and after the discharge of treated wastewater, the contents were as follows: Cu – 21.3, Zn – 81.3, Cr – 16.3, Mn – 193.4, Fe – 1,210.7 mg kg^{-1}. Based on the calculation of the geo-accumulation index, the examined sediments were classified as non-contaminated. The content of soluble metal forms in sediments is to a larger extent shaped by discharged purified sewage than the content of total forms, which is mainly related to the natural origin of metals as confirmed by statistical analyses (FA).

Keywords: Metals; Bottom sediments; Rivers; Wastewater treatment plants

1. Introduction

Progressive economic development, especially industrial production, agriculture, and strong urbanization, have a negative impact on the environment, causing a particular threat to the existence of natural surface water ecosystems [1–5]. Discharging the municipal and industrial wastewater directly into the surface water can pose a serious threat to the aquatic environment and, indirectly, also humans [6,7]. According to Samecka-Cymerman and Kempers [8], the quality of aquatic ecosystems is shaped to the greatest extent by treated wastewater discharged to receivers – mainly rivers. Wastewater can cause unfavorable changes in the aquatic environment, and their long-term introduction into the receiver can cause irreversible changes [9,10]. Chemical forms of elements, including metals, introduced into surface waters with sewage, accumulate in bottom sediments, in which much higher content can be recorded than in the water flowing through them, therefore it is necessary to carry out the research on the properties of bottom sediments deposited above and below the sewage discharge section [11]. The intensity of the migration of the elements in rivers is influenced by geochemical, physicochemical, climatic, and biological factors [12]. Processes occurring in the river environment, such as sorption/desorption, precipitation/dissolution, coagulation, and complexation reactions,

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affect the behavior of metals in water-sediment systems, that is, their concentration, reactivity, availability, and bioavailability [13]. According to Zheng et al. [14], about 90% of metals in the aquatic environment are associated with sediments and suspended solid particles. Increased content of elements in water sediments is one of the most important environmental problems due to their unfavorable impact on biological resources of the environment [15,16]. According to Singh et al. [17], sediments are important carriers of organic and inorganic contaminants and thus play an important role in determining the patterns of aquatic ecosystems pollution. According to Bielski [10], in order to demonstrate potential environmental changes in river sediments as a result of the sewage discharge from the treatment plant, it is advisable to conduct research on undeveloped sections of watercourses. Miakoto [18] argues that in fact, the total mixing of sewage at a short distance from the discharge occurs incidentally. Determining the distance, at which full mixing will take place, should be considered in a given river section in vertical and cross-section dimensions. According to Skorbiłowicz et al. [19], often when determining the size of mixing zones, solutions based on morphological parameters of water objects are used, among others, width of the river bed. In many European countries, mixing zones are only determined on the basis of river widths.

The study attempts to determine the impact of discharges from seven sewage treatment plants on the Biebrza ecosystem and its tributaries. The content of metals: Cu, Cr, Zn, Mn, and Fe was analyzed in bottom sediments above and below the cross-section of the treated wastewater discharge. Wastewater treatment plants were located in the following towns: Lipsk, Szczuczyn, Dolistowo, Sztabin, Goniądz, Rajgród, and Trzcianne – Poland.

2. Methods

2.1. Study area

The Biebrza River is a right-bank tributary of the Narew river, 155.3 km long, and the catchment area of 7,051.2 km^2 (Fig. 1). It is a typical lowland river with low slopes with a strongly meandering riverbed, creating numerous bends,

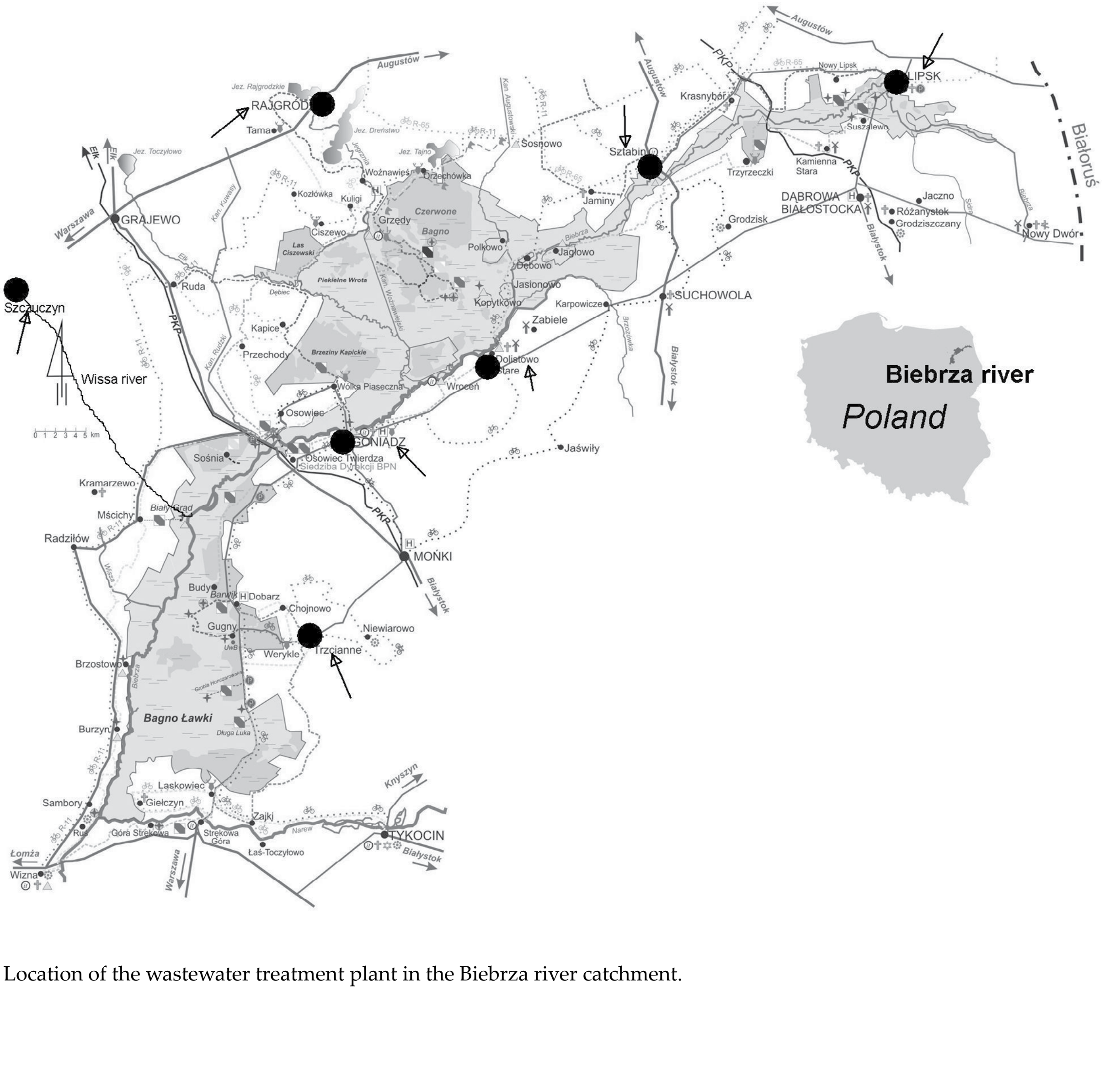

Fig. 1. Location of the wastewater treatment plant in the Biebrza river catchment.

and oxbow lakes. The river valley is distinguished by a high degree of naturalness, great natural and landscape values, the occurrence of many rare species of plants, animals and birds, and diversity of geo-morphological forms. Area of the studied catchment is located in the Biebrza National Park and is slightly affected by a man. Regional policy aimed at sustainable development of industry, taking into account the preservation of the uniqueness of the natural environment, also confirms the unique character of the studied area.

As part of the work, seven treatment plants were analyzed in the following cities: Lipsk, Szczuczyn, Dolistowo, Sztabin, Goniądz, Rajgród, and Trzcianne, which discharge treated sewage to Biebrza River and its tributaries (Fig. 1). Table 1 presents general data of the treatment plants studied.

2.2. Sampling and preparation of samples

On the Biebrza River and its tributaries (Wissa, Czarna Struga, Jerzgnia, and Muchawiec), 14 measurement points were located before and after discharge of treated wastewater in the following cities: Lipsk, Szczuczyn, Dolistowo, Sztabin, Goniądz, Rajgród, and Trzcianne (Table 1). Bottom sediment samples for laboratory tests were collected in 2015 at distances of 80 m before and after the point of treated sewage discharge on Biebrza River, whereas on the tributaries – at distances of 40 m before and after the point of discharge of sewage. Samples of bottom sediments were collected in places, where no other sources of impact were observed in the vicinity of purified sewage collectors location.

2.3. Analytical procedures

In each point selected, several individual surface samples of bottom sediments (from 5 to 10 cm depth) were collected. After mixing the test material, a representative sample was obtained (mass approximately 1,000 g). The samples were then dried in the air to an "air-dry" state and stored until tested [20]. Before proceeding with chemical analyses, the bottom sediment sample was dried at 40°C and sieved through a 0.2 mm sieve. According to Förstner and Müller [21], fractions between 20 and 200 μm are suitable for assessing the impact of contamination. They constitute a representative majority in the sediment and thus determine the transport of toxic substances. Decision to select the <200 μm fraction for testing was also dictated by the fact that geochemical monitoring of Poland's water sediments is carried out in this fraction. Bottom sediments were mineralized using hydrochloric and nitric acid in a volume ratio of 3:1 in a closed CEM microwave system (CEM Corporation, USA) [22,23].

Simultaneously, the metal forms soluble in 1 mol dm^{-3} HCl were cold extracted from the samples of bottom sediments [24]. Hydrochloric acid (1) is one of the most commonly used reagents for non-biodegradable fractionation of metals from solid samples [25].

All determinations were carried out in triplicate. The content of metals in bottom sediments was determined by atomic absorption spectrometer AAS ICE 3500 Thermo Scientific Spectrometer (UK and USA). Results of sediment analyses were verified using a certified reference material NCS DC 73317a. Results of standard reference material measurements showed good agreement with certified values (Cu = 101%, Zn = 96%, Cr = 80%, Mn = 97%, and Fe = 98%).

Obtained results of the tested metals (Cu, Zn, Cr, Mn, and Fe) were given in relation to air-dry sediments.

2.4. Assessment of bottom sediments pollution degree

To assess the bottom sediments contamination degree, the proposed classification of water sediments in Poland was used [24] and compared to the geochemical background proposed by Turekian and Wedepohl [27] (Table 2). Degrees of pollution were also calculated using the geochemical index (I_{geo}).

Table 1
General data and coordinates of the sampled points in Biebrza river catchment

Location	Latitude	Longitude	General data on the wastewater treatment plant
Lipsk Augustów county	53°73′06N	23°38′31E	Mechanical–biological, embedded process of elevated biogens treatment, real average 24 h sewage flowrate – 250 $m^3\ d^{-1}$, treated wastewater is discharged to Biebrza
Szczuczyn Grajewo county	53°55′61N	22°29′66E	Mechanical–biological, real average 24 h sewage flowrate – 200 $m^3\ d^{-1}$, treated wastewater is discharged to Wissa
Dolistowo Mońki county	53°54′98N	22°90′01E	Mechanical–biological, real average 24 h sewage flowrate – 120 $m^3\ d^{-1}$, treated wastewater is discharged to Biebrza
Sztabin Mońki county	53°67′29N	23°09′97E	Mechanical–biological, real average 24 h sewage flowrate – 100 $m^3\ d^{-1}$, treated wastewater is discharged to Biebrza
Goniądz Mońki county	53°49′26N	22°73′30E	Mechanical–biological, embedded process of elevated biogens treatment, real average 24 h sewage flowrate – 70 $m^3\ d^{-1}$, treated wastewater is discharged to Czarna Struga
Rajgród Grajewo county	53°73′02N	22°70′36E	Mechanical–biological, real average 24 h sewage flowrate – 70 $m^3\ d^{-1}$, treated wastewater is discharged to Jerzgnia
Trzcianne Mońki county	53°31′85N	22°61′30E	Mechanical–biological real average 24 h sewage flowrate – 30 $m^3\ d^{-1}$, treated wastewater is discharged to Muchawiec

Table 2
Metal contents and acidity of bottom sediments (fraction 0.2 mm) after and before treated wastewater discharge point from selected treatment plants in Biebrza catchment

Treatment plant localization City, river	pH		Decomposition, extraction	Cu		Zn		Cr		Mn		Fe	
				[mg kg⁻¹s.m.]									
	Before	After		before	after	before	after	before	after	before	after	before	after
Lipsk (Biebrza)	7.1	6.9	*A*	41.7	50.4	123.7	140.6	17.9	28.3	155.6	231.7	1,095.2	1,213.9
			B	17.5	27.5	39.7	50.4	6.4	22.8	33.7	45.7	271.2	288.9
Szczuczyn (Wissa)	7.5	7.6	*A*	2.4	3.1	75.2	162.7	5.4	14.0	89.1	125.6	980.9	1,056.6
			B	1.2	1.5	33.1	39.2	1.7	1.9	26.5	33.9	239.1	283.6
Dolistowo (Biebrza)	7.3	7.5	*A*	3.3	4.3	16.7	17.4	10.7	12.3	171.3	219.4	1,006.0	1,079.5
			B	1.4	1.9	8.2	10.2	3.7	4.6	30.1	61.8	250.5	198.7
Sztabin (Biebrza)	6.4	6.6	*A*	16.5	54.7	35.5	48.0	12.5	15.6	163.6	221.2	1,063.2	1,241.8
			B	10.6	22.3	24.8	35.9	2.3	10.2	52.8	59.1	237.7	321.9
Goniądz (Czarna	7.1	7.6	*A*	5.6	20.7	35.2	108.8	8.1	13.3	64.3	125.3	1,042.4	1,567.9
Struga)			*B*	2.4	11.5	12.4	28.0	2.1	2.3	34.7	41.3	365.1	450.7
Rajgród (Jerzgnia)	7.1	6.9	*A*	7.7	12.1	31.4	39.8	7.9	8.4	141.0	198.7	1,034.2	1,243.9
			B	1.7	4.6	15.5	19.9	3.5	2.7	42.2	69.5	206.4	214.9
Trzcianna (Muchaw-	7.7	7.4	*A*	2.1	3.9	39.8	51.6	19.0	21.8	207.4	231.7	987.0	1,071.2
iec)			*B*	1.1	1.6	24.2	31.5	2.6	3.5	42.3	55.6	164.4	200.7
Arithmetic mean			*A*	11.3	21.3	51.1	81.3	11.7	16.3	141.8	193.4	1,029.8	1,210.7
			B	5.1	10.1	22.5	30.7	3.2	6.9	37.5	52.4	247.8	279.9
Standard deviation			*A*	14.3	22.3	36.6	55.8	5.2	6.7	49.4	47.7	41.6	178.0
			B	6.4	10.8	11.3	13.1	1.6	7.5	8.9	12.6	62.1	89.6
Variability coefficient			*A*	126.3	104.4	71.7	68.7	44.5	41.1	34.8	24.7	4.0	14.7
			B	125.3	106.4	50.3	42.7	50.2	108.7	23.8	23.9	25.1	31.9
Geochemical background			1	45		95		90		850		47,700	
			2	6		48		5		–		–	

A – decomposition in HCl and HNO_3, *B* – extraction in HCl; 1 – Turekian, Wedephol [27], 2 – Bojakowska, Sokołowska [26]

The geochemical index (I_{geo}) is defined using Eq. (1) [28]:

$$I_{geo} = \log_2\left(\frac{C_n}{1,5 \times B_n}\right) \tag{1}$$

where C_n is the measured content of the analyzed metal (mg kg^{-1}), B_n is the geochemical background concentration suggested by Turekian and Wedepohl [27] (Table 2). The constant 1.5 is the correlation coefficient of the background matrix due to the lithological variability. I_{geo} values are classified according to Müller [28] and are divided into seven classes: unclassified class 0 ($I_{geo} \leq 0$); uncontaminated to medium contaminated class 1 ($0 < I_{geo} < 1$); moderately contaminated class 2 ($1 < I_{geo} < 2$); medium or heavily contaminated class 3 ($2 < I_{geo} < 3$); heavily contaminated class 4 ($3 < I_{geo} < 4$); strongly to heavily contaminated class 5 ($4 < I_{geo} < 5$); very heavily contaminated class 6 ($I_{geo} \geq 5$).

2.5. Statistical analysis

The Shapiro–Wilk test was used to verify normal distribution. The results were considered statistically significant at the probability of making a mistake $p < 0.05$. To study the relationships between metals in bottom sediments and identify their sources, the Pearson correlation analysis was applied. Statistical analysis of clusters (CA) in the Ward version was used for analyses in order to investigate possible sources of heavy metals in bottom sediments based on data classification. Multidimensional statistical analysis (FA) has also been applied, which is often used to identify sources of sediment pollution in water media [29]. The number of factors was determined on the basis of the "scree criterion" and the "Kaiser criterion." In order to interpret results of the factor analysis, it was assumed that the relations of the original variable with the factor are strong when the absolute values of its charges are greater than 0.70. The purpose of factor analysis is usually the interpretation of the influence of individual factors on the variables studied. All statistical analyses were performed using the licensed software Statistica ver. 13.3 for Windows.

3. Results and discussion

3.1. Metals content in bottom sediments and contamination degree assessment

The pH of the aqueous environment is an extremely important factor greatly affecting the mobility of metals in waters. Smaland and Salomons [30] claim that solubility of microelements increases along with the decrease of pH value. Reaction of Biebrza bottom sediments oscillated around 6.4–7.6 pH, while those from Biebrza tributaries had 6.9–7.6 pH. Studies of sediment acidity revealed that treated wastewater discharged to the receiver only slightly changes the bottom sediments acidity. Different results were achieved by authors investigating the impact of the sewage treatment plant on Bug river bottom sediments; in all tested points after discharge of treated wastewater, sediment acidity was lower [11]. It was probably the consequence of chemical composition of wastewater supplied to the treatment plant and several times the higher load of that sewage.

Contents of Cu, Zn, Cr, Mn, and Fe in bottom sediments of Biebrza and its tributaries are presented in Table 2. Average metal content in bottom sediments (decomposition in HCl and HNO_3) from points before treated wastewater discharge amounted respectively to Cu – 11.3, Zn – 51.1, Cr – 11.7, Mn – 141.8, and Fe – 1,029.8 mg kg^{-1}. There is a clear increase in the amount of metals in sediments after discharge of treated wastewater: Cu – 21.3, Zn – 81.3, Cr – 16.3, Mn – 193.4, and Fe – 1,210.7 mg kg^{-1}. The research shows that the largest concentration of Cu, Zn, Cr, and Mn is introduced by the sewage treatment plant in Lipsk, in the test point after discharge of treated wastewater, the following contents were noted for: Zn – 140.6, Cr – 28.3, and Mn – 231.7 mg kg^{-1}. Among the analyzed treatment plants, the one localized in Lipsk is characterized by the highest amount of sewage discharged to the receiver (Table 1). In the case of copper, the highest content was recorded for the discharge of sewage in the sewage treatment plant in Sztabin (Cu – 54.7 mg kg^{-1}). The amount of metals in sediments may also result from the geochemical nature of a given element and the type of river catchment. This property was noticed in the case of iron in sediments after treatment plants in Goniądz (Fe – 1,567.9 mg kg^{-1}) and Rajgród (Fe – 1,243.9 mg kg^{-1}). The content of Fe in these bottom sediments is influenced by the catchments of Czarna Struga River and Jerzgnia River. These rivers flow through boggy areas abundant in iron compounds.

Metals in sediments occur in several different forms and are associated with a number of components [31]. In order to assess the degree of bottom sediments contamination with metals, it becomes necessary to determine their soluble forms. The use of single-stage HCl extraction allows for a relatively fast and simple method of estimating the mobile forms in aqueous environment. Moreover, according to Frankowski et al. [25] and Sutherland [32], diluted HCl acid is the most suitable elution reagent for determining the anthropogenic sources of metals in solid samples. In the bottom sediments (extraction with HCl) of Biebrza River and its tributaries, higher content of Cu, Zn, Cr, Mn, and Fe was found after discharge of treated sewage in relation to their content before discharge, but not threatening the aquatic environment of the tested watercourses. The highest contents of Cu (27.5 mg kg^{-1}), Zn (51.4 mg kg^{-1}), and Cr (22.8 mg kg^{-1}) in bottom sediments were recorded in Biebrza River after the discharge of treated sewage in the town of Lipsk (Tables 1 and 2).

Higher content of both forms of metals is also visible in points after discharge of sewage as compared to sites before discharge, which indicates the impact of the treatment plant on bottom sediments of the tested receivers in the absence of other metal sources. According to Zhang et al. [33], the presence of metals in a river can be associated with continuous discharge of municipal sewage. Variability coefficients for all metals ranged from 4.03% to 126.24%, which indicates a large variation in monitored metal content in river sediment samples (Table 2).

The performed research indicated the geochemical background exceeding according to the classification of water sediments in Poland [26] for medium Cu, Zn, and Cr contents, while in the case of Mn and Fe, amounts of these metals were on a natural level. On the other hand, according to the proposed background by Turekian and Wedepohl [27], there were no exceedances for average element contents, the exceedance of the background occurred only in two sediment samples for Cu (Lipsk and Sztabin) and Zn (Lipsk and Goniądz) (Table 2).

Analyzing results of the geo-accumulation index (Table 3) for all heavy metals tested (Cu, Zn, Cr, Mn, and Fe), which for all collected bottom sediment samples reached a negative value, thus according to the classification, these sediments can be considered as non-polluted (class 0).

Table 4 shows Cu, Zn, Cr, Mn, and Fe contents in sediments of selected rivers in Poland and in the world. Comparing these contents with the amount of metals in Biebrza sediments and its tributaries, it should be stated that they are similar or smaller. The exception is the upper Narew River, where there were smaller amounts of Cu, Zn, and Cr in bottom sediments than in the studied objects.

3.2. Interpretation of results using statistical analyses

In order to investigate the relationship between metal content in bottom sediments after discharge and the amounts of sewage discharged, Pearson's correlation analysis was performed (sewage volume – total Cu form $r = 0.36$, Zn $r = 0.70$, Cr $r = 0.46$, and soluble Cu form $r = 0.45$, Zn $r = 0.61$, and Cr $r = 0.66$). In addition, correlations between some metals Cu and Cr $r = 0.87$ as well as Cu and Zn $r = 0.65$ were revealed, which may indicate their common source of sewage [40,41].

In order to identify and confirm possible sources of metals in sediments, a multidimensional statistical analysis was used (Table 5). The analysis was done separately, the first one for soluble metal forms and the second for total forms. Results obtained were very interesting. As a result of factor analysis (FA), two factors for soluble forms and 2 factors for total metal forms were isolated. Table 5 shows values of factor loads, which are significant if they take the value >0.7. The first factor in the case of soluble forms explains 49% of the total variance and consists of five significant factor loads (sewage flow, Cu, Zn, Cr, and acidity).

Factor 1 is associated with the flow of sewage that transports Cu, Zn, and Cr to the bottom sediments. According to Liu et al. [42], a large amount of discharged heavy metals directly causes an increase in the content of metals in the soluble fractions, which is also reflected in riverbed sediments. The analysis of correlation coefficients confirmed the above relations in the system: sewage flow – content of metals in bottom sediments. The factor load describing the variable "reaction" got negative value (–0.75), which may, in addition to the sewage flow, influence the behavior of soluble forms of Cu, Zn, and Cr. When environmental conditions change (pH, redox potential, salinity, etc.), heavy metals present in the sediment become bioavailable or toxic to organisms in the aquatic environment [43].

The change of metals from the soluble fraction is influenced by the reaction of sediment, which is a key parameter controlling the behavior of heavy metals in sediments and may reduce the adsorptive capacity and then increase their mobility [44,45].

The second factor is more difficult to interpret, because the distinctive variable is Mn, for which the load is (–0.99), which may be related to leaching of natural Mn from bottom sediments. In the case of total metal forms, the system of factors assumed approximately reverse form compared to the forms of soluble metals. This second factor explaining only 31% of the variance is related to the penetration of total metal forms into the tested sediments. On the other hand, the first factor explaining 35% of the variance is related to Mn penetrating in conditions of lower pH. The origin of the total Mn forms may be partly natural, not related to supplied sewage.

Table 3
Value of geochemical index (I_{geo}) in bottom sediments of Biebrza River and its tributaries after discharge of treated wastewater

Biebrza river and its tributaries	Cu	Zn	Cr	Mn	Fe
			I_{geo}		
Lipsk	–0.42	–0.02	–2.25	–2.46	–5.88
Szczuczyn	–4.44	0.19	–3.27	–3.34	–6.08
Dolistowo	–3.97	–3.03	–3.46	–2.54	–6.05
Sztabin	–0.30	–1.57	–3.11	–2.53	–5.85
Goniądz	–1.71	–0.39	–3.34	–3.35	–5.51
Rajgród	–2.48	–1.84	–4.01	–2.68	–5.85
Trzcianne	–4.11	–1.47	–2.63	–2.46	–6.06

Table 4
Results of metals content in bottom sediments (mean and ranges) in selected rivers in Poland and in the world

Study object	Cu	Zn	Cr	Mn	Fe	Reference
			(mg kg^{-1} DM)			
Biebrza and its tributaries, Poland	21.3	76.1	16.3	193.4	1,210.7	Own results
	2.1–50.4	16.7–140.6	5.4–28.3	64.3–231.7	980.9–1,243.9	
Rivers in Poland	21.00	247.00	18.00	506.0	1,180.0	Lis and Pasieczna [20]
Upper Narew river, Poland	3.5	47.5	14.8	–	–	Skorbiłowicz [34]
Bystrzyca River, Poland	2.7–42.5	9.9–326.0	6.5–63.8	114.0–1,194.0	4,724.0–15.630	Polechońska and Klink [35]
Huaihe River, China	31.3	186.6	–	–		Wang et al. [36]
Suquia River, Argentina (2009)	8.34	82.5	–	340.0	7,892.0	Harguinteguyin et al. [37]
Yinma River, China	23.8	52.2–151.1	46.6	–	–	Guan et al. [38]
Gomti River, India	43.48	6,365	20.65	260.4	6,547.5	Singh et al. [39]

Table 5
Results of multivariate analysis (FA) of metal content (extraction with HCl and decomposition with HCl and HNO_3) in bottom sediments of Biebrza River and its tributaries after discharge of purified sewage

Variable	Factor 1	Factor 2	Factor 1	Factor 2
	Soluble forms (extraction with HCl)		Total forms (decomposition with HCl and HNO_3)	
Sewage flow	0.70	0.53	–0.10	0.86
Cu	0.93	0.15	0.60	0.70
Zn	0.70	0.57	–0.56	0.80
Cr	0.93	0.12	0.33	0.73
Mn	0.01	–0.99	0.91	–0.03
Fe	0.13	0.63	–0.19	0.02
Acidity	–0.75	0.56	–0.84	–0.13
% of variance	49	27	35	31

In connection with the above, a more important form of metals transported by wastewater to bottom sediments in their weakly bound soluble form, explaining almost 50% of the variance. Radomskaya et al. [46] claim that from an ecological point of view, metals in soluble forms are dangerous, because they are thermodynamically unstable and quickly convert as a result of dissolution, thereby increasing the rate of migration in the aquatic environment.

The total metal content in river sediments depends primarily on their naturally occurring amounts associated with geological origin materials and to a lesser extent on the amount of inputs introduced by humans and the ability of sediments to capture metals entering the system [43,47]. Essentially, heavy metals of anthropogenic origin migrate in the environment in the form of inorganic complexes or hydrated ions, that are then easily absorbed by sediment particles through relatively weak physical and/or chemical bonds [48].

Cluster analysis classified all analyzed sediments from sewage treatment plants to two interpretable groups according to their similar impact on bottom sediments such as cluster 1 (Goniądz) and cluster 2 (Sztabin, Rajgród, Trzcianne, Dolistowo, Lipsk, and Szczuczyn). An isolated object exhibited by cluster analysis is the purification plant in Goniądz. For a long time, the wastewater treatment plant in Goniądz required modernization based on a completely new biological treatment system [49]. Modernization was carried out, but the years of inadequate sewage treatment had an effect on bottom sediments near their discharge (Fig. 2).

4. Conclusions

- The highest concentration of Cu, Zn, Cr, and Mn is introduced by the sewage treatment plant in Lipsk, the following content was noted at the test point after discharge of treated wastewater: Zn – 140.6, Cr – 28.3, and Mn

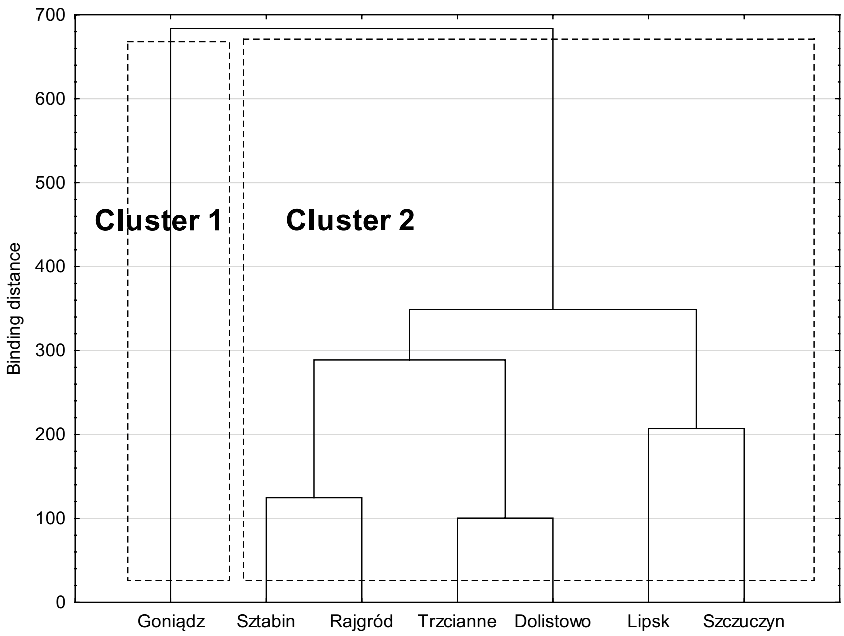

Fig. 2. Division of research objects based on cluster analysis (Ward) taking into account the content of metals in bottom sediments.

– 231.7 mg kg^{-1}. The largest amount of Cu is introduced by the sewage treatment plant in Sztabin – 54.7 mg kg^{-1} Cu was found at the point after discharge of sewage.

- The research showed that the content of total metal forms in the sediments was significantly higher compared to their soluble forms. Higher contents were also found for metals of both forms in sites after discharge of sewage in comparison to places before discharge, which indicates the impact of the treatment plant on bottom sediments of the tested receivers in the absence of other metal sources.
- It was shown that the geochemical background was exceeded according to the classification of water sediments in Poland (Bojakowska and Sokołowska [26]) for medium Cu, Zn, and Cr contents, while the amounts of Mn and Fe were on a natural level. There were no exceedances of the background values given by Turekian and Wedepohl [27] for average elemental content. Exceeding the background value occurred only in two samples of sediments in the case of Cu (Lipsk and Sztabin) and Zn (Lipsk and Goniądz).
- On the basis of calculations of the geo-accumulative index, the examined sediments were classified as non-contaminated (class 0).
- The calculations of Pearson's correlation showed the dependence between the content of metals in bottom sediments after discharge and the flow of discharged wastewater.
- The contents of soluble metal forms in sediments are to a larger extent shaped by discharged purified sewage than the content of total forms, which is mainly related to the natural origin of metals. The results of factor analysis (FA) confirmed the above thesis as demonstrated in the studied literature.
- The Ward analysis made it possible to separate the sewage treatment plant (Goniądz) from all of the plants studied. The operation of the plant changed over time until its modernization began.

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