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HEAVY METAL CONCENTRATIONS IN WATER AND BOTTOM SEDIMENTS OF SMALL WATER RESERVOIR IN KANIOW

KONCENTRACJA METALI CIĘŻKICH W WODZIE I OSADACH DENNYCH MAŁEGO ZBIORNIKA WODNEGO W KANIOWIE

Abstract: The paper presents the results of investigations on concentrations of ions of selected heavy metals (Fe, Cr, Zn, Ni, Mn, Cu, Pb, Cd, and Hg) in sediments and water in a small dammed reservoir located in Kaniow (the Swietokrzyskie Province, Poland) on the stream flowing from Borowa Gora (Borowa Mount). The sediments and water were collected from the upper, middle, and lower part of the reservoir. The samples were collected twice, first in July 2012, and then in March 2013. The content of trace elements in water did not exceed: 801 $\mu g \cdot dm^{-3}$ (Fe), 0.064 $\mu g \cdot dm^{-3}$ (Cr), 13.5 $\mu g \cdot dm^{-3}$ (Zn), 0.106 $\mu g \cdot dm^{-3}$ (Ni), 285 $\mu g \cdot dm^{-3}$ (Mn), 2.35 $\mu g \cdot dm^{-3}$ (Cu), 6.98 $\mu g \cdot dm^{-3}$ (Pb), and 3.35 $\mu g \cdot dm^{-3}$ (Cd). As regards bottom sediments, the maximum recorded concentrations of heavy metals were: 872 $mg \cdot kg^{-1}$ (Fe), 15.19 $mg \cdot kg^{-1}$ (Cr), 26.26 $mg \cdot kg^{-1}$ (Zn), 16.26 $mg \cdot kg^{-1}$ (Ni), 750 $mg \cdot kg^{-1}$ (Mn), 3.58 $mg \cdot kg^{-1}$ (Cu), 82.56 $mg \cdot kg^{-1}$ (Pb), 0.73 $mg \cdot kg^{-1}$ (Cd), and 0.0031 $mg \cdot kg^{-1}$ (Hg). An attempt to determine the mathematical relationship between the content of organic matter in sediments and heavy metals was made and the possibility of agricultural utilization of sediments after removal from the bottom was determined.

Keywords: heavy metals, bottom sediments, reservoir

Water reservoirs are the sites where intense deposition of suspensions transported by watercourses is observed. Sediments accumulated within the bowls of reservoirs contribute to the reduction of their capacity, and thus they limit the function those objects perform. Small water reservoirs are particularly affected by intensive silting [1, 2], as a result after a few years, or dozens of years of operation, they have to be

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subjected to dredging. Every time the reservoir is desilted, the bottom sediments need to be properly managed, which depends on their physical and chemical properties [3].

The chemical composition of bottom sediments results from many factors, both natural and anthropogenic ones. It primarily depends on the basin geological structure, the basin management and use, and also on climatic and hydrological conditions. Those are decisive for the pattern and intensity of the erosion processes in the basin, for the migration and accumulation of suspensions, and also of trace elements [4–7]. In non-industrialized basins, shallow deposits of minerals may provide a source of heavy metals, while in areas subjected to strong anthropogenic pressures, heavy metals originate in man's industrial and agricultural activities [8–10]. Uncontrolled discharges of domestic sewage and stormwater directly into rivers and reservoirs may become a major source of heavy metals. The investigations carried out by Bak et al., and also by Gorska and Sikorski [11, 12] indicate that stormwater from urban areas is strongly polluted with lead, zinc, nickel, chromium, cadmium, and copper compounds.

As a result of chemical and biochemical processes, noxiuos substances contained in bottom sediments can undergo desorption to water, which poses a great hazard to aquatic biota. At high flows, warp containing harmful substances can be deposited within the flood routes, and thus contaminate the areas adjacent to water [13, 14].

The study presents the characteristics of physical and chemical properties of bottom sediments and water from a small dammed reservoir located in Kaniow. The content of heavy metals was compared with the threshold values of permissible concentrations specified in the regulation of the Minister of the Environment, the guidelines developed by the Institute of Soil Science and Plant Cultivation (IUNG) and LAWA classification. The assessment of the content of heavy metals in the sediments will provide a basis to evaluate the possibility of agricultural use of sediments, and also the hazard they cause to the aquatic environment.

Material and methods

Facility description

Kaniow reservoir was put into operation in the 1980s. It was constructed by damming the watercourse flowing from the hill called Borowa Gora at km 0 + 920 with an earth dam, 80 m in length. It is a valley, flow-through reservoir, which serves recreational purposes. At the normal water level, the reservoir volume is 40.0 thousand m^3 and the water table area is 2.0 ha. The average depth of this water body is approx. 2.0 m. The basin area is equal to 7.37 km^2. The land use structure involves forests which dominate in the reservoir basin covering over 80 % of its area and forming spruce and fir, pine, and hornbeam and spruce dense complexes. Meadows constitute 8.1 %, arable land – 10.9 % and built-up area – 0.7 % of the area. Grain is the dominant crop, whereas root crops (mainly potatoes) have a lower share. In the reservoir basin, low-fertility soils of V and VI valuation class are mostly found. In the years 2001–2002, Kaniow reservoir was modernised. As a result of the construction works, the front dam of the reservoir was elevated and strengthened. The reservoir was also desilted.

Methodology of investigations

Samples of bottom sediments from Kaniow reservoir were collected twice, first in July 2012, and then in March 2013. Sampling was performed from the boat. Samples were collected into transparent cylinders, 57 mm in internal diameter and 1200 mm in length, using the Beeker-type sampler. It is equipped with a cutting head which allows closing the cylinder bottom, thus collecting the samples in undisturbed state. Water samples for analysis were collected, using the bathometer, at the middle of the water depth at the given site. Sites of bottom sediment and water sampling are shown in Fig. 1. The cylinders were transferred to the laboratory, then the warp was dried at the temperature of 60 ^{o}C. After that, it was ground in a mill to a fraction below 0.063 mm, and finally subjected to complete mineralisation. The total content of ions of selected heavy metals (Pb, Cr, Cd, Cu, Ni, Zn, Fe, and Mn) in sediment and water samples was determined. Depending on the level of concentrations and the matrix received, the determination was performed using the atomic absorption spectrometry method with SavantAA Sigma or SavantAA Zeeman spectrometers.

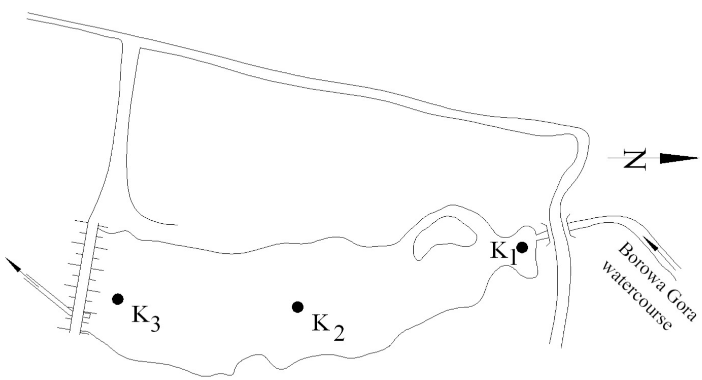

Fig. 1. Outline of Kaniow reservoir with water and bottom sediment sampling sites

The granulometric composition of sediments was determined with the sieve method and the areometric Casagrande's method modified by Pruszyński. 1.5 g of anhydrous sodium carbonate (Na_2CO_3), acting as deflocculant, were added to the solution in the form of sediment suspension. The analysis provided information on the percentage content of argillaceous ($d \leq 0.002$ mm), dust ($0.002 < d \geq 0.05$ mm), and sand ($0.05 < d \geq 2$ mm) fractions. The percentage content of organic matter was determined by sample annealing.

The quality assessment of bottom sediments in Kaniow reservoir was performed by comparing the content of heavy metals accumulated in the sediments with the values given in the binding Regulation of the Minister of Environment of 9 Sept. 2002 [J. of Laws No. 165, item 1359] [15] and the guidelines drawn up by the Institute of Soil Science and Plant Cultivation (IUNG) in Puławy [16]. Employing the guidelines developed by IUNG makes it possible to indicate the possibility of sediment use in agriculture, depending on the chemical composition and granulometric variation of sediments.

In order to assess the degree of contamination of the aquatic environment components, German LAWA classification was employed [17]. In this classification, seven purity classes were specified with reference to bottom sediment contamination with heavy metals. Permissible content of heavy metals for individual classes is shown in Table 1.

Table 1

Permissible content of heavy metals in sediments in accordance with LAWA classification

Metal	Purity class							Sediment classification
	I	I–II	II*	II–III	III	III–IV	IV	
Zinc	≤ 100	≤ 200	≤ 400	≤ 800	≤ 1600	≤ 3200	3200	I – non-contaminated
Lead	≤ 25	≤ 50	≤ 100	≤ 200	≤ 400	≤ 800	800	I–II – non-contaminated/ moderately contaminated
Copper	≤ 20	≤ 40	≤ 80	≤ 160	≤ 320	≤ 640	640	II – moderately contaminated
Nickel	≤ 30	≤ 60	≤ 120	≤ 240	≤ 480	≤ 960	960	II–III – moderately contaminated/ heavily contaminated
Chromium	≤ 80	≤ 160	≤ 320	≤ 640	≤ 1280	≤ 2560	2560	III – heavily contaminated
Cadmium	≤ 0.3	≤ 0.6	≤ 1.2	≤ 2.4	≤ 4.8	≤ 9.6	9.6	III–IV – heavily/very heavily contaminated
								IV – very heavily contaminated

* Recommended permissible value.

Results of investigations

On the basis of analyses of granulometric composition, it was found out that bottom sediments of Kaniow reservoir comprise finely grained deposits with a low content of organic matter that does not exceed 2 % (Table 2). In samples K_2 and K_3, grains 0.25–0.5 mm in diameter (medium sand) constituted 62 % and 53 %, respectively, of the whole sample mass. Dust and argillaceous fractions in both samples did not exceed 0.2 %. In sample K_1, collected at the upper part of the reservoir, grains of 0.05–0.25 mm range (fine sand, 58 % of the mass sample) and 0.002–0.05 mm range (dust fraction, 14 % of the mass sample) prevailed.

Analysis of heavy metal content in sediments showed that the highest variation in results, in all samples, was found for nickel and lead (Table 2). The content of those metals in the sediments did not exceed 16.26 $mgNi \cdot kg^{-1}$ and 82.56 $mgPb \cdot kg^{-1}$, additionally, the highest values both for nickel and lead, were observed at station K_2, and the lowest values – at station K_1 for nickel, and K_3 – for lead. A wide variation in results is also observed for chromium, zinc, copper and cadmium. The highest content of chromium was noted at K_2, and the lowest – in the samples collected in the upper part of the reservoir (station K_1). Zinc content in samples did not exceed 26.26 $mgZn \cdot kg^{-1}$. The maximum value of this element compounds was found at station K_3 in 2013. Copper content in the samples did not exceed 3.56 $mgCu \cdot kg^{-1}$, and cadmium 0.79 $mgCd \cdot kg^{-1}$. Additionally, in 2012, the maximum cadmium content was found at station K_1, and a year later – at K_3. The highest content of iron compounds was discovered in bottom sediments collected in the central part of the reservoir (866 $mgFe \cdot kg^{-1}$ – 2012, 881 $mgFe \cdot kg^{-1}$ – 2013), the lowest iron content was found in the samples from the lower part of the reservoir (762 $mgFe \cdot kg^{-1}$ – 2012, 734 $mgFe \cdot kg^{-1}$ – 2013). A similar situation was observed for manganese compounds. Mercury content ranged from 0.002 to 0.003 $mgHg \cdot kg^{-1}$.

Table 2

Content of heavy metal ions in bottom sediments

Station	Fe	Cr	Zn	Ni	Mn	Cu	Pb	Cd	Hg	Content of organic substances
	$[mg \cdot kg^{-1}]$									[%]
2012										
K_1	828	8.45	22.00	6.94	701	3.56	51.25	0.73	0.003	1.79
K_2	866	15.19	18.43	14.98	750	2.25	82.56	0.55	0.003	0.39
K_3	762	10.23	24.54	9.03	690	3.30	35.86	0.62	0.002	0.35
2013										
K_1	852	8.98	20.47	7.36	717	2.98	53.15	0.79	0.003	2.00
K_2	881	14.62	17.50	16.26	758	2.19	77.36	0.58	0.003	0.28
K_3	734	11.16	26.26	9.85	673	3.54	39.16	0.69	0.002	0.45

As regards water samples, such a great variation in the content of individual compounds of heavy metals was not observed, as it was the case for sediments. Chromium and lead ions were characterised by the highest variation. The highest content of these metals was found in water samples collected from sites denoted as K_1 for chromium (0.06 $\mu gCr \cdot m^{-3}$ – 2012 and 2013), and K_3 for lead (6.98 $\mu gPb \cdot m^{-3}$ – 2013). Iron, zinc, manganese and cadmium ions showed a similar range of variation. The highest values for iron and also zinc compounds were noted at station K_1 both in 2012 and 2013. The highest concentrations of manganese and cadmium were observed in the samples collected at the dam-adjacent part of the reservoir, whereas the lowest – in water samples collected next to the reservoir inlet, both in 2012 and in 2013. The content of these elements ranged 229–285 $\mu gMn \cdot m^{-3}$ and 2.66–3.35 $\mu gCd \cdot m^{-3}$ (Table 3). The content of nickel and copper demonstrated the lowest variation throughout the whole measurement cycle. The content of these elements in water ranged 0.09–0.11 $\mu g \cdot m^{-3}$ for nickel, and 2.11–2.35 $\mu g \cdot m^{-3}$ for chromium. In all samples of concern, mercury content was below the detection threshold.

Table 3

Content of heavy metal ions in water

Station	Fe	Cr	Zn	Ni	Mn	Cu	Pb	Cd	Hg	pH	Suspension
	[μg · kg^{-1}]										[g · m^{-3}]
2012											
K_1	801	0.06	13.51	0.10	229	2.11	5.21	2.66	—	7.40	17.68
K_2	649	0.06	12.21	0.10	229	2.11	6.11	3.06	—	7,20	12.54
K_3	702	0.05	12.21	0.09	244	2.35	6.52	3.35	—	7.25	15.25
2013											
K_1	743	0.06	13.26	0.10	264	2.25	4.37	2.66	—	7.35	18.11
K_2	693	0.04	12.97	0.11	273	2.15	6.23	2.97	—	7.40	11.11
K_3	721	0.05	12.35	0.09	285	2.32	6.98	3.25	—	7.20	19.78

The pH of the water sampled for testing fluctuated around the near neutral values, and the content of suspensions did not exceed 19.78 g·m^{-3} (Table 3).

Discussion of results

Table 4 shows the content of heavy metals in the bottom sediments of Kaniow reservoir. It can be stated that in accordance with the LAWA classification, bottom sediments did not exceed the permissible level in any sample. With respect to chromium, zinc, nickel and copper, the threshold values for class I of deposits cleanliness were not exceeded. Only for lead (stations K_1 and K_2) and cadmium (stations K_1 and K_3), bottom sediments of the reservoir were classified as moderately contaminated.

Table 4

Classification of bottom sediments from Kaniow reservoir

Station	Cr	Zn	Ni	Cu	Pb	Cd	Hg	Criterion
K_1	I	I	I	I	II*	II*	—	LAWA classification
K_2	I	I	I	I	II*	I–II	—	
K_3	I	I	I	I	I–II	II*	—	
K_1	—	0	0	0	I	I	—	IUNG guidelines
K_2	—	0	I	0	II	I	—	
K_3	—	0	0	0	I	I	—	
K_1	A	A	A	A	B	A	A	Ministerial regulation
K_2	A	A	A	A	B	A	A	
K_3	A	A	A	A	A	A	A	

* Recommended permissible value.

In accordance with the guidelines developed by the Institute of Soil Science and Plant Cultivation (IUNG), sediments deposited in the lake basin of Kaniow reservoir can be classified as uncontaminated, with the natural content of trace metals, for zinc, nickel and copper. With respect to lead (except for station K_2) and cadmium, the reservoir bottom sediments can be classified as soils with elevated metal content. The sediments collected from the central part of the reservoir (station K_2) should be classified as weakly contaminated as regards the lead content. Therefore, while planning the agricultural use of the sediments, it is necessary to exclude certain horticultural crops, due to the hazard of the chemical contamination of plants. Nonetheless, the cultivation of cereals, root crops and fodder is allowed on so fertilised land.

In accordance with the soil quality standards set in the regulation [15], permissible limits were exceeded only for lead (stations K_1 and K_2). Thus, sediments deposited on the reservoir bottom correspond to soils classified as farmland (group B) as regards chemical composition.

Table 5 shows the content of heavy metals in bottom sediments from two small dammed reservoirs located in the Swietokrzyskie Province (Suchedniow reservoir and Kielce artificial lake), also from Krempna water reservoir, which is characterised by a percentage content of forests in the total basin area similar to that of Kaniow reservoir, and finally Zeslawice reservoir, the basin of which is agricultural in character as arable land constitutes approx. 80 % of its area.

Table 5

Content of heavy metal ions in selected small water reservoirs

Fe	Cr	Zn	Ni	Mn	Cu	Pb	Cd
[mg · kg^{-1}]							
Suchedniow reservoir							
10911–21948	37.36–63.92	177.49–216.94	29.01–31.41	499.76–698.45	26.39–42.97	59.39–110.02	5.02–10.75
Artificial lake in Kielce							
—	3.7–64	5.2–68	—	—	1.2–28	34.2–291	2.32–22.6
Krempna reservoir							
—	38.2–70	39.7–79.5	28.3–52.3	—	14.2–33.2	9.3–17.2	0.14–0.32
Zeslawice reservoir							
—	29.0–29.9	55.0–72.6	5.9–9.0	—	5.1–7.7	9.7–13.9	0.27–0.41

Comparing the sets of data in Table 5 and Table 2, it can be concluded that bottom sediments of Kaniow reservoir were contaminated with heavy metals to a far lesser extent than bottom sediments of Suchedniow reservoir and Kielce artificial lake. The latter are located in urban areas and subjected to strong anthropogenic pressure. In addition, their function is to receive stormwater, which undoubtedly affects the quality of sediments in those reservoirs. Bottom sediments of Kaniow reservoir are characterised by a lower content of Cr, Zn, Ni and Cu when compared with sediments from Krempna reservoir. The content of Pb and Cd compounds was higher than in the sediments of Kaniow reservoir. A similar situation was observed when bottom sediments from Kaniow and Zeslawice reservoirs were compared.

The literature data [18] show that heavy metals can be absorbed by sediment organic matter. The results of statistical analyses indicate the occurrence of a strong correlation dependence, which is statistically relevant for the level $p < 0.05$, for the pairs: Fe – organic matter and Ni – organic matter. Correlation coefficients for these pairs were 0.94 for iron and –0.87 for nickel (Fig. 2a and b). In all remaining cases, this dependence was not statistically significant.

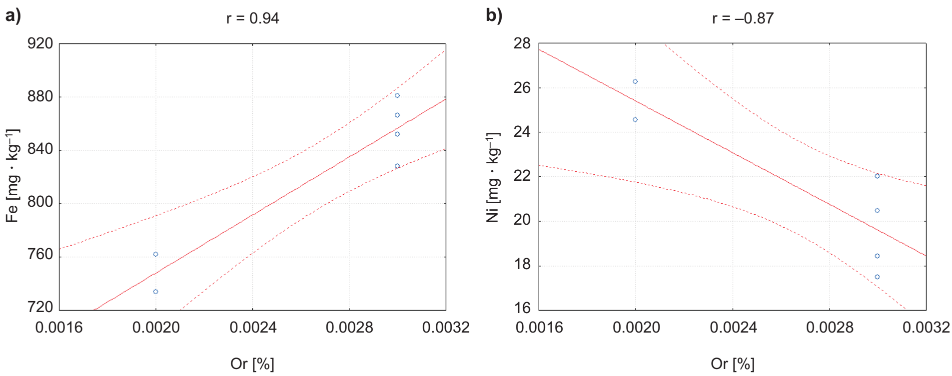

Fig. 2. Correlation dependence: a) Fe – organic matter; b) Ni – organic matter

The waters of Kaniow reservoir satisfy the basic chemical requirements (content of heavy metals) that should be met by potable water. In the investigations, the highest permissible values of concentrations of heavy metals, stipulated in the Regulation of the Minister of Health of 27 March 2007 [19], were not exceeded.

Conclusions

1. The bottom sediments of Kaniow reservoir are only weakly contaminated with heavy metals, additionally spatial differentiation in their concentrations can be observed. It should be noted that the highest concentrations of Fe, Cr, Ni, Mn and Pb were found in the sample collected in the central part of the reservoir. In other samples, the content of those metals was much lower. At present, it is not possible to adequately explain the reason for that difference, therefore it is necessary to continue monitoring the state of the reservoir bottom sediments.

2. In accordance with the LAWA classification, the content of heavy metal ions in the reservoir bottom sediments did not exceed the permissible limits.

3. Values of lead and cadmium concentrations in all analysed samples corresponded to level I–II contamination in accordance with the IUNG classification. For the

remaining elements, it was the 0 level (except for station K_2, where level I contamination was observed). II level indicates weak soil contamination, therefore it is possible to grow only cereals, root crops and fodder on such land, due to the hazard of the chemical contamination of plants. Significant correlation was found between iron and organic matter, and also nickel and organic matter.

4. The concentrations of ions of heavy metals in Kaniow reservoir water do not exceed the maximum limits for potable water, in accordance with the Regulation of the Minister of Health of 27 March 2007.

5. The examined sediments contain a substantial amount of sandy material and small amounts of particulate and argillaceous materials. The sandy fraction in the samples constituted from 86 % to 99.8 % of the total mass.

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KONCENTRACJA METALI CIĘŻKICH W WODZIE I OSADACH DENNYCH MAŁEGO ZBIORNIKA WODNEGO W KANIOWIE

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Abstrakt: W artykule przedstawiono wyniki badań stężeń jonów wybranych metali ciężkich (Fe, Cr, Zn, Ni, Mn, Cu, Pb, Cd, Hg) w osadach i wodzie małego zbiornika zaporowego zlokalizowanego w miejscowości Kaniów na cieku od Borowej Góry. Do badań pobrano osady i wodę z części górnej, środkowej i dolnej zbiornika. Próby pobrano dwukrotnie, po raz pierwszy w lipcu 2012 r., a następnie w marcu 2013 r. Zawartość pierwiastków śladowych w wodzie nie przekraczała: 801 $\mu g \cdot dm^{-3}$ (Fe), 0,064 $\mu g \cdot dm^{-3}$ (Cr), 13,5 $\mu g \cdot dm^{-3}$ (Zn), 0,106 $\mu g \cdot dm^{-3}$ (Ni), 285 $\mu g \cdot dm^{-3}$ (Mn), 2,35 $\mu g \cdot dm^{-3}$ (Cu), 6,98 $\mu g \cdot dm^{-3}$ (Pb), 3,35 $\mu g \cdot dm^{-3}$ (Cd). W przypadku osadów dennych maksymalne odnotowane stężenia metali ciężkich wynosiły: 872 $mg \cdot kg^{-1}$ (Fe), 15,19 $mg \cdot kg^{-1}$ (Cr), 26,26 $mg \cdot kg^{-1}$ (Zn), 16,26 $mg \cdot kg^{-1}$ (Ni), 750 $mg \cdot kg^{-1}$ (Mn), 3,58 $mg \cdot kg^{-1}$ (Cu), 82,56 $mg \cdot kg^{-1}$ (Pb), 0,73 $mg \cdot kg^{-1}$ (Cd), 0,0031 $mg \cdot kg^{-1}$ (Hg). Podjęto również próbę określenia matematycznej zależności między zawartością części organicznych w osadach dennych zbiornika a metalami ciężkimi oraz określono możliwość rolniczego wykorzystania osadów po ich wydobyciu z dna zbiornika.

Słowa kluczowe: metale ciężkie, osady denne, zbiornik wodny