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CHANGEABILITY OF HEAVY METALS CONTENT IN THE SEDIMENT OF THE WATER RESERVOIR IN THE 1996–2005 YEARS

ZMIENNOŚĆ ZAWARTOŚCI METALI CIĘŻKICH W OSADACH DENNYCH ZBIORNIKA WODNEGO W LATACH 1996–2005

Abstract: The presented study was aimed to analyze the variability of the selected heavy metal content in bottom sediments from a dam reservoir in Krempna, located in the upper part of the river Wisloka, in the Subcarpathian Voivodeship. The concentrations of the analyzed heavy metals in the examined sediments were variable. The copper content ranged from 8.4–49.16 mg $\cdot$ kg^{-1}, zinc 28–98 mg $\cdot$ kg^{-1}, chromium 8.7–70 mg $\cdot$ kg^{-1}, nickel 20.53–74.5 mg $\cdot$ kg^{-1}, lead 7.7–64.3 mg $\cdot$ kg^{-1} and cadmium 0.1–0.6 mg $\cdot$ kg^{-1}. The heavy metal concentrations in the bottom sediments of the Krempna reservoir were referred to the limit values that inform whether the material is contaminated. The contents of heavy metals did not exceed the limit content. The analyzed material was characterized by elevated concentrations of copper, chromium, nickel and lead, far beyond the geochemical background of the Polish sediments given by the Polish Geological Institute. Particularly high concentrations of nickel qualify the sediment as the class III, ie as contaminated. In the analyzed study period of 1996–2005 the bottom sediments showed no clear tendency to excessive accumulation of the examined elements. Heavy metal concentrations fluctuated in different years of the sediment collection, however there was no clear decreasing or increasing trend.

Keywords: bottom sediments, heavy metals, dam reservoir

Heavy metals, due to their specific characteristics, are a potential threat to all living organisms. They can occur in different forms in aquatic environment: as water-soluble compounds or associated with the particles of the solid phase (mineral suspension of bottom sediments) [1]. Soluble forms of metals are precipitated as a result of oxidation processes, creation of different chemical compounds and sorption by organic and

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mineral fraction of sediments. At present, the chemical composition of sediments is significantly affected by the intensity of agricultural use of catchments, by elution of residues of fertilizers and plant protection products from fields and meadows, transportation, dust emissions and sewage discharge, which leads to the increase in the heavy metal concentration in sediments [2–5]. Despite the temporary immobilization of metals in sediments, they are a potential threat to the aquatic environment.

Geochemical composition of sediments accumulated on the bottom of rivers and reservoirs is a good indicator of surface water purity [6, 7]. Observation of changes in sediments allows to determine the changes occurring in watercourses.

Properties of sediments from running waters are different than those from stagnant water sediments. Sediments from artificial reservoirs, which are intermediate between rivers and lakes, are characterized by yet other qualities. Dam reservoirs are strongly influenced by the catchment's morphology, hydrological conditions, chemical composition of water, as well as by flora and fauna of the supplying streams [8]. Hydrological conditions, especially changes in water flow velocity in the dammed river section affect the diversity of heavy metal content in the reservoir's sediments [9]. High water levels in rivers and streams flowing directly into reservoirs cause significant leaching of chemicals, removing of soil material from catchments and introducing of nutrients. The deposition of heavy metal-contaminated slurry onto floodplain soils during floods or due to excavation of sediments during dredging of reservoirs constitutes a threat to the terrestrial environment [10].

Silting of reservoirs is one of the main limiting factors for their proper operation. Small objects are particularly exposed to rapid loss of capacity in favor of the fine-grained mineral material accumulated in the reservoir bowl [11, 12]. The analysis of the heavy metal concentration accumulated in bottom sediments allows to identify the source, speed and the route of distribution of elements in the reservoir and is the basis for determining the secondary water pollution . This is particularly important in the case of small reservoirs, due to the rapid rate of silting and the necessity of periodic dredging of these reservoirs [13].

This study was aimed to investigate the variability of the selected heavy metal concentration in bottom sediments from the dam reservoir in Krempna, located in the upper part of the river Wisloka.

Material and methods

Bottom sediments were collected 4 times in the period of 1996–2005 from the dam reservoir located in Krempna. Bottom sediment samples were collected within three zones of the reservoir: at the inlet, in the middle and at the outlet (near-dam zone). The sampling sites were located outside the flow riverbed and three samples from each zone were collected (Fig. 1). The material was sampled from under the water table using the Ekman's bottom sediment probe. In order to average the sampled material, 6 subsamples were collected, which then were mixed to form the final sample. The sediments were collected from the 0–15 cm layer.

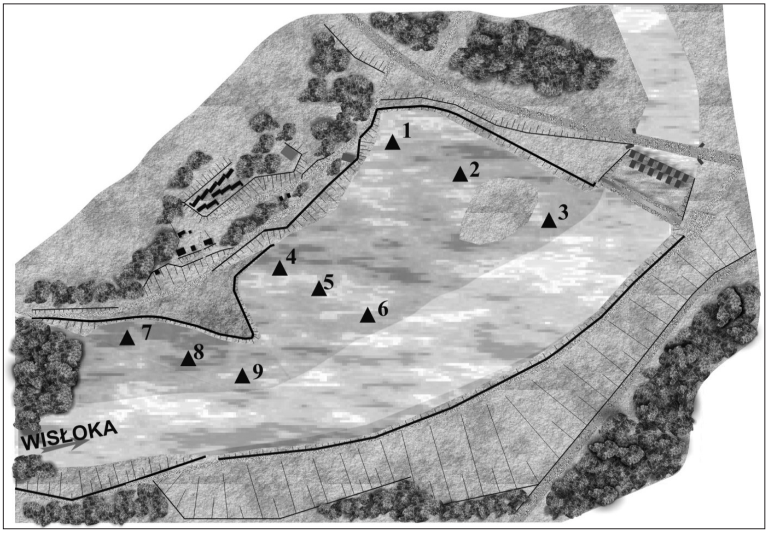

Fig. 1. The plan of the Krempna reservoir on the Wisloka river with marked bottom sediment sampling sites

The resulting material was dried and the concentration of chromium, nickel, copper, zinc, cadmium and lead was determined by AAS. The results were subjected to statistical analysis using a repeated measures ANOVA and HSD Tukey's test, using the R software for the calculations and drawing graphs [14].

The studied object is located in the Krempna locality, 35 km from Jaslo, on the river Wisloka, which is the second order tributary of the Vistula. The total length of the Wisloka is 163.6 km and the catchment area is 4110.2 km^2. To the Krempna locality, where the reservoir is located, the river is only 18.6 km long. The reservoir's dam closes the sub-catchment with an area of 165.3 km^2, located in the south-western part of the Subcarpathian Voivodeship.

The upper Wisloka catchment is located within the Magura Nappe, which is mostly composed of slate and sand flysch. The surface formations in this area are composed of residual and slope clays, formed by physical weathering of bedrock. These are medium deep soils, mostly acidic with low nutrient content. The catchment area is predominated by woodlands. The forest-occupied area accounts for about 80 % of the catchment, which is due to its mountainous nature. A significant part of forests is included in the Magura Nature Park. Meadows and pastures are often situated in gentle hills or less steep slopes (14 %). Difficult growing conditions and infertile soils limit the agriculturally used land to small areas of gentle slopes and locally wide bottoms of the river Wisloka. The total area of arable land represents only 4 %, the remaining *ca* 2 % of the catchment is occupied by roads and less crowded, mostly rural, housing [11].

The reservoir in Krempna, located in the upper part of the Wisloka river in km 145 + 023 of its course, was put into operation in 1972. The reservoir, which was constructed at the request of the Krempna Municipality, plays recreational functions and enables the operation of a small hydropower plant. A 145 m long earth dam, with a four-span concrete weir, acts as the damming element. Below the existing reservoir there will be a designed large Katy-Myscowa reservoir. The reservoir in Krempna will serve as the preliminary reservoir.

In the first period of operation, the flooding area was about 3.2 ha and the volume was 119.1 thousand m^3. In 1987–1988 and in 2005 renovation works were carried out, because of the significant silting of the reservoir. Bottom material was partially deposited in the reservoir bowl, forming a left-bank beach and was disposed of on local farms.

Results and discussion

The examined sediments were characterized by varying concentration of the analyzed heavy metals (Fig. 2). The concentration of copper over the study period ranged from 8.4 to 49.16 mg $\cdot$ kg^{-1}. The least variable concentrations of copper in all analyzed samples were recorded in 2002. The lowest content was recorded in 1996 in the section located at the inlet to the reservoir. Within ten years of the study, the concentration of zinc was 28–98 mg $\cdot$ kg^{-1}. The concentration of this metal was the highest in 2002, particularly in the sites located near the inlet and the mainstream. These values were about 40 % higher than those obtained in 1996. The smallest amounts of zinc were found in the sediment samples collected in the first year of the study. The content of chromium ranged from 8.7 to 70 mg $\cdot$ kg^{-1}. The smallest amounts of chromium, recorded in 1999, were over twice lower than the ones obtained in 2002 and 1996, and over 4-times lower than the values recorded in 2005. Accumulation of this metal increased at the outlet from the reservoir. The nickel content ranged from 20.53 to 74.5 mg $\cdot$ kg^{-1} over the whole study period. The highest concentrations were recorded in 2002 in all samples, while a significant decrease was observed in 2005. The concentrations of lead ranged from 7.7 mg $\cdot$ kg^{-1} to 64.3 mg $\cdot$ kg^{-1} over the study period. The highest value (about 60 mg $\cdot$ kg^{-1}) was observed in the first year of the study at the outlet from the reservoir. The remaining results were similar to each other. The cadmium concentrations ranged from 0.1 to 0.6 mg $\cdot$ kg^{-1}. The cadmium concentration was even over the 9-year period in the examined sediment samples at the outlet of the reservoir. The highest cadmium concentration was recorded in 2002 at the inlet – it was almost 2–4-times higher than in 1996.

The repeated measures ANOVA test was performed, in order to show statistically significant differences between the values detected in each year of the study for the selected heavy metals. The calculated test statistics (F) and probability values (p) (Fig. 2) indicate a rejection of the null hypothesis for all analyzed groups of elements (Cu, Zn, Ni, Cr, Pb, Cd) in favor of the alternative hypothesis and thus demonstrate the differences between the groups in different years. Moreover, a HSD Tukey's test was performed – a so-called post-hoc test, used when the analysis of variance (ANOVA) showed that the groups are significantly different. HSD is used to indicate the differing groups. The test involves the calculation of a "p" value for each pair of groups, which indicates the significantly different pairs, when it is lower than 0.05 (Table 1).

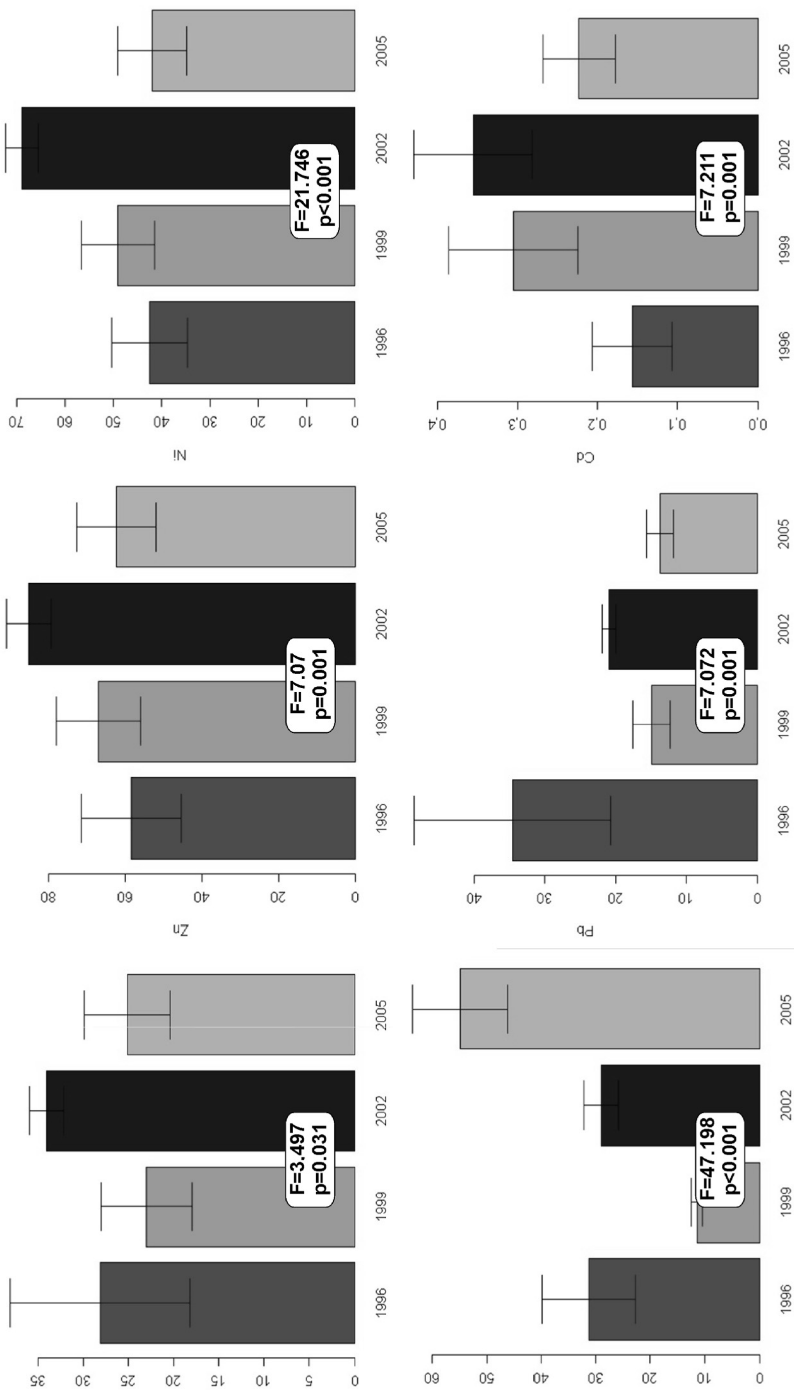

Fig. 2. Mean values and the values of the confidence interval and ANOVA statistics for the examined heavy metals in each year of the study

Table 1

Summary of "p" values calculated using the HSD test for heavy metals analyzed in each year of the study

Year	1996	1999	2002	2005	1996	1999	2002	2005
	Cu				Zn			
1996	—	—	—	—	—	—	—	—
1999	0.487	—	—	—	0.531	—	—	—
2002	0.365	**0.013**	—	—	**< 0.001**	**0.02**	—	—
2005	0.84	0.935	0.067	—	0.928	0.882	**0.002**	—
	Cr				Ni			
1996	—	—	—	—	—	—	—	—
1999	**< 0.001**	—	—	—	0.32	—	—	—
2002	0.924	**< 0.001**	—	—	**< 0.001**	**< 0.001**	—	—
2005	**< 0.001**	**< 0.001**	**< 0.001**	—	0.999	0.257	**< 0.001**	—
	Pb				Cd			
1996	—	—	—	—	—	—	—	—
1999	**< 0.001**	—	—	—	**0.008**	—	—	—
2002	**0.037**	0.645	—	—	**< 0.001**	0.702	—	—
2005	**< 0.001**	0.995	0.489	—	0.475	0.286	**0.022**	—

The changes in heavy metal concentrations in the sediments were most significantly influenced by the pre-sampling period in 2002. In 2002, a statistically significant increase in the concentration of Cu, Zn and Ni was recorded in the sediments, as compared to other years of the study, but this increase occurred only once and the heavy metal contents decreased in subsequent years.

When analyzing the cadmium concentrations, the statistically significant differences were detected between the concentrations recorded in 1996 and 1999, and 2002, as well as the difference between 2002 and 2005. This indicates that the situation is quite dynamic. In 1999 and 2002 the concentration of cadmium in the sediment samples was significantly higher than in 1996, then it declined significantly in 2005, as compared to 2002.

There are statistically significant differences between 1996 and the other years of the study shown in the analysis of lead concentration. This indicates that in 1999 there was a statistically significant decrease in the concentration of lead in the sediment and the resulting situation was sustained, as from the beginning of that year there were no statistically significant differences recorded.

There was a high change rate concerning the variability of chromium concentration in the examined sediments of the Krempna reservoir. There is a non-significant difference only between 1996 years and 2002 years. This means that in 1999 a significant decrease in chromium concentration was recorded, but this decrease occurred only once, and in 2005 there was a significant increase in the chromium concentration in the sediments.

The variability of the analyzed content of trace elements in the bottom sediments is influenced by the nature of the reservoir and the watercourse on which it is located. The examined object is a small reservoir on a river with large and abrupt floods. The resulting marginal left-bank part of the reservoir reduces the flow velocity and causes intense sedimentation of saltations, particularly in the phase of descending high water waves.

The examined heavy metal content in the bottom sediments of the reservoir in Krempna was referred to the limit values that inform whether the material is contaminated [15]. The concentration of copper, zinc, chromium, lead and cadmium was much lower than the limit values provided by the Act, the nickel content was higher, particularly in 2002 (63.5–74.5 mg $\cdot$ kg^{-1} d.m.), nevertheless it still did not exceed the threshold value.

Polish Geological Institute introduced a qualitative classification of bottom sediments, determining the thresholds of accumulated pollutants that affect the life processes of aquatic organisms (class I – slightly polluted sediments, class II – moderately polluted sediments, class III – polluted sediments) [6]. Exceeding the limit given for at least one harmful compound defines the sediment's quality (Fig. 3).

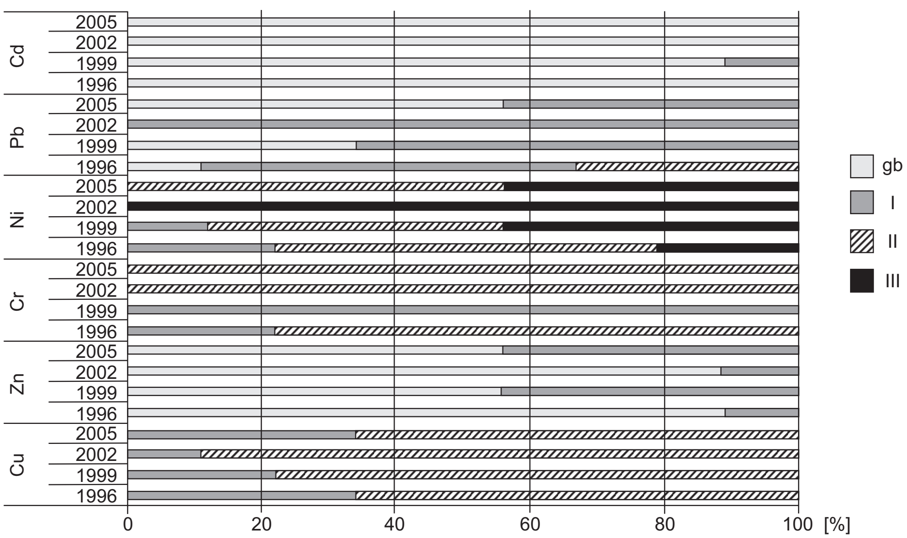

Fig. 3. Percentage contribution of the investigated sediments according to geochemical classification in particular years of the study; gb – geochemical background

The material collected in 1996 was moderately polluted in terms of copper, chromium and lead (class II), while in terms of the zinc concentration, the sediment was included into class I. In 1999 the bottom sediment contained lower concentrations of chromium and lead, therefore it was classified as moderately polluted. In 2002 the amounts of chromium increased to the level of the class II of pollution, while copper, zinc and lead remained at the same level. This trend was sustained in 2005. The concentration of nickel in the sediment collected over the period of 1996–2005 was very high, therefore it was evaluated as the class III. The cadmium content was low – of all collected samples only one was characterized by the exceeded geological background.

Conclusions

1. The examined bottom material showed no clear tendency to excessive accumulation of the analyzed elements during the period of 1996–2005. Metal concentrations fluctuated in different years, there were no clear decreasing or increasing trends, though.

2. The sediment from the examined reservoir was characterized by excessive content of copper, chromium, nickel and lead.

3. Due to the significant excess of nickel, the sediment was qualified as class III, ie as polluted.

4. Research on bottom sediments should be continued because of the potential risk to the running water, as this material is the best indicator of environmental risk. This will also allow to control the chemical composition of the material, which is disposed of by farmers on nearby agricultural lands.

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ZMIENNOŚĆ ZAWARTOŚCI METALI CIĘŻKICH W OSADACH DENNYCH WYBRANEGO ZBIORNIKA WODNEGO W LATACH 1996-2005

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Abstrakt: W pracy badano zmienność zawartości wybranych metali ciężkich w osadach dennych pochodzących ze zbiornika zaporowego w Krempnej, zlokalizowanego w górnym odcinku rzeki Wisłoki, w województwie podkarpackim. W latach 1996–2005 osad pobierano 4-krotnie. W uzyskanym materiale oznaczono zawartości chromu, niklu, miedzi, cynku, kadmu i ołowiu metodą ASA. Badane osady charakteryzowały się zmiennym stężeniem analizowanych metali ciężkich. Zawartość miedzi była w zakresie 8,4–49,16 mg · kg^{-1}, cynku 28–98 mg · kg^{-1}, chromu 8,7–70 mg · kg^{-1}, niklu 20,53–74,5 mg · kg^{-1}, ołowiu 7,7–64,3 mg · kg^{-1}, kadmu 0,1–0,6 mg · kg^{-1}. Stężenia badanych metali ciężkich w osadzie dennym zbiornika w Krempnej odniesiono do wartości dopuszczalnych, które powodują, że urobek jest zanieczyszczony. Zawartości metali ciężkich nie przekraczały zawartości dopuszczalnych.

Analizowany materiał wykazywał podwyższone stężenia miedzi, chromu, niklu i ołowiu, znacznie przekraczające tło geochemiczne osadów Polski wg PIG. Szczególnie wysokie stężenie niklu kwalifikują osad do III klasy jako zanieczyszczony. W analizowanym okresie badawczym 1996–2005 materiał denny nie wykazywał wyraźnych skłonności do nadmiernej kumulacji oznaczonych pierwiastków. Stężenia metali ciężkich ulegały wahaniom w poszczególnych latach badań, stwierdzono brak jednoznacznych trendów malejących czy rosnących.

Słowa kluczowe: osad denny, metale ciężkie, zbiornik zaporowy