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The effect of abiotic factors on the content and mobility of heavy metals in the sediment of a eutrophic dam reservoir (Dobczyce Reservoir, southern Poland)

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Abstract – The total concentrations and exchangeable phase of Cd, Pb, Cu, Zn, Mn, and Fe in the sediment of the Dobczyce Reservoir were studied. The Pb and Mn concentrations in the sediment were positively correlated with the content of organic matter, Cd and Cu with the clay silty and Mn with the clay fractions. The percentage of heavy metals in the exchangeable phase ranged from 2.2 to 54.0 for Cd, 0.6–5.1 for Pb, 0.9–7.3 for Cu, 0.7–16.8 for Zn, 0.7–55.6 for Mn, and 0.001–0.042 for Fe and showed a higher mobility of Cd, Mn, and Zn, than Pb, Cu, and Fe. The mobility of Cd, Pb, Cu, Zn, and Fe in the sediment seems to be affected by the redox condition of the near-bottom water

Key words: reservoir, sediment, heavy metals, organic matter, grain fractions, exchangeable phase

1. Introduction

Freshwater sediments act as an important accumulation place for heavy metals, where they are bound in various components, among which clay minerals and organic matter are of great importance since they have a high potential for adsorption of these metals (Salomons and Förstner 1984, El Ghobary and Latouche 1986, Helios Rybicka 1986). The specific form of binding determines the mobilization behaviour of the heavy metals (Helios Rybicka and Förstner 1986, Förstner et al. 1986, Helios Rybicka 1991). Exchangeable metals in sediment can easily be remobilized to solution following any change in the characteristics of the water. The exchangeable fraction includes metals adsorbed to exchange sites on the surface of sediment particles (Fiszman et al. 1984; cited after Lacerda et al. 1992). The proportion of exchangeable metals in a given sediment depends on numerous environmental variables. Among them redox conditions of the near-bottom water are important (Salomons and Förstner 1984, Fernex et al. 1986, Förstner et al. 1986, El Ghobary and Latouche 1986).

The aim of the present work was to study the concentrations of heavy metals in the sediment of the eutrophic, stratified dam reservoir and their mobility (exchangeable phase). Redox conditions of the near-bottom water in this reservoir change during the year, so it could be expected that the mobility of the heavy metals in the sediment might also change. The relations between the heavy metal content and factors which may affect their distribution in the sediment (organic matter and granulometric composition) were also studied.

2. Study area

The Dobczyce Reservoir (49°52' N, 20°02' E, alt. 270 m) was built in 1986 at the 60th kilometre of the River Raba, about 25 km south of Cracow (Polish Western Carpathians, southern Poland). It is 10 km in length, the mean depth is 11 m (max. c. 30 m), the surface area is about 1000 ha, and its capacity is 99.2 10^6 m^3. In average, the water is exchanged 3.6 times a year (Mazurkiewicz 1988). The summer stratification, and spring and autumn circulation are characteristic of this reservoir. During stratification reductive conditions of the near-bottom water are created. Also after the period of algal bloom, when decomposition processes of organic matter occur, the content of dissolved oxygen in the near-bottom water is low (G. Mazurkiewicz unpubl.).

Almost the entire area of the Raba basin is composed of Tertiary sandstone shale formations of the Magura series and of Submagura beds (Pasternak 1968, 1969). These sandstones are resistant to leaching and determine a small migration of chemical components in the greatest part of the catchment. Most of the montane part of the basin is composed of loam soil with a small or medium content of skeleton grain. The direct catchment of the Dobczyce Reservoir is covered by fine sands soils originating from flysch rocks.

3. Material and methods

Sediment samples from the reservoir were taken from seven stations, which were located along its long axis (fig. 1). The depths at these stations were 3, 8, 13, 18, 17, 21, and 26 m respectively. The samples were collected during the summer stratification (5 July 1994) and autumn circulation (9 November 1994) with a polythene corer (diameter 4 cm). Each sample was divided into the upper (0–3 cm) and lower layer (3–10 cm) in which the heavy metal concentration (total amount and exchangeable phase) as well as the content of organic matter were analyzed. Concentrated HNO_3 was used to extract the total metal content from the sediment samples (Helios Rybicka 1986). To analyse the exchangeable cations one part of the sediment was extracted for 2 h shaking with 1M ammonium acetate, at pH 7.0, and solid/solution ratio of 1:20 (Calmano and Förstner 1983; cited after Förstner et al. 1986). The concentrations of Cd, Pb, Cu, Zn, Mn, and Fe were determined using a Perkin-Elmer 403 atomic absorption spectrophotometer.

The content of organic matter in the sediment samples was determined using the weight (loss of ignition) and chemical oxygen demand (COD) methods (APHA 1992). In the samples collected in July, the grain fractions were determined using the method of Bonyoncosa-Casagrande in Proszyński's modification (Lityński et al. 1976). The following grain fractions were determined: coarse (1.0–0.05 mm), clay silty (0.05–0.002 mm), and clay (<0.002 mm). To determine the relations between the heavy metal concentration and the content of organic matter or the grain fractions, the coefficients of correlation were calculated by one-way ANOVA (Blalock 1977).

Fig 1. Location of the sampling stations (1-7) in the Dobczyce Reservoir

4. Results

The statistical calculations showed that Pb and Mn concentrations in the bottom sediment were related to the content of organic matter and Cd, Cu, and Mn with the clay silty or clay fractions. In the 3–10 cm layer of the sediment a positive correlation between the percentage of organic matter and the content of Pb in July ($P<0.05$, $r=0.98$, $n=6$) and Mn in both terms ($P<0.05$, $r=0.59$, $n=13$) was found. A positive correlations between clay silty fraction and the content of Cd ($P<0.02$, $r=0.80$, $n=6$) and Cu ($P<0.05$, $r=0.70$, $n=6$), and clay fraction and the content of Mn ($P<0.001$, $r=0.90$, $n=6$) in the 3–10 cm layer of the sediment were also found. The percentage of organic matter in the sediment ranged from 4.6 to 8.9% (determined by the weight method) and from 1.4 to 3.3% (determined by the COD method).

In the sediment of the reservoir the clay silty fraction was dominant (55–82%) (with the exception of Station 7, where in the 3–10 cm layer 41% was calculated) (fig. 2). In the case of the clay and coarse fractions the following percentages of the total amount were recorded: 13–37 and 5–14% respectively (with the exception of Station 7, where in the 3–10 cm layer the coarse fraction was 39%). A slight decrease in the clay silty fraction and increase in the clay fraction along the course of the reservoir were observed.

The percentage of heavy metals in the exchangeable phase in the sediment ranged from 2.2 to 54.0 for Cd, 0.6–5.1 for Pb, 0.9–7.3 for Cu, 0.7–16.8 for Zn, 0.7–55.6 for Mn, and 0.001-0.042 for Fe (Table I). The following sequence of mobility of the heavy metals may be suggested on the basis of the maximum values of the above data: Fe (<1%) < Pb and Cu (<10%) < Zn (<20%) < Cd and Mn (<60%).

In the sediment of the Dobczyce Reservoir differences in the content of heavy metals in the exchangeable phase between July and November (with the exception of Fe) were obtained (figs 3 and 4). In July under reductive properties, generally a high content of Mn and low one of Cd, Pb, Cu, and Zn in the exchangeable phase

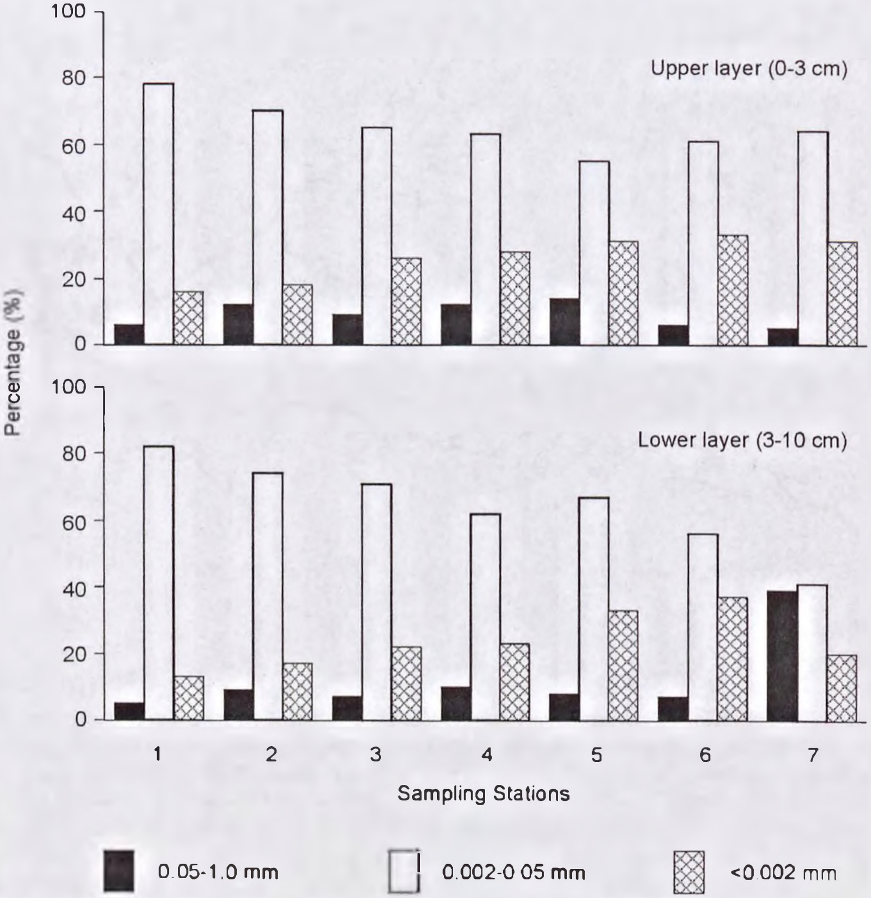

Fig. 2. The granulometric composition of the bottom sediment of the Dobczyce Reservoir in July 1994.

was observed in both layers. In November the behaviour of Cd and Mn was distinct. Low content of Mn and high one of Cd in the exchangeable phase were recorded. In November in the case of Pb, Cu, and Zn at most of the sampling stations their content in the exchangeable phase was greater than in July. However, for instance at Station 6 in the 0–3 cm layer a large decrease in the content of Pb and Zn in the exchangeable phase was noted. There were no distinct differences in the content of Fe in the exchangeable phase between July and November.

Table I. Range of concentrations of Cd, Pb, Cu, Zn (µg g^{-1}), Mn, and Fe (mg), and the exchangeable phase (EP; %) of these metals in the upper (0–3 cm) and lower (3–10 cm) layer of the bottom sediment of the Dobczyce Reservoir.

Elements	Layers							
	0–3 cm				3–10 cm			
	Conc.		EP		Conc.		EP	
	min.	max	min	max	min.	max	min	max.
5 July 1994								
Cd	0.7	1.2	2.2	10.0	0.6	0.9	5.0	16.7
Pb	38.7	50.3	0.6	1.3	27.4	45.2	0.7	1.3
Cu	37.1	58.0	1.2	3.1	36.3	52.2	0.9	4.0
Zn	244.0	397.6	0.7	11.3	270.9	454.7	2.9	9.2
Mn	0.6	1.6	17.5	55.6	0.6	1.1	28.1	50.1
Fe	7.7	22.6	0.007	0.016	11.2	20.6	0.001	0.009
9 November 1994								
Cd	0.5	1.0	14.0	54.0	0.5	1.0	14.0	36.7
Pb	16.1	40.2	0.8	4.5	19.0	43.0	1.0	5.1
Cu	35.7	54.7	3.1	6.2	39.7	50.9	1.8	7.3
Zn	205.5	454.3	7.6	16.8	284.6	367.6	7.6	16.8
Mn	0.5	1.5	0.7	9.4	0.3	1.5	3.4	13.9
Fe	13.4	26.2	0.003	0.042	13.9	24.6	0.004	0.013

5. Discussion

The content of heavy metals in the bottom sediment of the Dobczyce Reservoir was compared with the data normally used as a standard for the geogenic background (Turiekian and Wedepohl 1961; cited after Helios Rybicka 1986). The concentrations of Cd, Pb, and Zn in the sediment of this reservoir were higher than the values of the geogenic background (c. 3 times for Cd, 2 for Pb and 3,5 for Zn).

The content of the heavy metals in the sediment of the Dobczyce Reservoir was lower than in the Goczałkowice and Kozłowa Góra reservoirs which are located on the border of the Upper Silesian Industrial Region (a region of high industrial development and population density). In the Goczałkowice Reservoir the content of heavy metals in sediment ranged from 0.0 to 18.0 µg g^{-1} for Cd and from 0.3 to 120.0 µg g^{-1} for Pb (Kwapuliński et al. 1991). In the Kozłowa Góra Reservoir the following mean values of heavy metals were recorded: 9.0 µg g^{-1} for Cd, 354.0 µg g^{-1} for Pb, and 716.0 µg g^{-1} for Zn (Reczyńska-Dutka 1985). A high level of heavy metals was also recorded in the Rybnik Reservoir in the Rybnik Coal Basin (Loska et al. 1994). In the 0–10 cm layer of the sediment the following ranges of metals were noted there: 3.4–53.2 µg g^{-1} for Cd, 26.1–811.8 µg g^{-1} for Cu, 22.8–204.6 µg g^{-1} for Pb, 84.7–2105.0 µg g^{-1} for Zn, 0.17–2.80 mg g^{-1} for Mn, and 3.3–48.8 mg g^{-1} for Fe. In the bottom sediments of Lake Piaseczno, which is not exposed to industrial emission, the content of Pb was similar whereas Cu (6.0–15.0 µg g^{-1}) and Mn (0.11–0.24 mg g^{-1}) had lower concentrations than those recorded in the sediment of the Dobczyce Reservoir (Górniak et al. 1993).

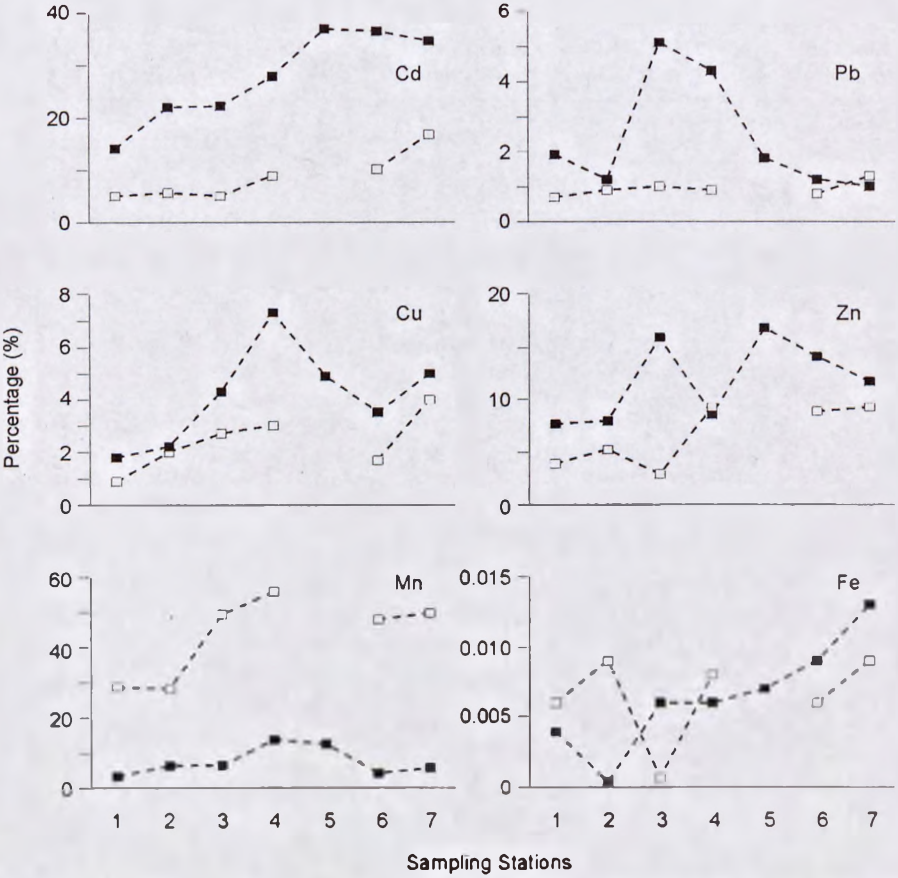

Fig. 3. The percentage of heavy metals in the exchangeable phase in the upper layer of the bottom sediment (0–3 cm) in the Dobczyce Reservoir on 5 July (open squares) and 9 November 1994 (solid squares).

Atmospheric pollution in the surroundings of the Dobczyce Reservoir may be one of the reasons of the higher content of some heavy metals in the bottom sediment. This area is affected by short- (metallurgical industry; the Tadeusz Sendzimir Steel Works in Cracow) and large-range emissions (power plant complexes in Jaworzno and Trzebinia) (Manecki and Tarkowski 1993). In the atmospheric precipitation in the area of the Dobczyce Reservoir zinc was found in the highest average monthly concentration (>106 μg L^{-1}) (Turzański and Bik 1993). Considerable amounts (>20 μg L^{-1}) of Pb and Cu were also found in the precipitation.

The results demonstrate that the content of Pb and Mn in the sediment of the Dobczyce Reservoir were particularly connected with the amount of organic matter, Cd and Cu with the clay silty and Mn with the clay fractions. Also Drbal (1991) found a significant dependence between the content of Cu, Pb, Cr, Zn and that of organic matter in the sediments of South Bohemian ponds. The bottom sediments of the Dobczyce Reservoir were rich in clay silty and clay fractions which favour

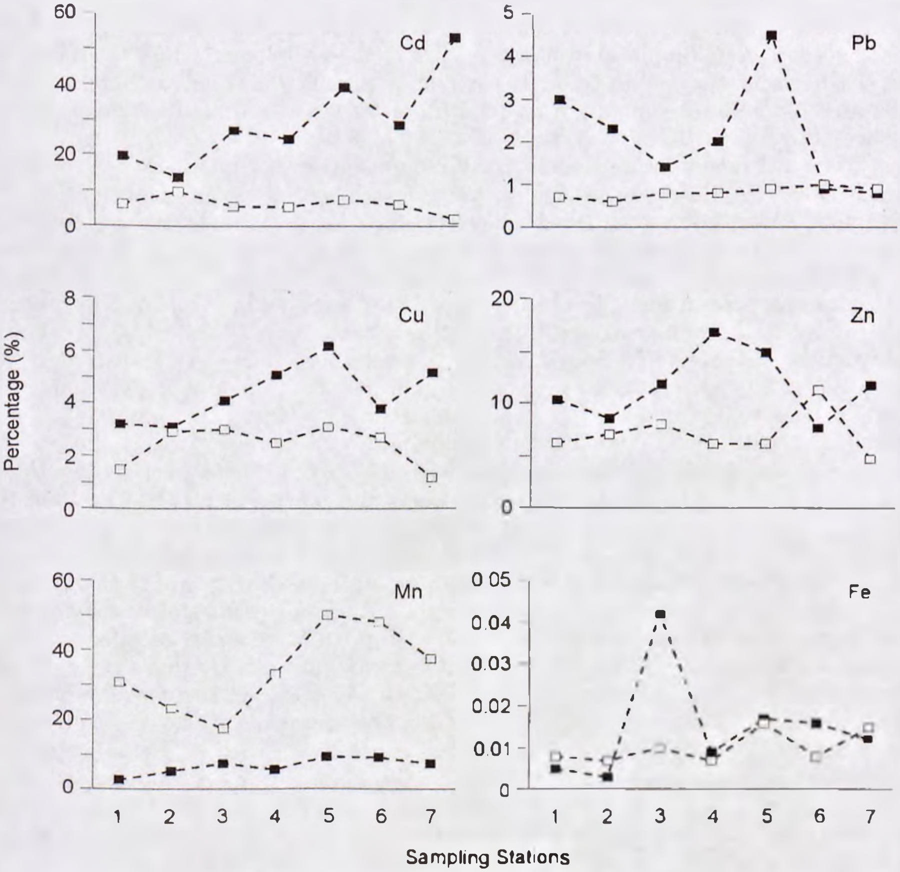

Fig. 4. The percentage of heavy metals in the exchangeable phase in the lower layer of the bottom sediment (3–10 cm) of the Dobczyce Reservoir on 5 July (open squares) and 9 November 1994 (solid squares).

heavy metal accumulations. Together the clay silty and clay fractions make up to 86–95% of the total sediment. According to Helios Rybicka (1983), in many cases the amount of metals in the <2 μm clay fractions of sediment is several times higher than in the clay silty <63 μm one. This is due to the high sorption capacity of clay minerals. These are characterized by large surface areas per unit mass and are considered to be the major reason for enrichment of heavy metals in clays (El Ghobary and Latouche 1986). In the Dobczyce Reservoir at Station 7 in the 3–10 cm layer a high percentage of coarse fraction was noted. This was connected with the soil particles which were found in the sediment samples. It should be noted that the relations between the content of Cd, Pb, Mn, and Cu and organic matter and clay silty or clay fractions were recorded mainly in the lower layer of sediments of this reservoir. It may suggest that in the upper layer of the sediment some other physical or chemical parameter affects the content of heavy metals.

The study of the mobility of heavy metals in the sediments of the Dobczyce Reservoir showed higher mobility of Cd, Mn, and Zn than of Pb, Cu, and Fe. These results are similar to those obtained by Helios Rybicka (1986). She studied the phase specific bounding form of heavy metals in the sediments of the River Vistula. On the basis of the mobilization behaviour of metals she divided them into two groups: (1) mobile elements such as Cd, Mn, and Zn, and (2) metals strongly bound to the sediment particles such as Pb, Cu, Cr, and Fe.

The results demonstrate that the mobility of some heavy metals in the sediment of the Dobczyce Reservoir seems to be affected by the redox conditions of the overlying waters. These differed in the studied period (reductive in July and oxidative in November). The content of dissolved oxygen in the overlying water ranged from 1.6 to 4.2 mg L^{-1} in July and from 6.2 to 8.8 mg L^{-1} in November while pH values ranged from 7.3 to 8.0 (Mazurkiewicz unpubl.). The greater part of manganese was connected with the exchangeable phase under the reductive condition of the overlying water during the summer It is well known that the behaviour of Mn is related to the redox conditions of the medium (Förstner et al. 1986, Fernex et al. 1986). El Ghobary and Latouche (1986) in their study noted that in the sediment, under a highly reductive condition of the overlying waters, a high percentage of Mn was associated with the exchangeable fraction. According to Lu and Chen (1977; cited after Drbal 1991), the release of Mn and Fe from the sediment increases with the increasing reductive properties of the environment. Also Li et al. (1969; cited after El Ghobary and Latouche 1986) pointed out that in the sediment cores, under reductive conditions Mn is mobilized into the pore water and can diffuse into the near-bottom water. The present results also show that at most stations in the sediments Cd, Pb, Cu, and Zn were more mobile under an oxidative condition of the near-bottom water in the autumn. Changes in the redox condition of the near-bottom water from reductive to oxidative increase the mobility of such elements as Cd, Hg, Pb, Cu, and Zn in the sediments (Förstner et al. 1986). According to Lu and Chen (1977; cited after Drbal 1991), with increasing oxidative properties of the environment the release of Cd, Pb, Cu, and Zn from the sediment increases. Helios Rybicka (1991) found that Cd, Pb, Cu, and Zn under reductive conditions are turned into more stable compounds of sediments, e.g. an organic sulphide.

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