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THE INFLUENCE OF ZINC-LEAD ORE MINING INDUSTRY ON THE LEVEL OF THE BIAŁA PRZEMSZA BOTTOM SEDIMENTS CONTAMINATION

Witold NOCOŃ [a*], Katarzyna NOCOŃ [b], Krzysztof BARBUSIŃSKI [c], Joanna KERNERT [d]

[a] Dr.; Faculty of Energy and Environmental Engineering, the Silesian University of Technology, Konarskiego 18A, 44-100 Gliwice, Poland
* E-mail address: *wknocon@polsl.pl*

[b] MSc; Institute of Environmental Engineering Polish Academy of Sciences, Skłodowskiej-Curie 34, 41-819 Zabrze, Poland

[c] Prof.; Faculty of Energy and Environmental Engineering, the Silesian University of Technology, Konarskiego 18A, 44-100 Gliwice, Poland

[d] MSc; Institute of Environmental Engineering Polish Academy of Sciences, Skłodowskiej-Curie 34, 41-819 Zabrze, Poland

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Abstract

In this paper the concentrations of Zn, Pb, Cd, Cr, Cu, Ni, Mn and Fe in bottom sediments from the chosen sector of the Biała Przemsza are showed. Samples were collected in three series at six samplings from the Biała Przemsza and one sampling from the Biała. The estimation of the level of sediments contamination is done using two classifications. From the tributary of the Centuria to the tributary of the Biała, concentrations of trace metals in river sediments are at the level of geochemical background. Below the tributary of the Biała, where industrial wastewater is discharged, very high concentrations of lead, cadmium and zinc were observed. The maximum contents of these metals were: 51370 mg/kg d.w. (Zn), 16980 mg/kg d.w. (Pb) and 148 mg/kg d.w. (Cd). Contamination of bottom sediments by Zn, Pb and Cd below the Biała, according to LAWA classification allows to classify them as "very strongly contaminated". According to Polish law these sediments can be classified as "contaminated".

Streszczenie

W pracy przedstawiono wyniki badań zawartości Zn, Pb, Cd, Cr, Cu, Ni, Mn i Fe w osadach dennych wybranego odcinka rzeki Biała Przemsza oraz dokonano oceny stopnia ich zanieczyszczenia w oparciu o dostępne klasyfikacje jakości osadów. Na odcinku od ujścia potoku Centuria do ujścia rzeki Biała zawartość metali była na poziomie tła geochemicznego, natomiast na odcinku poniżej rzeki Biała, gdzie wprowadzane są ścieki przemysłowe, występowały bardzo wysokie stężenia Pb, Cd i Zn. Maksymalne zawartości wynosiły: 51370 mg/kg s.m. (Zn), 16980 mg/kg s.m. (Pb) oraz 148 mg/kg s.m. (Cd). Zawartość cynku, kadmu i ołowiu w osadach dennych poniżej ujścia Białej pozwala, zgodnie z klasyfikacją LAWA, zakwalifikować je jako „bardzo silnie zanieczyszczone". Również zgodnie z polskim ustawodawstwem osady te mogą być zaliczone do zanieczyszczonych.

Keywords: **The Biała Przemsza; Heavy metals; Bottom sediments.**

1. INTRODUCTION

Sediments are the result of sedimentation of the allochtonic material, formed outside the sedimentation area and autochthonous material, formed in the area of sedimentation. The allochtonic materials are: sand, mud and gravel as a result of destruction of bottom and banks of rivers and lakes, as well as mineral and organic suspended matter introduced into water from surface runoff, tributaries and municipal and industrial wastewater [1]. The autochthonous material are the inorganic and organic substances such as calcium carbonate, hydroxides of iron and manganese, phosphorus compounds precipitated from water as well as phyto- and zooplankton [2].

In the Upper Silesia area a strong influence of human activities on the state of rivers contamination is observed. Streams flowing through the central part of the Upper Silesia are characterized by very high rates of pollution originating from industrial and municipal wastewater [3-5].

Heavy metals, due to their wide application in various industry branches, pose high risk to the environment. As a result of self-purification processes in surface water, dissolved forms of heavy metals during sorption and other biochemical processes move to bottom sediments, what results in water quality improvement and increase of heavy metal amounts in sediments [2]. The content of heavy metals in bottom sediments is a good indicator of the level of the aquatic environment contamination.

The Biała Przemsza is the last river in the Silesian agglomeration which retained its natural character, especially when it comes to the shape of riverbed. Despite many centuries of mining exploitation in the river catchments area which led to irreversible changes in the aquatic environment, natural areas located near the Biała Przemsza are one of the most valuable in the Silesia region. Within this river basin there is highly developed mining and metallurgical zinc-lead ore industry. It is therefore clear that it will exert a negative impact on the state of purity of surface water, and their bottom sediments.

So far, the contamination of the Biała Przemsza is treated rather marginally, and the last published research showing results of studies of sediments contamination with heavy metals date back more than ten years [6]. In this context, this research aim was to determine the level of bottom sediments contamination of the Biała Przemsza with heavy metals (Zn, Pb, Cd, Cr, Cu, Ni) and Fe and Mn.

2. BASIN CHARACTERISTICS

The Biała Przemsza is the beginning (together with the Czarna Przemsza) of the Przemsza river. The basin area is about 880 km^2, the length of this river is 64 km. The river source is a moor near Wolbrom at 380 m above sea level, and the end (the connection with the Czarna Przemsza) at 242 m above sea level on the border of Sosnowiec and Mysłowice, in the place which is called "Three Emperors Triangle".

Land of the Biała Przemsza encompasses several geographic regions from the bordering of the Silesia Upland and the Krakow-Częstochowa Upland [7]. The largest industrial complex which operates in the Biała Przemsza basin is Mining and Metallurgical Plant "Bolesław" which is located near Olkusz. The Olkusz region is famous for zinc and lead ore exploitation and processing. In the ancient times this city was called "the Silver City" because of occurrence of silver ore. The tradition and history of zinc mining and smelting stretches back to the 12th century when in Old Olkusz the King Kazimierz the second set up the mining settlement [8]. It can, therefore, be assumed that human activity in the Biała Przemsza has lasted over 900 years.

3. SAMPLING LOCALIZATION AND METHODOLOGY

Samples of sediments were collected during three sampling series from the sector of the river between a tributary of the Centuria and the tributary of the Sztoła there were six samplings. Samples of sediments were also collected from the Biała river.

BP1 – located below the connection of the Biała Przemsza and the Centuria in the village of Zagórze (Fig. 1.). Relatively small anthropogenic transformations influence on low river pollution with specific substances. However, due to agriculture development in both catchments there is possible higher phosphorus and nitrogen pollution.

BP2 – this sampling is located above the tributary of the Biała river in the village of Rudy, in the Błędowskie Forests. The river contamination may be caused by agriculture influence and possibility of uncontrolled discharges of municipal wastewater.

B1 – the Biała river, about 1 km above its tributary to the Biała Przemsza (Fig. 2.). This sampling is located in the village of Łazy in the environmentally protected area. This river is the largest source of the Biała Przemsza pollution, because through the Dąbrówka Canal industrial wastewater from Mining and

Metallurgical Plant "Bolesław" in Bukowno is discharged.

BP3 – is located in Okradzionów, above Small Water Electric Plant (Fig. 3.). Wastewater from households as well as surface runoff are discharged to the Biała Przemsza and the most of all higher concentrations of suspended matter from the Biała river are observed.

BP4 – is below Small Water Electric Plant in Okradzionów. The characteristic of contamination is the same as at BP3. Samples were collected below the connection of bypass from water mill and the main stream of the Biała Przemsza.

BP5 – located in the town of Sławków (Fig. 4.). High concentrations of suspended matter and the influence of municipal wastewater are still observed.

BP6 – the Sztoła estuary (the village of Burki). This sampling is located in the forest on the border of Śląskie and Małopolskie voivodeships.

Bottom sediments were collected during three series in February, May and October 2009, from the surface layer (about 5 cm). Samples were dried, sieved (0.5 mm) and grinded in agate mortar. After that they were mineralized, using spectral pure nitric acid, in Microwave Mineralizer Magnum, Ertec. Concentrations of Zn, Pb and Fe were measured using Atomic Absorption Spectrometer Avanta Sigma, GBC. Concentrations of Cd, Cu, Ni and Mn were measured by Atomic Absorption Spectrometer mod. 1100, Perkin-Elmer. In both cases it was air-acetylene flame. Because of very wide range of indicated elements concentrations and the minimization of measurement errors by maintaining the linearity of the method, Zn, Pb and Cd were determined using two calibration curves. In case of the other elements, concentrations were determined on one calibration curve, if it was necessary using the dilution. In case of Cr it was necessary to concentrate samples (in the microwave mineralizer). Ranges for calibration curves were chosen based on the producers instructions.

Figure 2.
B1 (1 km above the tributary to the Biała Przemsza)

Figure 3.
BP3 (Okradzionów, above Small Water Electric Plant)

Figure 1.
BP1 (below the tributary of the Centuria)

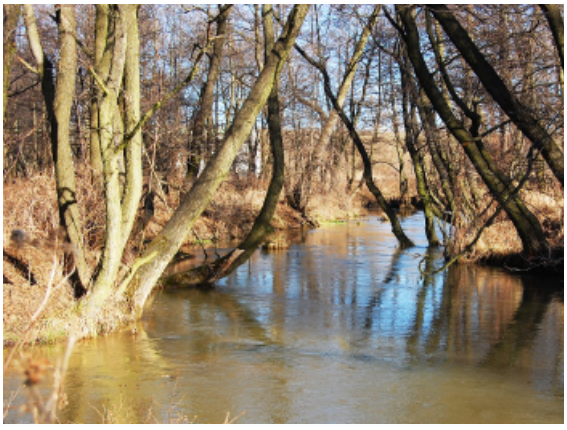

Figure 4.
BP5 (Sławków)

Table 1.
Concentration of metals in bottom sediments of the Biała Przemsza and the Biała river [mg/kg d.w.]

Sampling	Zn	Pb	Cd	Cr	Cu	Ni	Mn	Fe
02.2009								
BP1	-	-	-	-	-	-	-	-
BP2	36	14	1.2	<2	3	4	220	1370
B1	27260	6090	97.6	6	29	16	511	20570
BP3	37240	11980	133.8	14	127	32	1002	45900
BP4	37740	12430	137.2	16	142	38	1027	55790
BP5	15950	4620	58.0	6	37	16	480	20530
BP6	2145	650	10.4	4	17	12	90	5160
05.2009								
BP1	-	-	-	-	-	-	-	-
BP2	151	42	1.8	5	6	6	276	3380
B1	44570	12910	151.5	11	57	45	890	46080
BP3	34680	16980	135.6	13	50	44	985	50140
BP4	35100	14030	118.2	20	60	55	1017	50690
BP5	1940	1000	7.4	3	6	46	167	4500
BP6	7300	3800	31.4	5	29	15	254	13090
10.2009								
BP1	26	16	0.4	2	5	<2	37	1420
BP2	42	13	0.4	<2	3	<2	50	1500
B1	12990	3460	51.4	3	72	3	502	13190
BP3	51373	14350	148.2	15	173	17	1027	55520
BP4	42109	15600	132.7	20	292	22	1059	52140
BP5	1880	730	6.0	13	14	3	162	3000
BP6	-	-	-	-	-	-	-	-

4. RESULTS

Metal concentrations in bottom sediments of the Biała Przemsza (BP1 – BP6) and the Biała (B1) are shown in Table 1.

In terms of metal content in bottom sediments the Biała Przemsza can be divided into two characteristic sections. The first, from the river source to the estuary of the Biała river (BP1, BP2), where concentrations of heavy metals are at the level of geochemical background, and the second, under this estuary (BP3 – BP6), where significant enrichment of Zn, Pb, Cd, Fe and other metals in bottom sediments is observed. The highest concentration of these metals at BP3 and BP4 was noticed.

Concentration of Zn ranged from 26-151 mg/kg d.w. at BP1 and BP2 to 34680-51370 mg/kg d.w. at BP4 and BP4 in Okradzionów. Down the river course Zn concentrations in sediments were lower. In Sławków they ranged from 1880 to 15950 mg/kg d.w. and in the area of the Sztoła estuary from 2150 to 7300 mg/kg d.w. Pb content changed from 14 to 42 mg/kg d.w. in the sector from the Centuria estuary to the Estuary of the Biała, and from 11980 to 16980 mg/kg d.w. in Okradzionów (BP3, BP4). Pb contamination decreased through the river course, similar as in case of Zn. In Sławków it was 733-4620 mg/kg d.w. and at BP6 650-3800 mg/kg d.w. Also high concentrations of Cd in bottom sediments were observed. At BP3 and BP4 Cd content varied from 118 to more than 148 mg/kg d.w. Although at BP5 and BP6 its concentrations, as in case of Zn and Pb, were lower they were still very high. At BP3 and BP4 a rise of other metal concentrations was observed, but not so visible as Zn, Pb and Cd. At B1 concentrations of Zn, Pb and Cd were also very high (Zn: 12990-44570 mg/kg d.w., Pb: 3460-12910 mg/kg d.w., Cd: 51.4-151.5 mg/kg d.w.).

5. DISCUSSION

Strong contamination of the Biała Przemsza bottom sediments below the estuary of the Biała is observed. It indicates that the mining and processing of zinc-lead ore industry plays a decisive role in the pollution of the Biała Przemsza. The farther from the introduction of wastewater which contain very high con-

centrations of undissolved zinc, cadmium and lead, a decrease in the content of these elements in bottom sediments of the river is observed.

To have a complete view of the level of the Biała Przemsza bottom sediment heavy metals contamination, results of research were compared to threshold values of the elements contained in the Regulation of the Minister of Environment from 16th April 2002 [9] (Table 2) and LAWA classes for river sediments [10] (Table 3).

Table 2.
Concentrations of metals included in the Minister of Environment of 16 April 2002 that qualify sediments as contaminated

Element	Concentration
Zn	concentration equal to or greater 1000 mg / kg of dry weight
Pb	at a concentration equal to or greater 200 mg/kg of dry weight
Cd	concentration equal to or greater 7.5 mg/kg of dry weight
Cr	concentration equal to or greater 200 mg/kg of dry weight
Cu	concentration equal to or greater 150 mg/kg of dry weight
Ni	concentration equal to or greater 75 mg/kg of dry weight

The Biała Przemsza, despite its indubitable natural values, is strongly transformed by human activity. Either Polish or German classification (marked with colours) give reasons to classify the sediments of the Biała and the Biała Przemsza as very strongly contaminated (Table 4). A comparison of these results to the literature data [6] shows that in the past few years significant increase of sediments pollution, especially in case of zinc, lead and cadmium has been observed. Also, in comparison to other Silesian Agglomeration rivers [1,11,12] bottom sediments of the Biała Przemsza are more contaminated, especially when it comes to the content of zinc, lead by cadmium. Very high concentrations of the most toxic and bioavaliable elements (lead and cadmium) define the Biała Przemsza as one of the most polluted rivers in Poland.

6. CONCLUSIONS

Results of research presented in the publication allowed to formulate the following conclusions:

1. The Biała Przemsza, from bottom sediments contamination point of view can be divided into two characteristic sectors – the sector from its source to the tributary of the Biała, and the sector below it, where very strong contamination of bottom sediments is observed in case of Zn, Pb and Cd.

Table 3.
LAWA classes for river sediments [mg/kg d.w.]

Element	I	I – II	II	II – III	III	III – IV	IV
Zn	100	200	400	800	1600	3200	> 3200
Pb	25	50	100	200	400	800	> 800
Cd	0.3	0.6	1.2	2.4	4.8	9.6	> 9.6
Cr	80	160	320	640	1280	2560	> 2560
Cu	20	40	80	160	320	640	> 640
Ni	30	60	120	240	480	960	> 960
I	Uncontaminated						
I – II	Not contaminated / Moderately contaminated						
II	Moderately contaminated						
II – III	Moderately contaminated / Strongly contaminated						
III	Strongly contaminated						
III – IV	Strongly / Very strongly contaminated						
IV	Very strongly contaminated						

Table 1.
Average concentrations of metals in sediments [mg/ks d.w.] of the Biała Przemsza and the Biała – a comparison to LAWA classes

Sampling	Zn	Pb	Cd	Cr	Cu	Ni	Mn	Fe
BP1	27	17	0.4	2	5	2	37	1418
BP2	76	23	1.1	3	4	5	182	2081
B1	28273	7486	100.2	7	53	21	634	26612
BP3	41097	14435	139.2	14	117	31	676	50521
BP4	38318	14019	127.7	19	165	38	1034	52873
BP5	6590	2117	23.8	7	19	22	270	9343
BP6	4720	2224	20.9	5	23	14	172	9126

2. The most important influence of bottom sediments contamination plays zinc-lead ore mining industry.
3. Concentrations of Zn, Pb, and Cd in the Biała Przemsza sediments, according to LAWA classification allow to classify them as "very strongly contaminated" as well as according to Polish law as "contaminated sediment".
4. Results of research justify finality of further works to revitalize the Biała Przemsza ecosystem through reducing the level of sediment contamination.
5. Very high levels of Zn, Pb and Cd contamination in bottom sediments allow to take into consideration the conception of recycle these trace metals as valuable materials.

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