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CHEMICAL COMPOSITION OF BOTTOM SEDIMENT IN THE RZESZÓW RESERVOIR

A chemical composition of bottom sediment in the Rzeszów reservoir was investigated. The concentrations of carbon (total, organic, mineral and carbonates), total nitrogen and phosphorus, organic matter, silica and some metals (iron, copper, zinc, lead and cadmium) were determined. The contamination of the reservoir by heavy metals was estimated based on geochemical classification. The changes in the sediment composition after 30 years of reservoir exploitation were discussed.

1. INTRODUCTION

Dam reservoir on the Wisłok River in the city of Rzeszów was constructed 30 years ago. Originally the reservoir had an area of 1.18 km^2 and the volume of $1.8 \cdot 10^6$ m^3. Its maximum depth reached 6 m (on an average 1.5 m) and its length was 6.8 km [1]. Due to an intensive deposition of rock material carried by the reservoir tributaries (the Wisłok and the Strug Rivers) its surface decreased considerably. Despite several reconstruction trials they did not bring any expected results and did not prevent the reservoir from degradation [2].

The quality of the reservoir water is bad [3]–[5]. In the years 1999–2000, phosphorus and nitrogen loads exceeded their permissible levels [5], [6]. Thick layer of bottom sediment occurs at a small depth and therefore in the periods of a temporary low water level in the river it is uncovered. Based on the examinations of conducted in the eightiets, the bottom sediments were classified as siliceous with relatively small amount of other mineral components [1].

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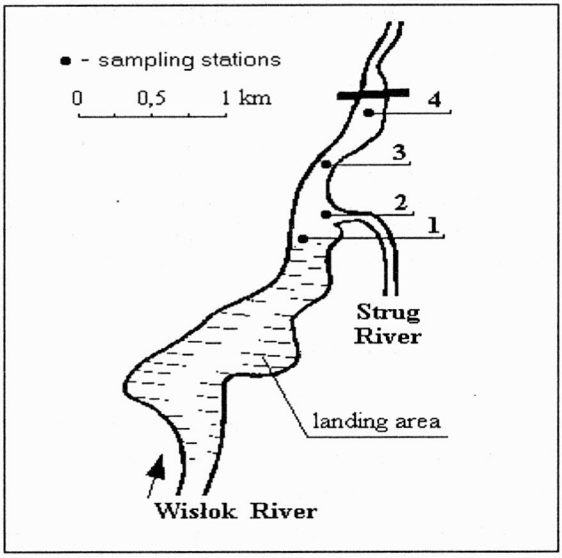
2. METHODS

Bottom sediment samples were taken in three series (from April to May 2003) at four sampling places (the figure) located in the whole area of the reservoir with a water depth not greater than 1 m. Surface (10 cm) layers of sediment were analysed after air-drying and milling. Thermal methods were used to determine organic matter (550 °C), carbon dioxide and silica (1100 °C). pH was measured potentiometrically. The residue was mineralized and then analysed for total phosphorus by colorimetric analysis and heavy metals (Fe, Cu, Ni, Pb, Zn and Cd) by means of atomic absorption spectrophotometry. In order to determine total content of nitrogen and carbon, the C,N Flash 1112 TermoQuest analyzer was used.



The Rzeszów reservoir with sampling places

3. RESULTS

The content of biogenic compounds (nitrogen and phosphorus), carbon compounds (total, organic, mineral and carbonates), organic matter, silica and pH in the surface bottom sediment were shown in table 1.

Sediment pH was rather neutral and ranged from 6.86 to 7.21. Silica was the predominant component, on an average 67.2% of dry weight (d.w.), and organic matter was the second main component, on an average 8.36% of d.w. But the content of organic matter completely did not correlate with the content of organic carbon, whose concentration ranged from 0.73 and 2.12% of d.w. (correlation coefficient r = 0.03;

level of significance, 0.05). The content of organic matter and the content of total carbon were not correlated either ($r = 0.02$). But the content of total carbon is strongly correlated with the content carbonates ($r = 0.91$). The loss of weight after sludge roasting at the temperature of 550 °C, which was the effect of organic matter ashing, could be probably caused by another chemical and physical processes (e.g. pore water removing or sulphide decomposition). This could affect the relationships examined decreasing the weight of sludge after its roasting. Nevertheless, this parameter is still useful and valuable indicator of organic matter in acquatic environment.

Table 1

Physicochemical characteristics of bottom sediment from the Rzeszów reservoir

Sampling place		pH	Fe	SiO_2	OM	CO_2	C_{tot}	C_{inorg}	C_{org}	N_{tot}	P_{tot}
		$pH_{(KCl)}$	[% of dry weight]								
series I	1	7.19	0.559	68.5	8.04	4.28	2.88	1.17	1.71	0.215	0.074
	2	7.10	0.547	67.5	6.41	1.96	1.71	0.53	1.18	0.061	0.078
	3	7.00	0.556	64.8	9.12	4.02	3.17	1.10	2.07	0.178	0.074
	4	7.14	0.560	65.5	8.39	4.89	3.08	1.33	1.75	0.172	0.078
series II	1	6.92	0.553	70.7	10.85	3.81	2.55	1.04	1.51	0.117	0.067
	2	6.86	0.564	58.0	4.72	3.55	2.72	0.97	1.75	0.098	0.080
	3	6.90	0.545	62.1	7.37	3.26	2.98	0.89	2.09	0.025	0.068
	4	7.21	0.469	79.7	8.78	1.74	1.20	0.47	0.73	0.038	0.028
series III	1	7.11	0.530	65.1	10.28	5.03	3.49	1.37	2.12	0.228	0.048
	2	7.16	0.534	67.2	7.63	1.95	1.61	0.53	1.08	0.067	0.049
	3	7.08	0.563	67.1	12.7	4.64	2.78	1.27	1.51	0.200	0.086
	4	7.05	0.560	70.3	6.08	3.51	2.67	0.96	1.71	0.180	0.079
Average		**7.06**	**0.545**	**67.2**	**8.36**	**3.55**	**2.57**	**0.97**	**1.60**	**0.132**	**0.0673**

The content of total carbon, iron, nitrogen, and phosphorus in dry weight averaged 1.6%, 0.55%, 0.13% and 0.07%, respectively. Total nitrogen content was correlated with total carbon content ($r = 0.88$) as well as with organic carbon ($r = 0.82$), while the correlation between phosphorus and organic carbon was rather weak ($r = 0.46$). There was a strong correlation between total phosphorus content and iron content ($r = 0.93$) which is confirmed by the chemistry of these elements (ferric ions precipitate inorganic phosphorus from water). Both nitrogen and phosphorus are the components of organic matter.

Comparison of the average values of the determined components to the values from the years 1980–1987 revealed that they did not differ substantially (table 2).

Table 2

Average concentrations of the components bottom sediment in the Rzeszów reservoir in the years 1980–2003 [% of dry weight]

Year	pH	C_{org}	N_{tot}	SiO_2	CO_2	OM	P_{tot}	Fe	N:P
1980–1983	7.28	2.02	0.20	–	–	–	0.003	1.18	67:1
1983	7.41	–	0.19	58	4.12	8	0.028	0.87	7:1
1986	7.38	–	0.17	69	2.04	7.2	0.028	0.42	6:1
1987	8.15	2.15	0.16	54	3.24	4.4	0.052	0.60	3:1
2003	7.06	1.6	0.13	67	3.55	8.4	0.067	0.55	2:1

Bottom sediments are still of silicate type because of SiO_2 content exceeding 50% of dry weight. Also organic matter was not changed considerably in spite of methodological differences (800 and 550 °C) [1]. Iron content from 1983 seemed to be on the same level – slightly below 1% of d.w. An average concentration of carbonates was within 3%. Total concentrations of nitrogen and phosporus changed only slightly. The same is valid for organic carbon, but because of too small number of results this component is not taken into account in discussion. In the last twenty years, a total nitrogen content decreased and a total phosporus content increased. The changes in nitrogen concentration were small, but in the case of phosphorus, its content seemed to increase considerably. This was confirmed by the investigations into the loads of biogenic compounds in the reservoir water. The ratio of nitrogen to phosphorus decreased [6]. Investigations carried out in 1999–2000 proved that phosphorus was more easily available than nitrogen. The ratio of these elements changed considerably with the age of the reservoir – from the value of 70:1 to the value of 13:1, respectively, in 1970 and at present. C_{org} : N_{tot} ratio, which is indicative of the rate of sediment mineralization, amounts to 10, 13 and 12 respectively in the years 1980, 1987 and 2003. This proves that the rate of mineralization is great in the shallow parts of the reservoir. In a deep area, the rate of this process is small because of oxygen defficiency and insufficient transparency [1].

In this study, total contents of copper, nickel, zinc, lead and cadmium were determined (table 3). The concentrations of heavy metals in the bottom sediment reflect the water contamination by these elements because most metal ions or their complex compounds are susceptible to precipitation due to sorption and oxidation processes. Bottom sediment is then a good indicator of water contamination in the reservoirs [7].

In order to evaluate the contamination of bottom sediment by heavy metals, geochemical classification according to Müller was used [7], [8]. In table 4, geochemical index values (I_{geo}) for the average concentrations of heavy metals analysed (C_{av}) and for maximum ones (C_{max}) were presented.

Table 3

Heavy metal content [mg/kg of d.w.] in the bottom sediment of the Rzeszów reservoir

Sampling place		Cu	Ni	Zn	Pb	Cd
Series I	1	19.4	31.2	101.8	32.4	0.61
	2	18.4	30.4	106.0	33.5	0.31
	3	20.7	31.6	95.6	28.6	0.49
	4	23.2	34.7	96.8	26.2	0.58
Series II	1	15.4	28.2	100.3	44.6	0.53
	2	16.1	32.3	111.7	46.8	0.36
	3	12.4	24.2	94.1	33.1	0.45
	4	6.8	6.4	34.5	28.4	0.56
Series III	1	16.0	25.8	69.9	32.2	0.48
	2	15.6	21.4	76.7	36.5	0.42
	3	20.2	33.2	110.3	36.7	0.47
	4	19.8	33.3	107.0	35.8	0.60

Table 4

Geochemical index (I_{geo}) for heavy metals in the Rzeszów reservoir bottom sediment

	Cu	Zn	Pb	Cd	Ni
C_{av}	17.0	92	34.6	0.49	27.7
$C_{min.}$	6.8	35	26.2	0.31	6.4
$C_{max.}$	23.2	112	46.8	0.61	34.7
Geochemical background	**45.0**	**95**	**20**	**0.3**	**68**
I_{geo} for C_{av}	–1.99	–0.63	**0.20**	**0.12**	–1.88
I_{geo} for C_{max}	–1.54	–0.35	**0.64**	**0.44**	–1.56

Geochemical background according to Turekian and Wadephole [7] was the basis for the calculations. Copper, zinc and nickel concentrations corresponded to zero geochemical class ($I_{geo} < 0$), hence the bottom sediment were classified as almost uncontaminated. Only lead and cadmium occurred in the concentrations corresponding to the first geochemical class ($0 < I_{geo} < 1$), i.e. the sediment was slightly contaminated.

To sum up: the bottom sediment of the Rzeszów reservoir is not contaminated by heavy metals. Water analyses proved that the concentrations of heavy metals did not exceed their concentrations in the water of the first class purity [3], [4]. Hence, the composition of bottom sediment can be considered to be the indicator of water contamination.

During the twenty-year span only lead concentration increased continually (table 5). Copper and zinc concentrations decreased to a natural level (Zn) or even below it (Cu). Taking into account the maximum concentrations of nickel and cadmium it can be concluded that their concentrations were constant.

Table 5

Average concentrations [mg/kg of d.w.] of heavy metals in the bottom sediments of the Rzeszów reservoir and in selected reservoirs of Podkarpackie Province

Year	the Rzeszów reservoir				
	Cu	Ni	Zn	Pb	Cd
1994	23	25	102	17	0,44
1995	29	40	144	29	0,61
2003	17	28	92	35	0,49
	the Wilcza Wola reservoir				
1994	6.6	7.2	50	7.6	0.27
1996	9.2	6.9	35	6.5	0.16
	the Ożanna reservoir				
	7.6	12.7	70	9.2	0.51
1997	5.3	9.1	63	7.6	0.46
	the Kamionka reservoir				
1994	4.3	5.6	56	7.1	0.67
	the Brzóza Królewska reservoir				
1994	2.7	2.9	26	2.9	0.13
	the Solina reservoir				
2000–2001	31	31.2	125	18.9	0.43

Comparing the metal concentrations in the Rzeszów reservoir with those in other reservoirs from the Podkarpackie Province we found that only in the Solina reservoir the metal concentrations are similar [9], [10]. In other reservoirs, the metal concentrations in bottom sediment are lower or considerably lower than in the Rzeszów reservoir. Only cadmium concentrations in the Ożanna and Kamionka reservoirs were below its natural content with the maximum values above 1–2 mg/kg of d.w. [4].

4. SUMMARY

Chemical composition of the bottom sediment in the Rzeszów reservoir did not change significantly in the space of years. Silica is its predominant component, the other mineral and organic components occurred in considerably smaller quantities. The concentration of biogenic elements in the bottom sediment reflect the load of these substances in water. The ratio of nitrogen to phosphorus decreased both in water and in bottom sediment with time. No progressive accumulation of organic matter was observed. In shallow parts of the reservoir, the rate of organic matter mineralization in the bottom sediment seemed to be significant.

The concentrations of heavy metals in the bottom sediment are not high. If geochemical classification is taken into account, zinc, copper and nickel do not contaminate the reservoir. Only cadmium and lead slightly contaminate sediment, and the concentration of lead has been increasing with time.

REFERENCES

[1] TOMASZEK J., *Chemizm osadów dennych zbiornika zaporowego w Rzeszowie*, Zeszyty Naukowe Politechniki Rzeszowskiej, Budownictwo i Inżynieria Środowiska, 1990, No. 68, z. 11, 101–111.

[2] TOMASZEK J., *Problems of preservation and land reclamation of the man-made lake on the Wislok River in Rzeszów*, Conference of the Polish Academy of Science, November 14–15, 1995, Zabrze, Poland, 133–150.

[3] *Raport o stanie środowiska w woj. rzeszowskim w 1994 r.*, Państwowa Inspekcja Ochrony Środowiska, Wojewódzki Inspektorat Ochrony Środowiska, Biblioteka Monitoringu Środowiska, Rzeszów, 1995.

[4] *Raport*: *Wody powierzchniowe a gospodarka wodno-ściekowa w województwie rzeszowskim*, Państwowa Inspekcja Ochrony Środowiska, Wojewódzki Inspektorat Ochrony Środowiska. Biblioteka Monitoringu Środowiska, Rzeszów, 1998.

[5] http://www.wios.rzeszow.pl/, *Klasyfikacja jakości wód w badaniach monitoringowych w 2002 r.*

[6] KOSZELNIK P., TOMASZEK J.A., *Obciążenie rzeszowskiego zbiornika zaporowego biogenami – bilans masowy*, II Ogólnopolska Konferencja Naukowo-Techniczna *Postęp w Inżynierii Środowiska*, Rzeszów-Polańczyk, 2001, 45–52.

[7] HELIOS-RYBICKA E., SIKORA W.S., WÓJCIK R., WARDAS M., STRZEBOŃSKA M., ADAMIEC E., ŁAGAN Ł., *Ocena zanieczyszczenia metalami ciężkimi osadów dennych górnej i środkowej Odry*, Gospodarka Wodna, 2000, 8, 300–304.

[8] KOSTECKI M., *Alokacja i przemiany wybranych zanieczyszczeń w zbiornikach zaporowych hydrowęzła rzeki Kłodnicy i na Kanale Gliwickim*, IPIŚ PAN, Zabrze, 2003.

[9] GRUCA-ROKOSZ R., BARTOSZEK L., TOMASZEK J.A., *Koncentracja metali ciężkich w osadach dennych zbiornika solińskiego*, III Ogólnopolska Konferencja Naukowo-Techniczna *Postęp w Inżynierii Środowiska*, Rzeszów-Polańczyk, 2003.

[10] TOMASZEK J.A., CZERWIENIEC E., *The chemistry of bottom sediments of the Solina Reservoir. The Regional Ecological Problems*, Scientific Works of International Institute Association of Regional Ecological Problems (IIAREP), Maria Curie-Skłodowska University Press, Lublin, 1996, 1, 181–190.

SKŁAD CHEMICZNY OSADÓW DENNYCH ZBIORNIKA ZAPOROWEGO W RZESZOWIE

Przebadano skład chemiczny osadów dennych zbiornika zaporowego na Wisłoku w Rzeszowie. Oznaczono w nich zawartość węgla (ogólną, organiczną, mineralną oraz węglanów), ogólne stężenia azotu i fosforu, substancji organicznej, krzemionki oraz żelaza, miedzi, niklu, cynku, ołowiu i kadmu. Oceniono stopień ich zanieczyszczenia metalami ciężkimi, wykorzystując klasyfikację geochemiczną. Wyniki omówiono pod kątem zmian, jakie zaszły w osadach dennych zbiornika po 30 latach jego eksploatacji.