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Horizontal, vertical and seasonal distribution of heavy metals in the water of a stratified dam reservoir (Dobczyce Reservoir, southern Poland)

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Abstract – The concentrations of heavy metals in the upper and lower part of the reservoir, at particular sampling dates, and in the water column, were different. The higher concentrations of Pb, Cu, and Fe in the upper part of the reservoir was caused by the greater input of these elements with the inflowing water of the River Raba. The concentrations of Cd and Pb showed the highest seasonal variability and Mn the lowest. The greatest vertical differences occurred during the period of summer stratification, Cd, Cu and Mn in May, and Pb, Zn, and Fe in July. Circulation of the water caused a levelling of the content of heavy metals in the water column.

Key words: dam reservoir, heavy metals, stratification, pH, redox conditions.

1. Introduction

Heavy metals which occur in reservoirs are subjected to many processes, which have an effect on their migration and differentiation of concentration. Metals in the particulate phase partially settle on the bottom. Dissolved trace metals undergo removal processes by, for instance, adsorption, uptake by biota, precipitation with calcium carbonate, or coprecipitation with iron hydroxides. During their fall through the water column a partial dissolution of metals may take place. In lakes with an anoxic hypolimnion there is a strong interaction between the metals and the redox cycle (Salomons and Förstner 1984, Kabata-Pendias and Pendias 1993).

The form in which heavy metals occur in a water environment are regulated by the physico-chemical parameters of the water (e.g. redox potential, water hardness) and the property of the metals themselves (Borg 1983, Förstner and Whittmann 1983, Salomons and Förstner 1984, Stephenson and Mackie 1988). The biological activity of algae also affect metal binding forms in the water (Sloof et al. 1995, Valenta et al. 1986, Revis et al. 1989, Golimowski et al. 1990).

The aim of these studies was to determine the horizontal, vertical, and seasonal variability of concentrations of selected heavy metals (Cd, Pb, Cu, Zn, Mn, and Fe) in the water of a eutrophic dam reservoir, typical of the submontane part of the Polish Carpathians.

2. Study area

The investigations were carried out on the Dobczyce Reservoir (49°52'N, 20°02'E, alt. 270 m) which was built on the River Raba (the Vistula catchment basin, southern Poland). The Dobczyce Reservoir constitutes a reservoir of drinking water for the city of Cracow. It is 10 km in length, has an area of c. 1000 ha, a mean depth of 11 m, and a volume of 99.2 10^6 m^3. The River Raba is its main tributary (88.6% of the total inflow). The water mass is changed in average 3.6 times a year (Mazurkiewicz 1988). The reservoir is eutrophic and dimictic. There are periods when algae develop very rapidly followed by a "clear-water" phases, i.e. when the phytoplankton biomass falls to very low levels. Circulation of the whole water mass takes place during spring and autumn. In the summer, stratification develops near the dam. In the hypolimnion reduction of the content of dissolved oxygen occurs and a reduction layer is formed (G. Mazurkiewicz unpubl.). It would appear that these factors may have an essential effect on the seasonal and vertical distribution of the content of heavy metals in the water of this reservoir.

3. Material and methods

The investigations were carried out in 1994 at two sampling stations (fig. 1). Station 1 was located in the upper part of the reservoir, c. 1 km from the mouth of the River Raba. The maximum depth was about 5 m, and no stratification occurred here. Station 2 was located in the lower part of the reservoir, near the dam, and was much deeper (max. 26.5 m) and underwent summer stratification. Samples of water were collected on four dates: during the spring circulation (12 April), in the initial period of stratification (10 May), during the summer stagnation (5 July), and the autumn circulation (9 November). The samples of

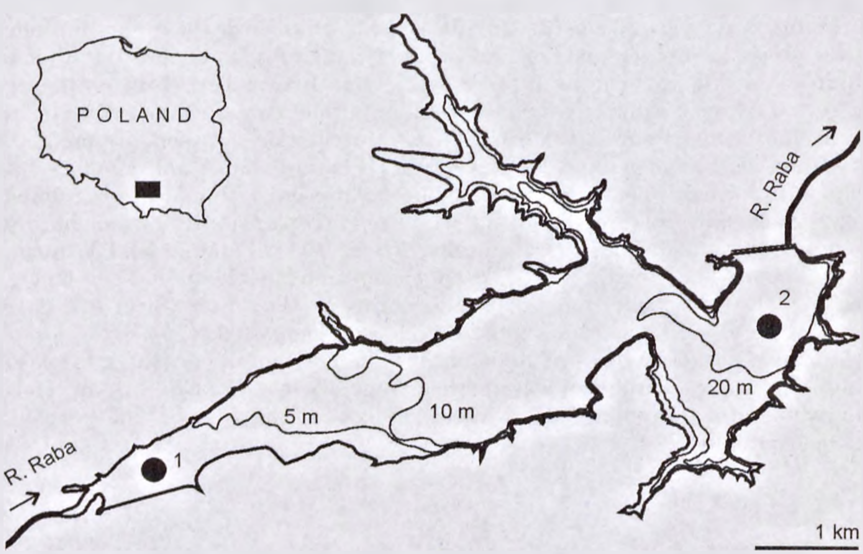

Fig. 1. The Dobczyce Reservoir. Location of the sampling stations (1, 2).

water were taken from the following depths: 0, 1, 2.5 m, and 1 m above the bottom (Station 1), and 0, 1, 5, 10, 15, and 1 m above the bottom (Station 2).

In the collected water samples the total concentrations of Cd, Pb, Cu, Zn, Mn, and Fe were determined. The microcomponents were concentrated by evaporating 1 L of water, acidified with HNO_3 (Pasternak 1971). The content of heavy metals in the dilution was determined by a Perkin-Elmer 403 model atomic absorption spectrophotometer. To estimate the significance of differences in the concentrations of heavy metals between particular stations and dates the Mann-Whittney test was used (Sokal and Rohlf 1987).

4. Results

No significant differences in the concentrations of Cd, Zn, and Mn between the studied sampling stations were found. Instead, there were differences in the concentrations of Pb, Cu, and Fe between the upper and lower parts of the reservoir: Pb in May (N_1=4, N_2=6, U=22, P<0.025) and in April (N_1=4, N_2=6, U=24, P<0.005), Cu in May (N_1=4, N_2=6, U=21, P<0.05) and July (N_1=3, N_2=5, U=14, P<0.05), and Fe in May (N_1=4, N_2=5, U=20, P<0.01). Higher concentrations of these elements were found in the upper part of the reservoir (with the exception of Cu in July) (Table I).

The concentrations of Cd and Pb in the lower end of the reservoir showed great variability. The highest concentration of Cd occurred during the autumn circulation (November) and in the initial period of stratification (May), whereas the a pronounced lower concentration of Cd was found during the summer stagnation (July). The highest content of Pb (similar to Cd) was found during the autumn circulation and the lowest during the summer stagnation. The concentrations of Cu,

Table I. Concentration of heavy metals (μg L^{-1}) in water in the upper and lower part of the Dobczyce Reservoir in 1994.

Elements	Station	Sampling dates							
		4 April		10 May		5 July		9 November	
		min.	max.	min.	max.	min.	max.	min.	max.
Cd	upper	0.03	0.07	0.03	0.19	0.02	0.02	0.08	0.10
	lower	0.02	0.06	0.02	0.10	0.03	0.06	0.07	0.09
Pb	upper	0.7	2.0	0.3	0.8	0.3	0.6	2.1	2.3
	lower	0.4	0.6	0.03	0.4	0.2	3.5	0.8	2.0
Cu	upper	1.8	2.0	3.3	5.3	1.9	2.4	1.0	2.2
	lower	1.5	2.5	0.4	3.5	2.4	5.9	0.6	2.5
Zn	upper	26.4	47.3	20.6	38.1	15.6	31.1	16.7	36.0
	lower	24.3	35.2	17.3	23.7	26.7	70.6	17.1	42.9
Mn	upper	9.6	48.0	32.1	61.0	6.5	36.9	14.5	29.4
	lower	4.0	29.8	4.7	70.8	7.2	24.2	10.9	24.3
Fe	upper	375.0	417.0	242.3	787.6	44.9	154.3	32.8	115.6
	lower	175.0	240.2	45.0	192.5	44.5	195.1	48.0	102.4

Zn, and Fe showed lower seasonal variability. They all had the same level, with the exception of the content of Zn in May (when it was the lowest), Cu in July and Fe in April (when they were the highest). No differences in the content of Mn between particular dates were found.

The circulation and stratification periods on the vertical distribution of the concentrations of heavy metals were found to have an effect. The smallest variability of the content of heavy metals occurred during circulations (Pb, Cu, Zn, and Fe during the spring one) (Table II). However, even during the period of water circulation no total levelling of the content of heavy metals in the water column occurred. The greatest vertical differentiation of the content of Cd, Cu, and Mn was found in May, and Pb, Zn, and Fe in July. It should be noted, however that a great variability in the concentrations of Cd, Cu, and Mn in May did not last throughout the stratification period and in July they were lower. Zinc was the element which showed a slight vertical differentiation. The highest concentrations of Pb, Cu, Zn, Mn, and Fe were found in the near bottom water and also of Cd, Pb, and Cu at a depth of 1 or 5 m. On the other hand, the lowest content of Pb, Cu, and Mn occurred under the thermocline (15 m), and Fe in the surface layer and at a depth of 1 or 5 m (fig. 2).

5. Discussion

The investigation showed that differences occurred in the content of Pb, Cu, and Fe between the upper and the lower part of the Dobczyce Reservoir. The higher level of these elements in its upper part was probably caused by the enhanced input of Pb, Cu, and Fe with the river inflow. Horizontal distribution of trace metals in the water of reservoirs was observed, among others by Pasternak (1971) (Goczałkowice Reservoir, southern Poland), Harding (1981) (Derwent Reservoir, northern England), and Sálanki et al. (1992) (Balaton-Zala system, Hungary). In general, a decrease in concentration of the studied metals along the long axis of the above-mentioned reservoirs was noted (similar to the Dobczyce Reservoir).

Cadmium was found usually in low concentrations in the water of the Dobczyce Reservoir. Higher concentrations occurred in May, during the period of algal bloom and in the autumn during the water circulation. The high content of Cd during the period of algal bloom in May was correlated with a large quantity of chlorophyll *a* at depths of 1 and 5 m (E. Wilk-Woźniak unpubl.). The relationship between a high concentration of Cd and chlorophyll *a* is explained by the specific binding of Cd to phytoplankton (Valenta et al. 1986, Golimowski et al. 1990). In general, two stages are thought to be involved in the kinetics of metal uptake. The first is very rapid, assumed to be passive (e.g. physical and/or chemical adsorption or ion exchange at the cell surface) and occurs immediately after initial contact with the metal. The second stage is slow and active, being related to some type of metabolic activity (Sloof et al. 1995). According to Revis et al. (1989), the uptake of heavy metals by algae is highly specific for both the metal concerned and the organism. The high concentration of Cd during the autumn circulation was probably caused by the high content of suspended matter in the water at this time (Mazurkiewicz unpubl.). Valenta et al. (1986) who studied the distribution of Cd, Pb, and Cu between the dissolved and particulate phase in the water of the Eastern Scheldt and the Western Scheldt Estuary found a higher content of Cd in the water during the period of enhanced load of particular matter. Cadmium was then bound to particulate matter.

Table II. Significance of the differences between sampling dates in the concentration of heavy metals in water of the Dobczyce Reservoir in 1994 (Mann-Whitney test; ns — not significant).

		10 May				5 July				10 November			
		N_1	N_2	U	P	N_1	N_2	U	P	N_1	N_2	U	P
12 April	Cd				ns				ns	6	6	31	0.025
	Pb	6	6	35	0.005				ns	6	6	36	0.005
	Cu				ns	6	5	29	0.005				ns
	Zn	6	6	36	0.005				ns				ns
	Mn				ns				ns				ns
	Fe	6	5	26	0.05	6	5	26	0.05	6	6	36	0.005
10 May	Cd					6	6	31	0.025				ns
	Pb					6	5	27	0.025	6	6	36	0.005
	Cu												ns
	Zn								ns	6	6	30	0.05
	Mn								ns				ns
	Fe								ns				ns
5 July	Cd									6	6	32	0.025
	Pb												ns
	Cu									6	5	29	0.005
	Zn												ns
	Mn												ns
	Fe												ns

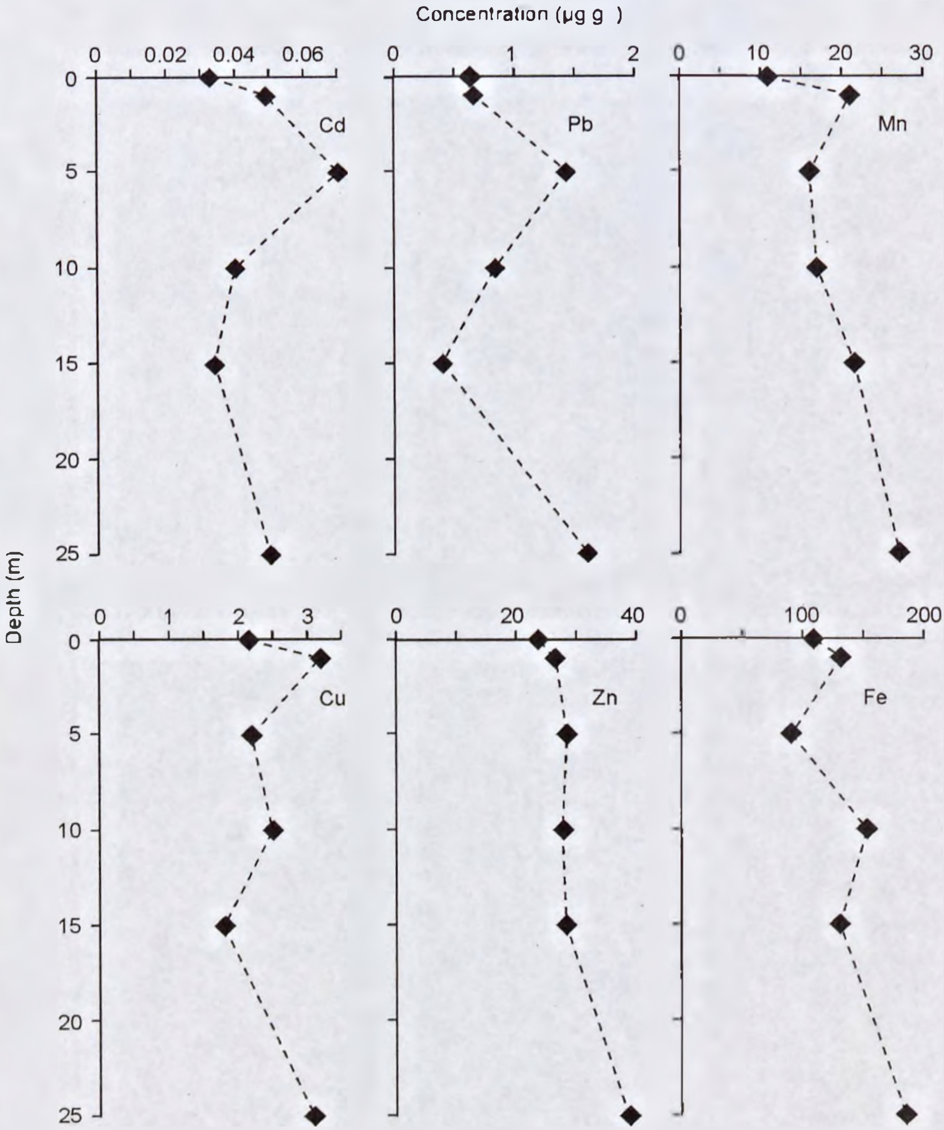

Fig. 2. Vertical distribution of the mean concentration of heavy metals in the lower part of the Dobczyce Reservoir from April to November 1994.

The concentration of lead showed the greatest seasonal variability. The highest concentration of Pb (similar to Cd) was recorded during the period of spring and autumn circulations, when a high level of suspended matter in the water of the Dobczyce Reservoir occurred (Mazurkiewicz unpubl.). Valenta et al. (1986) found that Pb showed a pronounced preference for all types of particulate matter and the highest content of Pb in the water of the Scheldt and the Western Scheldt Estuary was found in the period of the highest level of suspended matter.

The decrease in concentration of Zn in the initial period of stratification was probably due to the high pH value. The algal bloom which was present in this period in the lower part of the reservoir caused an increased oxygen level and pH value (up to 9.1). The binding forms of Zn depend to a high degree on the pH and at pH >8 $Zn(OH)_2$ is precipitated (Salomons i Forstner 1984, Dojlido 1995).

The highest concentration of Fe which was found in spring was probably caused by the input of this element with the river water. This would be suggested by the very high level of Fe in the upper part of the reservoir in April and May.

The processes of mixing and stratification affect the vertical differences in the concentrations of heavy metals. In general it may be said that mixing of the reservoir water mass caused the levelling of heavy metal concentration, whereas the stratification caused the differentiation of most of the heavy metals in the water column. The variability of concentrations of heavy metals during the summer stratification would seem to be caused by the pH and redox condition. The surface water of the Dobczyce Reservoir, in the zone of algal bloom was well oxygenated (max. 10.1 mg O_2 L^{-1}) and had a high pH (max. 9.1) in May. In the near-bottom water, however, the content of dissolved oxygen and the pH were lower (6.7 mg L^{-1} and 7.9, respectively). The lowest contents of dissolved oxygen (3.3 mg O_2 L^{-1}) and pH (7.3) in the near-bottom water were recorded in July (Mazurkiewicz unpubl.). At high concentration of dissolved oxygen and high pH undissolved compounds of Fe and Mn are created and precipitated. Such conditions favour the precipitation of metals with calcium carbonate and their coprecipitation or adsorption with Fe/Mn hydroxides (Salomons and Forstner 1984). The redox conditions of the near-bottom water also bring about release of Mn and Fe from the sediments (Forstner and Wittman 1983, Helios Rybicka 1991). The release of Mn and Fe increases with the increasing redox properties of the environment (Lu and Chen 1977, after Drbal 1991). These processes may explain the low content of Mn and Fe in the surface water and the high concentrations of the most of the elements in the near-bottom water in the Dobczyce Reservoir in the period of stratification. A relation between the Mn concentration and the oxygen content at the bottom and at the water surface was found by Drbal (1991) in the South Bohemian ponds during the vertical stratification.

To sum up, it may be stated that in the water of the Dobczyce Reservoir a variability existed in the concentrations of microcomponents along the long axis (especially Pb, Cu, and Fe), in various periods (Cd, Pb, Cu, Zn, and Fe), and in the water column (all the studied elements). Many factors had an effect on the above differentiation. Among them very important are: the dimictic character of the reservoir, the moving of the water mass along the reservoir, and the physico--chemical factors (pH, redox condition, suspended matter), as well as the biotic ones (activity of algae).

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