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ACCUMULATION OF SELECTED HEAVY METALS IN BOTTOM SEDIMENTS OF DOLNOŚLĄSKIE PROVINCE RESERVOIRS

Magdalena Senze, Monika Kowalska-Góralska, Ryszard Polechoński,
Przemysław Pokorny, Wojciech Dobicki

Summary. The research was aimed at description of the water and bottom sediments from dam reservoirs at Słup and at Lubachów that are used as a source of drinking water. The samples were checked for chemical reaction, concentrations of organic and mineral compounds, copper, lead, zinc and chromium. The bottom sediments from the Lubachów reservoir were found to have accumulated more copper and lead, whereas those from Słup – more zinc and chromium. The highest accumulation rates were discovered for lead at Lubachów and for chromium at Słup. As a general rule, metal concentrations were the lowest in the central parts of the reservoirs.

Key words: bottom sediments, water, dam reservoirs, heavy metals

INTRODUCTION

Dam reservoirs located in the south west of Poland are mainly used for flood control and they store water for drinking. Heavy metals reaching water ecosystems originate from geochemical processes, i.e. from natural weathering of ore-bearing rocks within the reservoirs' catchment basins, but also from anthropopression – population density or industrialization [Prosowicz and Helios--Rybicka 2002]. The metals present in the water of the Słup and Lubachów reservoirs come from the agricultural catchment, atmospheric precipitation, domestic sewage and, to some extent, sewage from a few industrial plants.

The two reservoirs in question are used as a source of drinking water and water used for household purposes. This was the rationale behind the chemical analysis of their bottom sediments. An attempt was also made to determine the accumulation rates for Cu, Pb, Zn and Cr in the bottom sediments.

MATERIAL AND METHODS

The research covered two dam reservoirs: Słup and Lubachów, which differ in age, morphometric parameters and the nature of their direct catchments. The Słup reservoir is located on the border of the Sudeten Foreland and the Silesian Lowland. It was created on the Nysa Szalona river valley, 8.2 km from the river source. The reservoir bowl and all of the hydro-engineering structures lie within a direct protection zone, because they are used to gather drinking water for the city of Legnica [Szulkowska-Wojaczek and Marek 1984]. The Lubachów reservoir is located in the commune of Walim, Wałbrzyski Poviat. It was built on the Bystrzyca river, 75 km from its source. The reservoir and its engineering structures are not subject to direct protection, although drinking water is drawn from there for the towns of Dzierżoniów, Bielawa and Pieszyce [Hammer 2001]. The reservoirs selected for the research have different morphometric features which are presented in Table 1.

Table 1. Morphometric characteristics of the Słup and Lubachów dam reservoirs

Reservoir parameter	Słup reservoir	Lubachów reservoir
Average depth, m	8.00	15.70
Maximum depth, m	18.05	36.00
Length, km	2.90	3.50
Volume, million m^3	31.52	8.00
Area, ha	408.00	51.0

The research was conducted on bottom sediments collected in the years 2000/2001 (Słup) and 2004/2005 (Lubachów) from three locations within each reservoir: within the backwater area (site No. 1), in the central section of the reservoir (site No. 2), and immediately before the dam (site No. 3). Sediment samples were mineralised in a mixture of nitric and perchloric acids at a ratio of 3 : 1 in a MARS 5 microwave oven. Water samples were collected 0.5 m above the reservoir bottom. Metal concentrations were determined using a VARIAN SpectrAA 220 atomic absorption spectrophotometer. The analysis results were checked for correctness by means of the LKSD-2 reference material (reference lake sediment, Canada Centre for Mineral and Energy Technology). The accumulation rate (*k*) was computed by dividing the metal concentration in the sediment (*Co*) by its concentration in over-bottom water (*Cw*). Also the reaction of the sediments in question, and the concentrations of mineral and organic compounds were established. Metal concentrations in the sediments are given in $mg \cdot dm^{-3}$ of dry mass (d.m.)

RESULTS AND DISCUSSION

The bottom sediments from the dam reservoirs in Lower Silesia vary greatly in terms of their chemical properties. The sediments from the Słup reservoir are neutral in **reaction**, ranging from 7.15 pH at sampling site 3 to 7.17 pH at sites 1 and 2. The only visible trend in this respect is a slight decrease in reaction along with the flow of water in the reservoir. A similar dependence was found to be true for the Lubachów reservoir. The reaction values oscillated there between 4.84 pH at site 3 and 4.95 pH at site 2.

The concentrations of **mineral compounds** were higher at Słup than at Lubachów (on average by 6.63 percentage points). For the first one the values ranged from 89.98% at site 3 to 92.71% at site 2, and for the other reservoir from 84.53% at site 1 to 85.06% at site 2. In the two reservoirs the concentrations were the highest in the central part of the bowl. In the Słup reservoir the content of mineral compounds decreased slightly along the course of the water; the opposite tendency was observed in the other reservoir. There were nearly twice as much organic compounds in the bottom sediments at Lubachów sites 1 and 2 as at Słup. For sites 3 the difference in the concentrations between the two reservoirs was not so pronounced. At Lubachów the concentration of **organic compounds** varied from 14.93% at site 2 in the central part of the reservoir to 15.47% in the backwater area (site 1). In contrast, the concentrations of organic compounds at Słup were very low, from 7.19% at site 2 to 10.02% at site 3.

Copper content in the Słup reservoir bottom sediments oscillated between 16.06 mg $Cu \cdot kg^{-1}$ at site 2 in the central part of the bowl and 44.20 mg $Cu \cdot kg^{-1}$ at site 3 (immediately before the dam) – Tab. 2. The figures for the Lubachów reservoir were much higher (from 36.26 mg $Cu \cdot kg^{-1}$ at site 1 up to 60.83 mg $Cu \cdot kg^{-1}$ at site 3) – Tab. 2. The highest concentration of copper ions in the Słup reservoir sediments was found near the dam (k = 10914), whereas in the Lubachów reservoir it was in the central part of the bowl (k = 17553). It was discovered in a multi-year research of the Goczałkowicki reservoir that copper concentration in its bottom sediments ranged from 5.00 mg $Cu \cdot kg^{-1}$ to 83.30 mg $Cu \cdot kg^{-1}$, i.e. it fell within the limits similar to those for the Słup and Lubachów reservoirs [Pasternak and Gliński 1972, Kwapuliński *et al.* 1991]. Pasternak & Gliński [1972] and Reczyńska-Dutka [1985], who analysed the bottom sediments from the Kozłowa Góra reservoir, reported copper concentrations oscillating between 6.80 mg $Cu \cdot kg^{-1}$ and 112.50 mg $Cu \cdot kg^{-1}$. The Cu concentration in the bottom sediments of the Rybnicki reservoir, as found by Loska *et al*. [2002], fell within the range of 34.25–56.72 mg $Cu \cdot kg^{-1}$, and in the Dobczycki reservoir, as discovered by Szarek-Gwiazda [1998], 35.70–58.00 mg $Cu \cdot kg^{-1}$. Copper concentrations found in the sediments of other lakes throughout Poland indicate significant resemblance to those at Słup and Lubachów [Gonet and Cieślewicz 1997, Smoleński 1999, Jankowski *et al.* 2002].

Tabela 2. Content of metals in bottom sediments

Sites (number)		Słup				Lubachów			
		Cu	Pb	Zn	Cr	Cu	Pb	Zn	Cr
1	x_o	29.92	30.95	114.57	44.14	46.73	36.01	42.34	24.71
	min	22.31	20.07	70.07	30.74	36.26	16.67	33.95	21.09
	max	40.16	38.48	164.61	67.78	60.01	68.38	49.82	28.08
	S	6.04	6.53	34.55	11.34	11.34	23.90	7.18	2.87
	V	0.20	0.21	0.30	0.26	0.24	0.66	0.17	0.12
	x_w	0.0043	0.0043	0.0262	0.0022	0.0063	0.0008	0.0142	0.0025
	k	6958	7198	4373	20064	7418	45012	2982	9884
2	x_o	28.86	30.87	105.63	40.11	56.17	35.24	43.95	25.34
	min	16.06	20.79	93.27	17.78	52.07	18.60	34.80	23.89
	max	38.82	41.36	139.90	57.75	59.01	67.46	62.20	27.67
	S	6.08	5.31	14.09	13.63	3.64	27.91	15.81	2.04
	V	0.21	0.17	0.13	0.34	0.06	0.79	0.36	0.08
	x_w	0.0045	0.0043	0.0263	0.0022	0.0032	0.0030	0.0171	0.0020
	k	6413	7179	4016	18232	17553	11747	2570	12670
3	x_o	40.38	52.65	134.87	51.01	50.91	27.58	48.44	25.69
	min	36.91	36.23	120.82	27.82	40.82	15.96	35.66	25.38
	max	44.20	78.93	156.25	73.98	60.83	47.79	62.45	25.92
	S	2.63	16.43	12.20	13.25	10.00	17.57	13.43	0.28
	V	0.07	0.31	0.09	0.26	0.20	0.64	0.28	0.01
	x_w	0.0037	0.0034	0.0239	0.0021	0.0092	0.0009	0.0179	0.0025
	k	10914	15485	5643	24290	5534	30644	2706	10276

x_o – mean content in bottom sediments ($mg \cdot kg^{-1}$); S – standard deviation, V – rate of variability; k – rate of accumulation; x_w – mean content in above bottom water ($mg \cdot dm^{-1}$)

Lead concentrations in the bottom sediments of the Słup reservoir ranged from 20.07 mg Pb·kg^{-1} at site 1 to 41.36 mg Pb·kg^{-1} at site 2 (Table 2), and at Lubachów from 15.96 mg Pb·kg^{-1} (site 3) to 68.38 mg Pb·kg^{-1} (site 1) (Table 2). Lead concentrations at Słup rose along the main water course, from 30.95 mg Pb·kg^{-1} at site 1 to 52.65 mg Pb·kg^{-1} at site 3, with a very small drop (by 0.08 mg Pb·kg^{-1}) at site 2. This trend was reflected in the increasing lead accumulation rate for the bottom sediments. A different situation was discovered at Lubachów, where the amount of lead in the sediments fell along the water course, but this was not reflected in the accumulation rate whose lowest value (11747) was recorded for the central part of the reservoir bowl. The lower lead content at Lubachów may be a result of a higher content of organic matter and a lower water reaction [Polechoński and Dobicki 2002]. The dam reservoirs in the south of Poland have been subject to research for many years. Thanks to this, it is possible to compare many of their environmental constituents, e.g. lead content which falls within the range determined for Lubachów and Słup [Pasternak and Gliński 1972, Kwapuliński *et al.* 1991, Szarek-Gwiazda 1998, Jankowski *et al.* 2002, Loska *et al.* 2002]. In many lakes classified as clean and in lakes subject to strong anthropopression a similar range of values has been found to be true [Gonet and Cieślewicz 1997, Smoleński 1999, Samecka-Cymerman and Kempers 2001, Polechoński and Dobicki 2002, Prosowicz and Helios-Rybicka 2002].

Zinc concentrations in the bottom sediments of the Lubachów reservoir ranged from 33.95 mg Zn·kg^{-1} (site 1) to 62.45 mg Zn·kg^{-1} (site 3) – Tab. 2. The figures for the Słup reservoir were twice as high (from 70.07 mg Zn·kg^{-1} – site 1 to 164.61 mg Zn·kg^{-1} – also site 1) – Tab. 2. At Lubachów, zinc concentrations grew along the water flow and at Słup the lowest concentration was recorded at site 2. In both reservoirs the lowest Zn accumulation rates were found at site 2, but it must be pointed out that at Słup the metal accumulated more intensely than at Lubachów. The bottom sediments of the Goczałkowice dam reservoir had from 66.50 to 414.00 mg Zn·kg^{-1} [Pasternak and Gliński 1972, Kwapuliński *et al.* 1991]. Zinc concentrations found in the Rybnicki reservoir fell within the range of 67.95–121.25 mg Zn·kg^{-1} [Loska *et al*. 2002], and in the Kozłowa Góra reservoir: 185.00–1,875.00 mg Zn·kg^{-1} [Pasternak and Gliński 1972, Reczyńska--Dutka 1985]. Lake sediments were found to contain similar amounts of zinc to those measured at Słup and Lubachów [Tatur 1986, Gonet and Cieślewicz 1997, Smoleński 1999, Polechoński and Dobicki 2002].

Chromium content in the surface layer of the bottom sediments in the Słup dam reservoir oscillated between 17.78 mg Cr·kg^{-1} (site 2) and 73.98 mg Cr·kg^{-1} (site 3), and at Lubachów – between 21.09 mg Cr·kg^{-1} (site 1) and 28.08 mg Cr·kg^{-1} (also site 1) – Tab. 2. The horizontal profile showed a slight increase in chromium concentration in the bottom sediments at Lubachów (similarly to zinc). Of interest are the changes in the *k* rate along the water course. The lowest Cr accumulation at Słup was recorded at site 2, whereas at Lubachów site 2 was the location with the highest accumulation. The concentration of the metal in the bottom sediments of the Rybnicki reservoir fell within the range of 25.10–101.56 mg Cr·kg^{-1} [Loska *et al.* 2002]. According to Pasternak and Gliński [1972] and Reczyńska-Dutka [1985], the sediments at Kozłowa Góra contained similar amounts of chromium: from 20.00 mg Cr·kg^{-1} to 105.00 mg Cr·kg^{-1}. The corresponding range for Goczałkowice was from 46.00 mg Cr·kg^{-1} to 173.00 mg Cr·kg^{-1} [Pasternak and Gliński 1972]. Sediments from lakes in western Poland, subject to anthropopression [Samecka-Cymerman and Kempers 2001], and from lakes in regions under weak anthropopression (north-eastern Poland) [Tatur 1986], were characterised by a range of chromium content similar to that found at Słup and Lubachów.

CONCLUSIONS

1. Cu, and Pb accumulated more intensely in the Lubachów, whereas Zn and Cr at Słup.
2. The highest accumulation rates found were for Pb at Lubachów and for Cr at Słup.
3. As a general rule, metals accumulated most weakly (the lowest accumulation rate *k*) in the central part of the reservoir bowls.

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KUMULACJA WYBRANYCH METALI CIĘŻKICH W OSADACH DENNYCH ZBIORNIKÓW ZAPOROWYCH DOLNEGO ŚLĄSKA

Streszczenie. Przeprowadzono badania wody i osadów zbiorników zaporowych Słup i Lubachów. Zbiorniki pełnią funkcję retencyjną, a pobierana z nich woda służy jako woda pitna. W pobranym materiale określono odczyn, poziom związków organicznych i mineralnych, miedzi, ołowiu, cynku i chromu. Zaobserwowano silniejszą kumulację miedzi i ołowiu w osadach ze zbiornika Lubachów, a cynku i chromu w zbiorniku Słup. Najwyższymi współczynnikami kumulacji charakteryzował się ołów w zbiorniku Lubachów i chrom w zbiorniku Słup. Generalnie metale najsłabiej kumulowały się w centralnej części zbiorników.

Słowa kluczowe: osady denne, woda, zbiorniki zaporowe, metale ciężkie