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Heavy Metal Contamination of Sediments from Recreational Reservoirs of Urban Areas and its Environmental Risk Assessment

Metale ciężkie w osadach dennych zbiorników rekreacyjnych na terenach zurbanizowanych i ocena ryzyka środowiskowego

Water reservoirs play important role in human environment, especially as a part of ecological networks in urban areas. Due to such localization they are subjected to the effects of the anthropogenic activities, introducing broad range of contaminants (e.g. heavy metals) through various pathways. The main aim of this study was to estimate heavy metal (Cd, Cr, Cu, Pb, Zn) contamination level in sediments of eight reservoirs in the Cracow urban area (Bagry, Nowohucki, Plaszowski, Dabski, Przylasek Rusiecki, Tyniec, Zakrzowek, and Zeslawice Reservoirs), and assess its potential environmental risk with use of various criteria (I_{geo} - geo-accumulation index, CF - contamination factor, PLI - pollution load index, TEC/PEC - threshold effect concentration/probable effect concentration). Furthermore, the role of reservoir catchment for sediment contamination (agricultural, industrial, and urbanized) was studied. Also, levels of metal contamination were compared with other recreational reservoirs in Poland (Jeziorsko, Barycz Dzierzno Duze, Pogoria III, Rusalka, and Sloneczne Reservoirs). The study revealed considerable variation in the chemical composition of bottom sediments, evidently depended on their localization. Results showed that the sediments of the Cracow area reservoirs and from the other urbanized catchments were moderately contaminated. Reservoirs from industrial catchments had a considerably higher content level, while water bodies localized in agricultural areas displayed low content of heavy metals. According to I_{geo} and CF sediments of Cracow area reservoirs were mostly Cd contaminated. However, Cd contents were relatively high in urban (Sloneczne) and industrial areas (Dzierzno Duze). The same situation was found in PEC values exceedances. In other cases, investigated heavy metals were mostly between the TEC and PEC values, which indicate moderate contamination of the sediments and moderate impact on biota. Therefore, further research and monitoring of sediments quality should be maintained in future seasons due to the use of water reservoirs throughout the year for recreational purposes.

Keywords: **heavy metals, recreational reservoirs, Cracow area, urban catchment**

Introduction

Water reservoirs play important role in human environment, especially as a part of ecological networks in urban areas, where they not only look good but also provide health benefits and act as reservoirs or conduits for biodiversity [1]. They are commonly used for various types of recreational activities by local residents (swimming, sailing, fishing, etc.), but also serve as habitat and breading area for wildlife species. Due to their localization in the municipal areas they are subjected to the effects of the anthropogenic activities introducing broad range of contaminants through various pathways.

Heavy metals are a special group of contaminants appearing in water reservoirs. They have ecological significance because of remaining in water and accumulating in reservoirs and entering the food chain. Their occurrence in the environment results primarily from anthropogenic activities [2]. The main input of heavy metals is connected with untreated sewage release, washed-out from dumping grounds, settlement of atmospheric dust as well as use of the plant protection agents in agriculture. Great amounts of heavy metals are also discharged by supplying water courses and eventually concentrated in bottom sediments [3]. Though natural processes that may enrich waters with heavy metals also play a key role in such habitats [4]. Some of reservoirs despite being located in areas heavily affected by industry preserved natural values, and sometimes even enriched them becoming as an attractive sites of the cities in urban areas.

The main aim of this study was to estimate the metal (Cd, Cr, Cu, Pb, Zn) contamination level in sediments of eight reservoirs in the Cracow urban area (Bagry, Nowohucki, Plaszowski, Dabski, Przylasek Rusiecki, Tyniec, Zakrzowek, and Zeslawice Reservoirs), and estimate its potential environmental risk with use of various criteria (I_{geo}, CF, PLI, TEC/PEC). Furthermore, the role of reservoir catchment for sediment contamination (agricultural, industrial, and urbanized) was studied. Also, the levels of metal contamination were compared with other recreational reservoirs in Poland (Jeziorsko, Barycz Dzierzno Duze, Pogoria III, Rusalka, and Sloneczne Reservoirs).

1. Study area

Eight reservoirs from the Cracow urban area were examined in the present study, and six others localized in different parts of Poland were chosen to provide a database for comparison and discussion of contamination issues in different types of catchments (Fig. 1). The choice of reservoirs outside of Cracow was dictated by availability of published datasets representing agriculture, industrial, and urban catchments in Poland with a pronounced anthropogenic impact (Table 1). For all of them air pollution, industrial and urban area surface run-off, erosion processes within agricultural areas, direct sewage discharges or pollution of tributaries are the main sources of various contaminants including heavy metals in water reservoirs [3, 5-7].

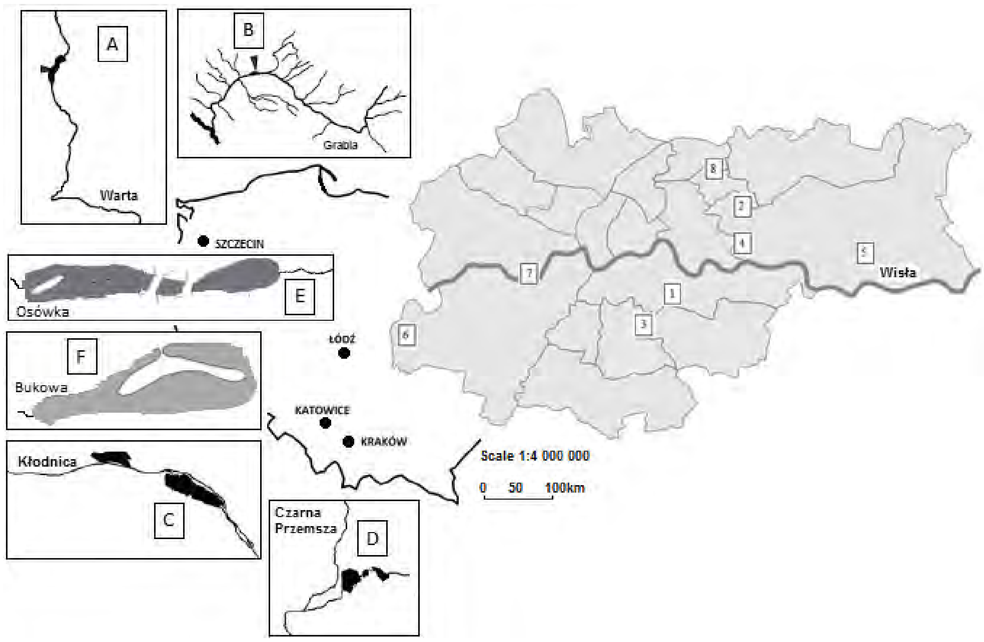

Fig. 1. Location of the studied reservoirs in the Cracow area: 1 - Bagry, 2 - Nowohucki, 3 - Plaszowski, 4 - Dabski, 5 - Przylasek Rusiecki, 6 - Tyniec, 7 - Zakrzowek, 8 - Zeslawice, and location of other reservoirs: A - Jeziorsko, B - Barycz, C - Dzierzno Duze, D - Pogoria III, E - Rusalka, F - Sloneczne

Rys. 1. Lokalizacja wybranych zbiorników wodnych na terenie Krakowa: 1 - Bagry, 2 - Nowohucki, 3 - Płaszowski, 4 - Dąbski, 5 - Przylasek Rusiecki, 6 - Tyniec, 7 - Zakrzówek, 8 - Zesławice, oraz lokalizacja pozostałych zbiorników: A - Jeziorsko, B - Barycz, C - Dzierżno Duże, D - Pogoria III, E - Rusałka, F - Słoneczne

Cracow (pop. 850,000) is located in the southern part of Poland with the area of approximately 327 sq. km. The city is located on the border of a few different physiographic regions (i.e. Cracow Upland, Carpathian Foothils, and Sandomierz Basin), and the Vistula is a main river here, flowing from west to east, over 41.2 km. An artificial oxbow lake, created during engineering works in the beginning of the 20th century on the channel of this river constitutes one of the studied reservoirs (Tyniec) [8]. Among the remaining reservoirs, two of them were created for industrial/water supply purposes (Nowohucki, and Zeslawice), and the rest of them are open pits resulted from the exploitation of sands, gravels, and limestones (Bagry, Plaszowski, Dabski, Przylasek Rusiecki, and Zakrzowek) [9]. All of them are localized within the Cracow borders and mostly used for swimming, sailing, and fishing. Water quality of these reservoirs has been described elsewhere [10].

To reservoirs with the urban catchment belong also the Rusalka and Sloneczne Reservoirs, situated in Szczecin (pop. 750,000, approximately 300 sq. km), in the north-western part of Poland. Water flowing from watercourse Osowka contributed to create an artificial reservoir, called Rusalka. The Sloneczne Reservoir is a flow water reservoir which was created artificially in the 1930s in the naturally swampy valley of watercourse Bukowa, after the settlement and drained surrounding areas. Both reservoirs are localized in Szczecin borders and used for recreation and fishing [5].

The agriculture catchment is represented by the Jeziorsko Reservoir located in the middle course of the Warta River between the towns Skeczniew and Warta. It was created in 1986 in order to regulate river flows and of agricultural land irrigation. The catchment area is covered by arable lands (42% of the land's surface), meadows and pastures (14%). The Barycz Reservoir which is retention reservoir is situated in the middle course of the Grabia River in Barycz city which is 25 km from Lodz. The catchment consists of arable land and orchards, which cover 63% of this area [3]. Both reservoirs are mostly used for recreation and fishing.

Silesian upland (3,900 sq. km) is located in the southern part of Poland. The industrial catchment is represented by the Dzierzno Duze Reservoir which was created in 1964 in the central part of the Klodnica valley by flooding two sand pits [11, 12]. The Pogoria III Reservoir located in the zone of influence of metallurgical plant and urban area supplied with water from the Czarna Przemsza River. The reservoir was also created in the post sand exploitation area in the 70s. The Dzierzno Duze Reservoir is used for sailing and flood control. The Pogoria III Reservoir is mostly used for water sports, recreation and fishing [6].

Table 1. **Surface area and main use of the water reservoirs**

Tabela 1. **Powierzchnia i użytkowanie badanych zbiorników wodnych**

Reservoirs	Surface area	Main use
Bagry	29 ha	swimming, sailing [13]
Nowohucki	17 ha	recreation [14]
Plaszowski	15 ha	fishing and recreation [13]
Dabski	3 ha	fishing, habitat of the rare species of plants and animals [13]
Przylasek R.	87 ha	swimming and fishing [13]
Tyniec	16 ha	fishing [15]
Zakrzowek	12 ha	swimming, diving, Special Protection Area within the Nature 2000 network [13]
Zeslawice	24 ha	fishing [16]
Rusalka	3 ha	recreation [5]
Sloneczne	5 ha	recreation and fishing [5]
Jeziorsko	4,300 ha	recreation and fishing [3]
Barycz	2.8 ha	fishing [3]
Dzierzno D.	516 ha	sailing and flood control [6]
Pogoria III	205 ha	water sports, recreation and fishing [6]

2. Experimental procedures

2.1. Materials and methods

Bottom sediment samples from the Cracow area reservoirs (Bagry, Nowohucki, Plaszowski, Dabski, Przylasek Rusiecki, Tyniec, Zakrzowek, and Zeslawice) were collected in summer of 2013. Sediment samples were collected from the surface layer (0÷5 cm), from sites selected according to best availability of the accumulated material, transported to the lab and kept in temperature 4°C before further analyses. In the laboratory samples were air dried at the room temperature, then crushed with mortar and pestle, and sieved through 2 mm sieve. Approximately 3 g of each sample was mineralized in *aqua regia* (HNO_3 and HCl, 1:3) according to ISO norm no. 11466:1995 (ISO 1995) [17]. Total metal contents (Cd, Cr, Cu, Pb, Zn) were measured use of atomic absorption spectrometry (AAnalyst 300 Perkin Elmer) according to ISO norm no. 11047:1998 [18], and the detection limit for each metal was 0.00005 mg/kg. Each measurement was performed three times, and an average value has been presented in the study. The evaluation of quality of the analytical part was performed using in-house control samples [19-21].

Samples from the Rusalka and Sloneczne Reservoirs were collected during periodic removal of bottom sediments in 2006. Samples were collected from the surface layer (0÷10 cm). Heavy metals (Cd, Cu, Pb, Zn) were analyzed using the method described elsewhere [5]. Briefly, samples were subjected to extraction in a mixture of concentrated acids (HNO_3 + $HClO_4$). The contents of heavy metals were determined by atomic absorption spectrometry (FAAS) using Salaar 929 spectrophotometer from Unicam.

Bottom sediment samples from the Jeziorsko and the Barycz Reservoirs were collected by a sediment core sampler only in the spring of 2007 from three stations (upper, middle and lower part) in each reservoir. Samples in the laboratory were homogenized, freeze dried at –40°C and mixed in proportion 1:1:1 to obtain the composed sample. Three heavy metals (Cu, Cd, Pb) were analyzed using the method described elsewhere [3]. Briefly, samples were subjected to extraction with *aqua regia* in closed microwaves system Milestone 1200 Mega. Measurements of heavy metal contents were performed by atomic absorption spectrometry using SOLAAR M6 (Unicam) spectrophotometer.

Sampling at the Dzierzno Duze and the Pogoria III Reservoirs was performed in 2007 and 2008 using sediment core sampler. Samples were collected in the zone along the reservoir axis and also in bays and in maximum depth locations. Then, sediments were dried at 105°C and homogenized using an agate mill. Five heavy metals (Cd, Cr, Cu, Pb, Zn) were analyzed using the ICP method (total digestion inductively coupled plasma) after digestion with $HClO_4$-HNO_3-HCl-HF at 200°C to fuming and diluted with *aqua regia* [22]. Content of Cr was determined using INAA method (instrumental neutron activation analysis).

2.2. Statistical analysis

General statistical analyses in this study were produced using Excel v. 2010. To explore the similarities and differences among metal content in sediments of investigated reservoirs principal components analysis (PCA) was performed using Statgraphics XV. Based on the PCA results, cluster analysis was performed (nearest neighbor method, squared Euclidean) to further quantify metal distribution patterns.

2.3. Classification criteria of heavy metals in sediments

Usually, as the first step of heavy metal assessment, the comparison with geological background is proposed. In environmental sciences geochemical background means "a relative measure to distinguish between natural element or compound concentrations and anthropologically-influenced concentrations in real sample collectives" [23], and different values are offered in literature [24, 25]. For Polish soils values given by Kabata-Pendias [26] are most commonly used (Cd 0.05÷÷0.35 mg/kg, Cr 5÷120 mg/kg, Cu 2÷60 mg/kg, Pb 3÷40 mg/kg, Zn 10÷120 mg/kg). Assessment of anthropogenic influences in environmental samples is usually performed with used of various geochemical criteria. One of the most commonly used is geo-accumulation index (I_{geo}) (Eq. (1)), in which the element concentration and the reference element in the sample are compared to geochemical background [27], with the scale consisting of 7 classes of the sample pollution, varying from 0 (unpolluted) to 6 (extremely polluted) [27].

$$I_{geo} = \log_2 C_n/1.5 \cdot B_n \tag{1}$$

where:
C_n - metal content in sediment sample,
B_n - the geochemical background value in sedimentary rocks - shales (Cd 0.3 mg/kg, Cr 90 mg/kg, Cu 45 mg/kg, Pb 20 mg/kg, Zn 95 mg/kg) [24].

Another method, which can be used to classify the quality of environmental samples, is contamination factor (CF) (Eq. (2)), where a mean concentration of a given element in samples is divided by pre-industrial concentration of the element [25]. CFs values below 1 indicate low contamination, those in the range of 1÷3 moderate contamination, 3÷6 considerable contamination, and > 6 very high contamination.

$$CF = C_{metal}/B_n \tag{2}$$

where:
C_{metal} - content of element in samples,
B_n - pre-industrial content of element (Cd 0.2 mg/kg, Cr 71 mg/kg, Cu 32 mg/kg, Pb 16 mg/kg, Zn 127 mg/kg) [28].

Furthermore, the extent of metals pollution can be assessed by employing the method on pollution load index (PLI) (Eq. (3)) for a site quality calculated as the following equation:

$$PLI = (CF1 \cdot CF2 \cdot CF3 \cdot CFn)^{1/n} \qquad (3)$$

where:
n - numbers of metals,
CF - contamination factor of each metal (as mentioned above).
The PLI < 1 indicates perfection, PLI = 1 denotes that only baseline levels of pollutants are present, while PLI > 1 would show deterioration quality [29].

To include ecotoxicological aspect in the sediment assessment, the ecotoxicological criteria have been used in this study, based on the two threshold values: TEC (below which harmful effects were unlikely to be observed) and PEC (above which harmful effects were likely to be observed). Additionally, when the heavy metal content is below the TEC then no toxic effects were expected, and sediment contamination can be tolerated by the majority of benthic organisms. Above the PEC level contaminants were assumed to have a detrimental impact to the majority of the benthic community. However, between the TEC and PEC sediments were neither predicted to be toxic nor nontoxic (Table 2) [30, 31].

Table 2. **Sediment quality objectives (TEC/PEC values)**
Tabela 2. **Kryterium ekotoksykologiczne (wartości TEC/PEC)**

Heavy metal	TEC/PEC, mg/kg
Cu	31.6/149
Cd	0.99/4.98
Pb	35.8/128
Cr	43.4/111
Zn	121/459

3. Results and discussion

Study revealed a considerable variation in metal composition of bottom sediments in the Cracow area (Table 3), with the values from close, or below to the detection limit, up to the highly elevated contents, well above geochemical background levels [26]. Among the measured metals in the Cracow area, Cd was the one with the most frequently exceeded geochemical background value while Cr, Cu and Zn contents did not exceeded background levels [26]. Among the remaining determined metals, the background level was exceeded only in the Tyniec Reservoir for Pb. Since, this reservoir is located near the ring road, road salting and the fuel spills are the major reasons of this sediment pollution. Comparison of metal contamination in the Cracow area with other recreational reservoirs in Poland displayed that sediments of other urban catchment reservoirs (Rusalka, Sloneczne) were more contaminated than sediments in the Cracow area, with the background levels exceeded for Cd and Pb, and also for Zn in the Rusalka Reservoir. It should be mentioned that contamination level in agricultural catchment (Jeziorsko and Barycz) was relatively low comparing to the other discussed water bodies, and no exceedances of geochemical background values were observed. Sediments of the industrial catchment reservoirs, represented by the Dzierzno Duze and the Pogoria III Reservoirs, were the most contaminated among the discussed ones. Cd, Pb and Zn contents exceeded geochemical background levels in these reservoirs; also Cu contents exceeded this level, however only in the Dzierzno Duze Reservoir. The data revealed that Cd, Cu, Pb contents were significantly higher compared to the reservoirs from the urban and agricultural catchment (Jeziorsko and Barycz). The values given in Table 3 showed that Cu and Pb contents were almost 50 times and Cd over 80 times higher than the values for agricultural catchment. Industrial catchment reservoirs were under a variety of anthropogenic impacts for several years so that the high content of heavy metals suggests human inputs [6, 15, 32]. Silesian upland belongs to the most transformed areas by human impact due to the complex changes in the natural environment, caused by industry concentration (especially mining) and population growth. Such changes usually alter water environment and cause water quality degradation [3]. The Dzierzno Duze Reservoir is situated in a highly industrial kind of land in the western part of Silesia surrounded by main roads and trees. This reservoir is mainly supplied by highly contaminated waters of the Klodnica River. However, in the nearest neighborhood of the Pogoria III Reservoir there are roads, forests and housing estates [6, 11, 12]. It should be also noted that high levels of metal contamination can pose additional threat due to the increasing acidification of environment, which is related to the increased mobility of heavy metals accumulated in bottom sediments [29].

Table 3. **Heavy metals content (mg/kg) in sediments from water reservoirs**
Tabela 3. **Zawartość metali ciężkich (mg/kg) w osadach dennych zbiorników**

Heavy metal	Urban										Agricultural		Industrial	
	Bagry	**Nowohucki**	**Plaszowski**	**Dabski**	**Przylasek R**	**Tyniec**	**Zakrzowek**	**Zeslawice**	Rusalka	Sloneczne	Jeziorsko	Barycz	Dzierzno Duze	Pogoria III
Cd	**	0.01	0.23	0.60	0.57	7.99	1.73	0.40	1.05	30.0	0.34	0.12	9.80	0.90
Cr	1.63	0.97	2.37	1.30	9.83	21.48	2.93	6.86	–	–	–	–	119.3	103.9
Cu	18.18	1.26	2.73	1.43	5.47	17.22	2.29	2.99	57.6	5.5	7.31	2.23	93.7	19.40
Pb	3.73	2.27	8.69	4.90	19.13	53.12	24.33	13.65	96.2	195	9.13	2.85	133.7	49.80
Zn	23.11	5.19	18.83	33.47	59.55	31.34	18.39	44.42	359.1	27.0	–	–	801.7	181.3

Explanation:
Bolded: reservoirs in the Cracow urban area
–: no data available
**: contents below detection limit

Performed cluster analysis (CA) for reservoirs in the Cracow area showed similarities among the investigated reservoirs, and enabled separation into groups with comparable metal composition of sediments. As CA (and following PCA) requires a complete matrix with no missing data, the detection limit was used to replace a non-detected cadmium content for the Bagry Reservoir.

The arrangement of the dendrogram (Fig. 2) identified the group of five reservoirs with the comparable distance including: Nowohucki, Plaszowski, Przylasek R., Zeslawice and Dabski Reservoirs. The catchments of particular reservoirs are different and vary due to their location. The Dabski Reservoir is located near the street connecting the city center with the other districts. Also, the Zeslawice Reservoir is located near the busy street. The Nowohucki Reservoir with the surrounding park is close to the green protective zone and the housing estates, same as the Plaszowski Reservoir. The Przylasek Rusiecki is situated in the vicinity of the old village of Wolica and Ruszcza in oxbow of the Vistula River [9]. However, among this group, two clusters of reservoirs should be distinguished. The first pair is characterized by sediments (Nowohucki and Plaszowski) with relatively low contamination, especially in case of the Nowohucki Reservoir, which is separated from the direct anthropogenic influence. The second cluster consists of two reservoirs (Przylasek R. and Zeslawice) localized in the vicinity of the metallurgical plant in Cracow and their sediments contain elevated contents of almost all metals.

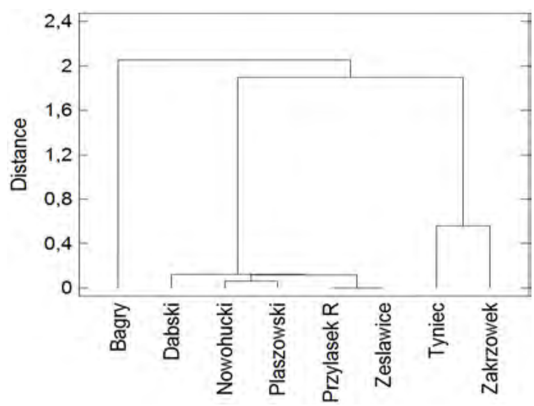

Fig. 2. Dendrogram of sediments investigation results for selected water reservoirs in the Cracow area

Rys. 2. Dendrogram wyników badań osadów dennych wybranych zbiorników krakowskich

According to the dendrogram, the cluster of two reservoirs (Tyniec and Zakrzowek) and one outlier (Bagry) were completely separate from the others. This separation has been also supported by the principal component analysis (PCA) results (Table 4). PCA revealed two components accounting for 77 and 18% of the total variance of the model. According to the PCA model the Tyniec and Zakrzowek reservoirs are strongly loaded onto axis PC2 (component loading > 0.5), while for the Bagry Reservoir the lowest component loading on this axis was noted. Sediments of the Tyniec Reservoir are the most contaminated among the local recreational water bodies, and its localization close to the Cracow ring road has undoubtedly the greatest impact on its status. However, the level of metal contamination especially for Pb and Zn is definitely lower than for other urban reservoirs (Rusalka and Sloneczne) in the Szczecin area. Higher metal contents, especially of lead, zinc, and copper for these reservoirs can be attributed to the contamination of the feeding water courses, flowing through the urban area. The difference in metal levels between Rusalka and Sloneczne depends on their location e.g. in the Rusalka Reservoir is much more zinc because the watercourse Osowka which supplies the reservoir is chemically and bacterial contaminated, while watercourse Bukowa flows through the western part of Szczecin contributed to the creation of the Sloneczne Reservoir. The Rusalka Reservoir is located close to parks and garden area. The Sloneczne Reservoir is surrounded by the housing estates [5]. However, it should be noted, that sediments of both reservoirs were acceptably contaminated compared to reservoirs located in industrial and agricultural catchments.

Table 4. **Principal component loadings (PCA) of individual water reservoir from the Cracow area**

Tabela 4. **Obciążenie składowych głównych (PCA) dla zbiorników krakowskich**

Reservoir	PC1	PC2
	77%	18%
Bagry	0.280408	–0.440966
Dabski	0.379802	–0.229992
Nowohucki	0.400370	–0.055940
Plaszowski	0.401514	0.002503
Przylasek R	0.394447	–0.103202
Tyniec	0.227842	0.667983
Zakrzowek	0.305848	0.530644
Zeslawice	0.393153	–0.105276

According to geo-accumulation index sediments from the Cracow area were Cr, Cu, Zn uncontaminated (0 class), and variably contaminated with Cd and Pb (1-5 class). The Cd *geo-accumulation index* value in sediments of the Nowohucki, the Plaszowski and the Zeslawice Reservoirs was less than 0, which means that according to this method sediments were Cd uncontaminated, while in the Tyniec Reservoir sediments were heavily to extremely contaminated (5 class). Also in the Tyniec Reservoir sediments were Pb uncontaminated to moderately contaminated (1 class). Other reservoirs in urban catchment areas (Rusalka, Sloneczne) were contaminated in a similar way to the Cracow area reservoirs. They were Cd extremely contaminated (6 class) (Sloneczne), Cu uncontaminated (0 class), Pb and Zn moderately to heavily contaminated (2-3 class). However, sediments from agricultural areas were uncontaminated (0 class). On the other hand, sediments from industrial areas were Cd heavily to extremely contaminated (5 class), Cr uncontaminated (0 class), Pb and Zn moderately to heavy contaminated (3 class) (Dzierzno Duze). The Pogoria III Reservoir (industrial area) showed less pollution than in the Dzierzno Duze Reservoir (Table 5).

Table 5. **Geo-accumulation index in sediments from water reservoirs**
Tabela 5. **Indeks geoakumulacyjny w osadach dennych zbiorników**

Heavy metal	Urban										Agricultural		Industrial	
	Bagry	**Nowohucki**	**Plaszowski**	**Dabski**	**Przylasek R**	**Tyniec**	**Zakrzowek**	**Zeslawice**	Rusalka	Sloneczne	Jeziorsko	Barycz	Dzierzno Duze	Pogoria III
Cu	0	0	0	0	0	0	0	0	0	0	0	0	1	0
Cd	**	0	0	1	1	5	2	0	2	6	0	0	5	1
Pb	0	0	0	0	0	1	0	0	2	3	0	0	3	1
Cr	0	0	0	0	0	0	0	0	–	–	–	–	0	0
Zn	0	0	0	0	0	0	0	0	2	0	–	–	3	1

In the Cracow area contamination factor values varied from low to high contamination. On this basis, only the Bagry and the Nowohucki Reservoirs had low contamination (CF < 1). The Tyniec and the Zakrzowek Reservoirs had the highest values of Cd (CF > 6 very high contamination). The same situation was found in other urban catchment reservoir (Sloneczne). Moreover, the Rusalka and the Sloneczne Reservoirs had very high contamination of Pb (CF > 6). It should be noticed that according to I_{geo} index the values of Cd displayed similarities between Cracow area reservoir (Tyniec) and urban catchment reservoir (Sloneczne) and showed extreme contamination. In agricultural areas mostly C_f values were low, but moderate value of Cd was found in the Jeziorsko Reservoir. However, due to I_{geo} index sediments in these areas were uncontaminated. Situation was slightly different in industrial areas. Contamination factor values varied from low to high contamination. The Dzierzno Duze Reservoir had the highest values of Cd, Pb and Zn (CF > 6) due to an extensive use of these heavy metals in different types of metallurgy, paper or leather industry (Table 6). Also according to I_{geo} index sediments in the Dzierzno Duze Reservoir were Cd, Pb and Zn contaminated.

According to the pollution load index the lowest index values were noted for Nowohucki Reservoir (the Cracow area) and the Barycz Reservoir (agricultural area), which means that sediments were uncontaminated (< 1 perfection). Also, according to I_{geo} index sediments from the Nowohucki and the Barycz Reservoirs were uncontaminated, and CF had low contamination values. The highest PLI index (> 1 deterioration quality) was in the rest of studied reservoirs.

Table 6. **Contamination factor in sediments from water reservoirs**
Tabela 6. **Współczynnik zanieczyszczenia w osadach dennych zbiorników**

Heavy metal	Urban										Agricultural		Industrial	
	Bagry	**Nowohucki**	**Plaszowski**	**Dabski**	**Przylasek R**	**Tyniec**	**Zakrzowek**	**Zeslawice**	Rusalka	Sloneczne	Jeziorsko	Barycz	Dzierzno Duze	Pogoria III
Cu	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	1-3	< 1	< 1	< 1	1-3	< 1
Cd	**	< 1	1-3	1-3	1-3	> 6	> 6	1-3	3-6	> 6	1-3	< 1	> 6	3-6
Pb	< 1	< 1	< 1	< 1	1-3	3-6	1-3	< 1	> 6	> 6	< 1	< 1	> 6	3-6
Cr	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	–	–	–	–	1-3	1-3
Zn	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	1-3	< 1	–	–	> 6	1-3

PEC values were exceeded in Cracow area (Tyniec) for Cd, also in urban area (Sloneczne) for Cd and Pb, and in industrial area (Dzierzno Duze) for Cd, Cr and Zn which point out the possible harmful effects on benthic organisms. In other cases, investigated heavy metals were mostly between the TEC and PEC values, which indicate moderate contamination of the sediments and moderate impact on biota [30]. The quality of sediment environment has a direct impact on the bioavailability of metals deposited in bottom sediments [33], which can be re-activated due to changes in pH, dissolved oxygen and redox potential [34] (e.g. the most mobile and easiest soluble is Cd at value pH 6.5, whereas with the higher acidification other metals can be activated - Zn and Cu), or bioaccumulated (e.g. Cr as insoluble oxides) [26]. Also, sediments exposition for atmospheric conditions, as well as the decomposition of organic matter with the involvement of microorganisms can cause the metals release from sediments that originally occurred under deoxidized or anaerobic conditions [35]. Since, additionally metal mobility is controlled by complexing factors such as dissolved organic substances and inorganic anions [36] threat for biota should be studied carefully in each of the presented reservoirs.

Conclusions

Different catchment areas can greatly modify contamination in the water reservoirs. Heavy metal content in bottom sediments of recreational reservoirs in the Cracow area, and also other parts of Poland reflects the nature of their catchment area. Higher contents are recorded in industrial areas than in agricultural due to their association with runoff from residential, commercial and industrial land uses as well as from road runoff. Obtained results in reference to catchments, rivers and reservoir characteristics showed that the biggest reservoir (Dzierzno Duze) situated in a highly industrial catchment, had the highest potential for heavy metal accumulation. On the other hand, the largest agricultural catchment

(Jeziorsko) had low content of heavy metal contamination, whereas the lowest was reported in the Barycz Reservoir (agricultural catchment). According to I_{geo} index and CF values sediments form the Cracow area reservoirs were mostly contaminated with Cd. However, Cd contents were relatively high in other urban area (Sloneczne) and industrial area (Dzierzno Duze), while agricultural areas were Cd uncontaminated. The same situation was found in PEC values exceedances. In other cases, investigated heavy metals were mostly between the TEC and PEC values, which indicate moderate contamination of the sediments and moderate impact on biota. Moreover, the lowest pollution load index was found in the Nowohucki Reservoir (the Cracow area) and the Barycz Reservoir (agricultural area). In spite of heavy metal contamination in sediments, all water bodies are used for recreational purposes throughout the year, especially the Cracow area reservoirs which were assessed for water quality [10]. However, further research and monitoring of sediments quality should be maintained in future seasons due to possible release of metals into water, which can pose a threat for local biota.

References

[1] Ignatieva M., Stewart G.H., Meurk C., Planning and design of ecological networks in urban areas, Landscape Ecological Engineering 2011, 7, 17-25.

[2] Loska K., Wiechuła D., Cebula J., Changes in the forms of metal occurrence in bottom sediment under conditions of artificial hypolimnetic aeration of Rybnik Reservoir, Southern Poland, Polish Journal of Environmental Studies 2000, 9, 6, 523-530.

[3] Urbaniak M., Zieliński M., Wesołowski W., Zalewski M., PCB and heavy metal contamination in bottom sediments from three reservoirs of different catchment characteristics, Polish Journal of Environmental Studies 2008, 17, 6, 941-949.

[4] Förstner U., Wittmann G.T.W., Metal Pollution in the Aquatic Environment, Springer-Verlag, Berlin, Heidelberg, New York, Tokyo 1983.

[5] Niedźwiecki E., Wojcieszczuk T., Poleszczuk G., Meller E., Malinowski R., Sammel A., Chemical composition of bottom sediments in water reservoirs „Rusałka" and „Słoneczne" located within the area of Szczecin municipality and the possibilities of their utilization, Zeszyty Problemowe Postępów Nauk Rolniczych 2007, 520, 353-362 (in Polish).

[6] Rzetala M., Rahmonov O., Malik I., Oleś W., Pytel S., Study on use of artificial water reservoirs in Silesian upland (southern Poland) as element of cultural landscape, Ekológia (Bratislava) 2006, 25, 1, 212-220.

[7] Rzymski P., Klimaszyk P., Niedzielski P., Poniedziałek B., Metal accumulation in sediments and biota in Malta Reservoir (Poland), Limnological Review 2013, 13, 3, 163-169.

[8] Rutkowski J., Vistula River Valley in the Cracow Gate during the Holocene, In: Evolution of the Vistula River Valley durig the last 15 000 years, part II, Geographical Studies, Poland, 1987, 31-50.

[9] Ciszewski D., Posiask-Karteczka J., Żelazny M., Heavy metals in bottom sediments of artificial water reservoirs in the Cracow area, Polish Journal of Environmental Studies 1998, 7, 2, 1-73.

[10] Zemelka G., Water quality in recreational reservoirs in the Cracow area, Technical Transactions Environment Engineering 2015, 18, 1-Ś, 157-165.

[11] Kostecki M., Allocation and transformations of selected pollutants in dam reservoirs of the hydro-junction of the Kłodnica and Gliwice canal, IPIŚ-PAN 2003, 57, 124 (in Polish).

[12] Kostecki M., Smyłła A., Starczewska A., Sanitary assessment of water reservoir Dzierżno Duże, Archiwum Ochrony Środowiska 2000, 26, 4, 57-73 (in Polish).

[13] Pietrzyk-Sokulska E., Water reservoirs in post-mining quarries - new component of city's landscape attractiveness, Prace Komisji Krajobrazu Kulturowego Nr 14, Komisja Krajobrazu Kulturowego PTG 2010, 264-272 (in Polish).

[14] Dzieszyński R., Franczyk J., The Encyclopedia of the Nowa Huta area, Encyklopedia Nowej Huty, Towarzystwo Słowaków w Polsce, Kraków 2006 (in Polish).

[15] Pociask-Karteczka J., Changes of water relations in the Krakow area, Zeszyty Naukowe Uniwersytetu Jagiellońskiego MCXLIV, Prace Geograficzne 1994, 96, 1-38 (in Polish).

[16] Michalec B., Pęczek K., Determination of silting degree of water reservoirs at Zesławice, Scientific Review Engineering and Environmental Sciences 2008, 2, 40, 178-184 (in Polish).

[17] ISO 1995. Soil quality - Extraction of trace elements soluble in aqua regia, International Organization for Standarization, Geneva.

[18] ISO 1988. Soil quality - Determination of cadmium, chromium, cobalt, copper, lead, manganese, nickel and zinc - Flame and electrothermal atomic absorption spectrometric methods, International Organization for Standarization, Geneva.

[19] Miśkowiec P., Łaptaś A., Zięba K., Soil pollution with heavy metals in industrial and agricultural areas: a case study of Olkusz District, Journal of Elementology 2015, 20, 2, 353-362.

[20] Zemelka G., Water reservoirs in the Cracow area - are they suitable for recreation? I Kongres Młodych Ludzi Nauki - wizja, nauka, postęp - publikacje pokonferencyjne, Kraków 22.06.2015, 120-124.

[21] Zemelka G., Heavy metal contamination in sediments from different recreational reservoir catchments in Poland, 16th International Multidisciplinary Scientific Geoconference & Expo SGEM 2016, Conference Proceedings, Water Resources, Forest, Marine and Ocean Ecosystems, Hydrology & Water Resources 2016, 1, 375-381.

[22] Rzętała M., Jaguś A., Rzętała M.A., Rahmonov O., Rahmonov M., Khak V., Variations in the chemical composition of bottom deposits in anthropogenic lakes, Polish Journal of Environmental Studies 2013, 22, 6, 1799-1805.

[23] Matschullat J., Ottenstein R., Reimann C., Geochemical background - can we calculate it? Environmental Geology 2000, 39, 990-1000.

[24] Turekian K., Wedepohl K., Distribution of the elements in some major units of the Earth's crust, Geological Society of America, Bulletin 1961, 72, 175-192.

[25] Martin J., Meybeck M., Elemental mass-balance of material carried by major world rivers, Marine Chemistry 1979, 3, 7, 173-206.

[26] Kabata-Pendias A., Pendias H., Biogeochemistry of Traces Elements, WN PWN, Warszawa 1993 (in Polish).

[27] Muller G., The heavy metal pollution of the sediments of Neckars and its tributary, A Stock taking Chemische Zeit 1981, 150, 157-164.

[28] Hakanson L., An ecological risk index for aquatic pollution control. A Sedimentological approach, Water Research 1980, 14, 975-1001.

[29] Tomilson D., Wilson J., Harris C., Jeffrey D., Problems in assessment of heavy metals in estuaries and the formation of pollution index, Helgol Meeresunlters 1980, 33, 566-575.

[30] Persaud D., Jaagumagi R., Hayton A., Guidelines for the protection and management of aquatic sediment quality in Ontario, Water Resources Branch, Ontario Ministry of the Environment, Toronto, Ontario 1992.

[31] Zemelka G., Contamination and environmental risk assessment of heavy metals in the sediments of the Dobczyce Reservoir and its tributaries, Geomatics and Environmental Engineering (in review) 2017.

[32] Owen B.R., Sandhu N., Heavy metal accumulation and anthropogenic impacts on Tolo Harbour, Hong Kong, Marine Pollution Bulletin 2000, 40, 2, 174-180.

[33] Lu X., Werner I., Young T., Geochemistry and bioavailability of metals in sediments from northern San Francisco Bay, Environment International 2005, 31, 593-602.

[34] Czaplicka-Kotas A., Ślusarczyk Z., Zagajska J., Szostak A., Analiza zmian zawartości jonów wybranych metali ciężkich w wodzie Jeziora Goczałkowickiego w latach 1994-2007, Ochrona Środowiska 2010, 32, 4, 51-56.

[35] Zoumis T., Schmidt A., Grigorova L., Calmano W., Contaminants in sediments: Remobilisation and demobilization, Science of The Total Environment 2001, 266, 1-3, 195-202.

[36] Wojtkowska M., Content of selected heavy metals in water and riverbed sediments of the Utrata river, Environment Protection Engineering 2011, 37, 3, 55-62.

Streszczenie

Zbiorniki wodne pełnią ważną rolę w środowisku człowieka, zwłaszcza na obszarach miejskich, gdzie nie tylko dobrze wyglądają, ale również zapewniają korzyści zdrowotne oraz pełnią funkcję zbiorników lub ostoi dla różnorodności biologicznej. Ze względu na ich usytuowanie na obszarach miejskich zbiorniki te narażone są na działania antropogeniczne z różnych działań, które wprowadzają zanieczyszczenia (np. metale ciężkie). Głównym celem badań było oszacowanie poziomu zanieczyszczenia metali ciężkich (Cd, Cr, Cu, Pb, Zn) w osadach dennych ośmiu zbiorników zlokalizowanych na terenie Krakowa (Bagry, Nowohucki, Płaszowski, Dąbski, Przylasek Rusiecki, Tyniec, Zakrzówek, Zesławice) oraz oszacowanie potencjalnego zagrożenia dla środowiska przy zastosowaniu różnych kryteriów (I_{geo} - indeks geoakumulacyjny, CF - współczynnik zanieczyszczenia, PLI - wskaźnik ładunku zanieczyszczenia, TEC/PEC - wartość progowa/wartość prawdopodobna). Ponadto wzięto pod uwagę charakter zlewni badanych zbiorników (rolniczy, przemysłowy i zurbanizowany) w zanieczyszczeniu osadów dennych oraz porównano poziomy zanieczyszczenia metali ciężkich z innymi zbiornikami rekreacyjnymi w Polsce (Jeziorsko, Barycz, Dzierżno Duże, Pogoria III, Rusałka i Słoneczne). Badania wykazały znaczne różnice w składzie chemicznym osadów dennych, co zdecydowanie zależało od lokalizacji zbiorników. Osady denne w zbiornikach na terenie Krakowa i w zlewni zurbanizowanej były umiarkowanie zanieczyszczone. Zbiorniki ze zlewni przemysłowych miały znacznie wyższą zawartość metali ciężkich, podczas gdy zbiorniki zlokalizowane na obszarach rolnych charakteryzowały się niskimi zawartościami. Zgodnie z indeksem I_{geo} i CF, osady denne zbiorników wodnych w Krakowie były głównie zanieczyszczone kadmem. Stosunkowo wysokie stężenia tego metalu zaobserwowano również na obszarach miejskich (Słoneczne) oraz przemysłowych (Dzierzno Duże). Podobną sytuację stwierdzono przy przekroczeniach wartości wskaźnika PEC. Jednakże w przypadku większości zbiorników poziomy metali ciężkich w osadach dennych znajdowały się pomiędzy wartościami TEC i PEC, co sugeruje umiarkowane zanieczyszczenie. W związku z tym należy prowadzić dalsze badania oraz stale monitorować jakość osadów dennych zbiorników, zwłaszcza że są one wykorzystywane w celach rekreacyjnych przez cały rok.

Słowa kluczowe: **metale ciężkie, zbiorniki rekreacyjne, Kraków, miejskie zlewnie**