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Influence of cadmium and lead partitioning in water and sediment on their deposition in the sediment of a eutrophic dam reservoir

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Abstract

This study was conducted in the submontane and eutrophic Dobczyce Reservoir (southern Poland). Cadmium and lead concentrations in the water and sediment were relatively low. The partitioning coefficient (Kd) indicated that dissolved Cd and Pb dominated in the water column at depths of 1 and 15 m, and that they were present in the particulate phase in near-bottom water. The relation of dissolved Cd and Pb with physical and chemical parameters of the water is discussed. Binding forms of Cd and Pb in the sediment showed that Cd was potentially a more “mobile’ element than Pb; therefore, Cd had probably accumulated in the sediment in considerably lower amounts than Pb (K=8400 and K=33000, respectively).

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INTRODUCTION

It has been recognized that the partitioning of Cd and Pb in water plays a fundamental role in their transport in aquatic ecosystems. This has been described in detail in rivers (Förstner 1986, Golimowski et al. 1990, Samanidou and Papadoyannis 1992, Foster and Charlesworth 1996, Rondeau et al. 2005) and lakes (Sigg 1985, Sigg et al. 1991, Kleeberg and Schubert 2000, Taillefert et al. 2000, Nguyen et al. 2005), but rarely in dam reservoirs (Polukhina et al. 1998, Quintal et al. 2000, Skwarczek and Helios-Rybicka 2004).

Spatial and temporal changes in element concentrations in river water depend on changes in constituent inputs and discharge (Laureano and Navar 2002). During transport, environmental changes (i.e., properties of the particle's surface, pH, Eh, salinity, concentration of organic and inorganic complexing agents affect the element distribution between dissolved and particulate phases (Förstner, 1986; Sigg et al. 1991, Webster et al. 1998, Abate and Masini 2002, Gouvea et al. 2005). The dominant phase in which Cd and Pb occur in unpolluted or polluted river water is not clear. According to Förstner (1986), dissolved Cd dominated in polluted rivers, due to a higher concentration of complexing agents, while in less polluted systems, particulate Cd dominated. According to Audry et al. (2004), in polluted rivers (Garonne River, France) Cd and Pb were dominant in the particulate phase. Cadmium and lead can form various complexes in soft water. Cadmium primarily occurs with chloride, hydroxide, sulfide or cyanide, while Pb primarily occurs with hydroxide, chloride, or phosphate. Bicarbonate and cyanide rarely form complexes with lead (Quintal et al. 2000).

A part of the trace elements deposited in bottom sediment can be remobilized under changing environmental conditions. The binding strength of metals with different solid phases can be determined using operationally defined sequential extraction procedures. The methods developed by Tessier et al. (1979), or variations of this procedure, have been used in a wide range of hydrological and limnological studies to estimate the potential mobility of metals (Dawson and Macklin 1998, Loska et al. 2000, Głażewski 1991, Sobczyński and Siepak 2001, Fytianos and Lourantou 2004).

The aim of the present study, conducted in a submontane and eutrophic dam reservoir (Dobczyce Reservoir, southern Poland), was to determine:

- the Cd and Pb partitioning in the water,
- the operationally defined Cd and Pb phase specific binding form in the bottom sediment
- the influence of Cd and Pb partitioning in water and sediment on their accumulation in the sediment.

STUDY AREA

The submontane and eutrophic Dobczyce Reservoir (49° 52’N, 20° 02’E, alt. 270 m) was built on the Raba River (Wisła basin, southern Poland) in 1986, as a drinking water reservoir for the greater Cracow area. The reservoir has an area of 9.85 km^2, a volume of 108 Gl, and a mean depth of 11.0 m (max. about 27 m) at the standard damming level (269.9 m a.s.l.) (Amirowicz 1998). Mean water residence time is equal to 0.34 yr. The Raba River supplies 88.6% of the total inflow, according to Mazurkiewicz-Boroń (2002). The reservoir is currently dimictic in its lower, deeper part – the Dobczyce Basin. Ranges of the chosen physical and chemical parameters of the water in the Dobczyce Basin from April to September 1998 are presented in Table 1. Their detailed description was given by Szarek-Gwiazda and Mazurkiewicz-Boroń (2002) and Mazurkiewicz-Boroń (2002). The summer of 1998 was very rainy and may be

Table 1

Ranges of selected physical and chemical parameters in the water column of the Dobczyce Reservoir in 1998

	Depth (m)		
Parameter	**1**	**15**	**25**
Conductivity (μS cm^{-1})	269-291	251-294	245-300
pH	8.3-9.0	7.8-8.5	7.6-8.4
Dissolved O_2 (mg O_2 dm^{-3})	8.6-12.4	2.2-11.9	1.2-11.3
CO_2 (mg dm^{-3})	0-3.2	0-10	0.5-15
Alkalinity (°N)	5.3-6.3	4.9-6.6	4.8-7.2
Sulphate (mg dm^{-3})	13.8-27.6	20.2-27.6	21.0-31.7
N-NO_3 (mg dm^{-3})	0.7-1.6	0.8-1.7	0.5-1.7
N-NH_4 (mg dm^{-3})	0.22-0.33	0.21-0.23	0.23-0.87
PO_4 (mg dm^{-3})	0.03-0.07	0.01-0.08	0.01-0.06
Ca (mg dm^{-3})	37.7-42.5	33.6-42.9	9.3-43.2
Mg (mg dm^{-3})	6.2-7.7	6.5-7.4	6.3-21.5
COD (mg O_2 dm^{-3})	2.0-2.6	1.7-2.5	1.7-5.7
BOD_5 (mg O_2 dm^{-3})	1.1-9.0	0.6-8.3	0.8-7.7
Suspended matter (mg dm^{-3})	3.8-58.5	1.8-60.7	7.2-116.2

called a “wet” season. Higher quantities of suspended matter were found in the near-bottom water of the reservoir from the summer months until November. Mixing of water occurred in April and October, while stratification began in May and finished at the end of September. The water was alkaline and well oxygenated in winter, during spring and autumn mixing, and in the epilimnion during summer stagnation. In the near-bottom water, oxygen depletion was observed from June to the end of September. The metalimnion occurs between the depths 6-8 m. In the sediment of the Dobczyce Reservoir, silty and clay fractions predominate, and the organic matter content is low (4.8-8.4%; Szarek-Gwiazda and Mazurkiewicz-Boroń 2002).

There is no large industrial plant in the catchment basin of the Raba River, and contamination occurs primarily from municipal sewage from three small towns (less than 18,000 of inhabitants) as well as from waste water from villages (with no sewage systems) lying in the surroundings of the reservoir. An earlier study by Szarek-Gwiazda (1998 a,b) identified slight contamination of the water and sediment of the reservoir by Cd, Pb, Cu and Zn.

MATERIAL AND METHODS

Sample collection

Water samples were taken from the water column (depths: 1m - epilimnion, 15 m - upper layer of the hypolimnion, and 1 m above the bottom – (ca. 25 m) in the near-bottom water) at Station 3, located in the Dobczyce Basin (depth: ca. 26 m) about 200 m from the dam, from April to October (except for July) in 1998 (Fig. 1). The total concentrations of Cd and Pb, and the partitioning between dissolved and particulate phases, were determined for each sample. Water samples were stored in 1 l polyethylene bottles.

In order to calculate the coefficient of Cd and Pb accumulation in the sediment on the same dates and at the same station, sediment samples (0-3 cm layer) were collected with a polyethylene corer (diameter 4 cm) into plastic cups. The total metal concentrations were analyzed. Sediment samples were also taken from Stations 1, 2, and 4 on 19 May and 12 August 1998. In all samples collected on these dates, total Cd and Pb concentrations and phase-specific binding forms of Cd and Pb were determined.

Analytical methods

Water samples were filtered through glass fiber filters (Whatman GF/C 0.45 µm) within a few hours after sampling. 1 l of both unfiltered and filtered water was conserved with HNO_3 of high quality (3 ml acid per 1 l of water). As the concentrations of the microelements in the water samples were much lower than

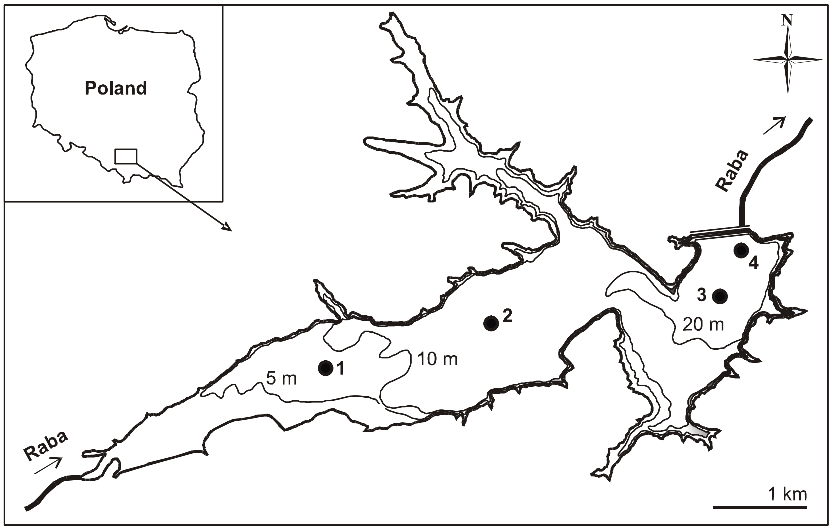

Fig. 1. The study sampling station in the Dobczyce Reservoir.

the ASA-technique detection limits, samples were pre-concentrated by evaporation. The residue was placed in a 10 ml volumetric quartz flask and filled to the mark with double-distilled water. All samples were collected and analyzed in duplicate.

Samples of sediment used for total Cd and Pb determination were dried at 105°C for ≥ 24 hr, and then homogenized using the Planetary Mill "Pulverisettle 5" with teflon grinding balls. Approximately 0.5 g of dry sediment sample was digested with 15 ml conc. HNO_3 in tubes on a heated block of a Tecator Digestion System 12 in conjunction with an Autostep 2000 controller set to 120°C for 2 hr. After digestion, the concentration in the tubes was filtered through a 0.45 µm filter into a 50 ml volumetric quartz flask and filled to the mark with double-distilled water.

Sediment samples used for the determination of metal partitioning were gently hand-ground to break up aggregates. Analyses for the phase-specific binding form of Cd and Pb in the sediment were carried out according to the method of Förstner and Calmano (1982). Six fractions of operationally defined phase-specific binding forms (F1 – exchangeable, F2 – carbonate, F3 – easily reducible, i.e. Mn oxide, amorphous Fe hydroxides, F4 – moderately reducible, i.e. mainly poorly crystalline Fe oxy-hydroxides, F5 – organic/sulphides, and F6 – residual) were analyzed. These fractions were extracted in the following steps:

F1 – The sediment sample (0.5 g dry weight) was extracted by 2 h of shaking with 1 M ammonium acetate (CH_3COONH_4), pH 7.0, at room temperature with a solid/solution ratio of 1:20.

F2 – The residue from F1 was leached by 5 h of shaking with 1 M sodium acetate (CH_3COONa) adjusted to pH 5.0 with acetic acid, at room temperature and with a solid/solution ratio of 1:20.

F3 – The residue from F2 was leached by 12 h of shaking with 0.1 M hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) adjusted to pH 2.0 with HCl, at room temperature and with a solid/solution ratio of 1:100.

F4 – The residue from F3 was extracted by 24 h of shaking with 0.2 M ammonium oxalate $(NH_4)_2C_2O_4$ and 0.2 M oxalic acid $H_2C_2O_4$; adjusted to pH 3.0 with HNO_3, at room temperature with a solid/solution ratio of 1:100.

During extractions 1–4, the samples remained in the centrifuge vessels. After each extraction, the solutions were centrifuged with 3500 rpm and then filtered through a 0.45 μm mesh filter.

F5 – The residue from F4 was transferred into a 100-ml beaker; 30% H_2O_2 was added, and digested at 85 ^{o}C. The addition of H_2O_2 was repeated until the solution stopped bubbling. Then the solution was evaporated until nearly dry. 50 ml of 1 M ammonium acetate was then added and the solution was shaken for 2 h. After shaking, the solution was centrifuged.

F6 – The residue from F5 was digested with 65% nitric acid (HNO_3) for 2 h, at 120^{o}C and with a solid/solution ratio of 1:100.

Cadmium and lead concentrations were determined using a Perkin - Elmer 403 atomic absorption spectrophotometer equipped with a Graphite Furnace (HGA - 74). Analysis of blank samples was conducted to check the purity of reagents. All analyses were corrected for blanks. In order to estimate the accuracy of the sequential extraction scheme employed, the sum of concentrations from the six steps was compared with values obtained for the total Cd and Pb concentrations. The following agreement was found: Cd 89-108%, Pb 96-112%.

Statistics

The partitioning coefficient (Kd) was calculated as the ratio of the concentration of the element in the particulate to the dissolved phases for the studied water depth. The cumulation coefficient (K) was calculated as the ratio of the mean element concentration in sediment to the mean element concentration in water.

RESULTS

Water

Cadmium and lead concentrations in the water of the Dobczyce Reservoir were rather low. Their vertical variability changed throughout the studied period (Figure 2). Cadmium concentrations showed little vertical variability (CV - 6.9%)

during the spring mixing (April) and in May, but were observed to be higher during stagnant periods(CV: 42.5-93.3%). During this time, Cd concentration was lower at the depths of 1 and 15 m, and higher in the near-bottom water (up to 0.32 µg l^{-1} in September). High vertical variability in Cd concentrations was also found during autumn mixing (October) with the highest concentrations in the epilimnion.

Lead concentration showed little vertical variability during both the spring mixing (April) and in May (Figure 2). Greater vertical variability occurred from August to October when Pb concentration was lower in the epilimnion and the upper layer of the hypolimnion, and higher in the near-bottom water.

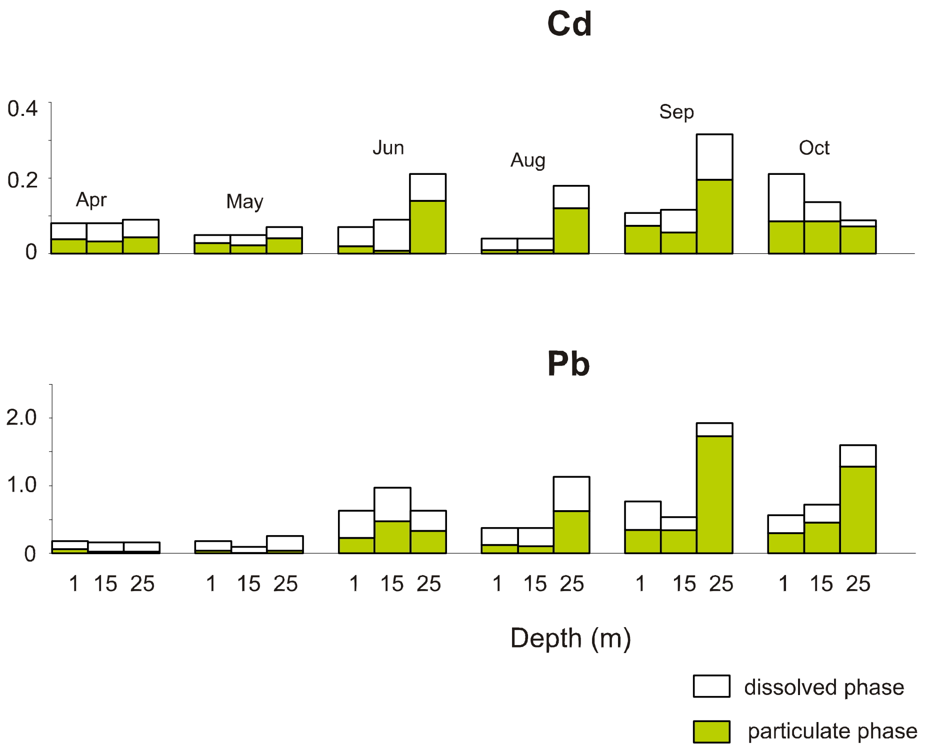

Fig. 2. Partitioning of Cd and Pb between dissolved and particulate phases (in: µg l^{-1}) in the water column (depths: 1 m - epilimnion, 15 m - upper layer of the hypolimnion, and 25 m - 1 m above the bottom) at Station 3, located in the Dobczyce Basin, in 1998.

Values of the partitioning coefficient for Cd and Pb are given in figure 3. Overall, dissolved Cd dominated in the epilimnion (1 m) and upper layer of the hypolimnion (15 m), while Cd in particulate phase dominated in the near-bottom water. Particulate cadmium was only dominant at a depth of 1 m in May and September, and at a depth of 15 m in October. Dissolved Pb dominated in the whole water column from April to June (Fig. 3). An increase in the concentration of particulate Pb was found in the near-bottom water in August, at a depth of 15 m in September and October, and at 1 m in October. In the annual median values of the partitioning coefficient (Kd), Cd and Pb dominated in the dissolved phase at the depths of 1 and 15 m (Kd for Cd was 0.8 and 0.7, and for Pb, 0.5 and 0.7, respectively), and in the particulate phase in the near-bottom water (Kd: 1.8 for Cd and 1.2 for Pb).

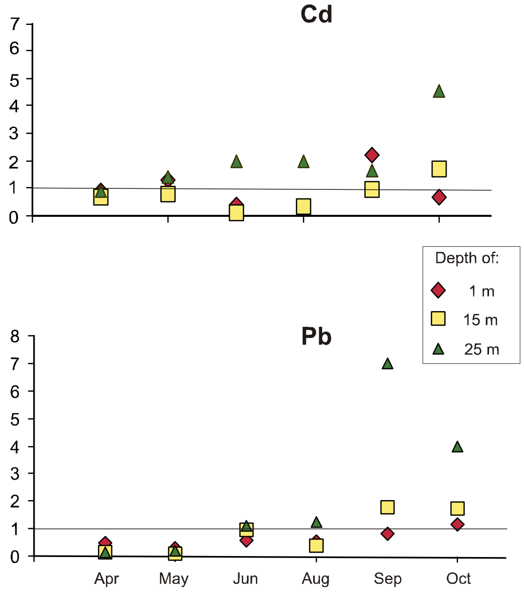

Fig. 3. Partitioning coefficient (Kd) of Cd and Pb in the water column (depths: 1 m - epilimnion, 15 m - upper layer of the hypolimnion, and 25 m - 1 m above the bottom) at Station 3, located in the Dobczyce Basin, in 1998.

Correlation coefficients of Cd and Pb concentrations with some water column parameters were calculated (Table 2). The content of dissolved Cd was positively correlated with the concentration of PO_4 and Ca (depth of 1 m), CO_2 (depth of 1 m, and in the near-bottom water), N-NH_4 and COD (near-bottom water), and negatively correlated with pH (depth of 1 m and in the near-bottom water) and the amount of dissolved oxygen (near-bottom water). The content of dissolved Pb was negatively correlated with the pH (depth of 15 m), the amount of dissolved oxygen (the depths of 1 m and in the near-bottom water), and PO_4 concentration (the near-bottom water). The content of particulate Cd was positively correlated with Mn and Fe concentrations in the near-bottom water (r=0.71 and r=0.79, respectively). Particulate Pb content was positively correlated with the content of Fe (r=0.77), and the quantity of suspended matter (r=0.83).

In mean annual concentrations, ca. 53% of the total amount of Cd and 40% of Pb were found in the particulate phase in the water of the Dobczyce Reservoir. The above results show that Cd tends to accumulate in the reservoir bottom sediment to a higher degree than Pb.

Table 2

Correlation coefficients between dissolved Cd and Pb and chosen physical and o-chemical parameters in the water column of the Dobczyce Reservoir in 1998, calculated for Station 3 (only significant values are given)

	Depth (m)	pH	Dissolved O_2 (mg O_2 dm^{-3})	Sulphate (mg dm^{-3})	PO_4 (mg dm^{-3})	N-NH_4 (mg dm^{-3})	CO_2 (mg dm^{-3})	Ca (mg dm^{-3})	COD (mg O_2 dm^{-3})
Cd dissolved	1	-0.78	ns	ns	0.55	ns	0.95	0.74	ns
	15	ns	ns	ns	ns	ns	ns	ns	ns
	25	-0.82	-0.73	ns	ns	0.81	0.73	ns	0.81
Pb dissolved	1	ns	-0.70	ns	ns	ns	ns	ns	ns
	15	-0.57	ns	ns	ns	ns	ns	ns	ns
	25	ns	-0.55	ns	0.59	ns	ns	ns	ns

ns – not significant

Sediment

Sediment Cd and Pb concentrations are presented in Table 3. Cd and Pb concentrations were relatively low throughout the study. There were considerable differences in Cd concentrations between Stations 1-4 as well as in Station 3 in the studied period.

Table 3

Cadmium and lead concentrations (µg g^{-1} dry weight) in the 0-3 cm layer of bottom sediment in the Dobczyce Reservoir at Station 3 (from April to October) and at Stations 1-4 (on 19 May and 12 August)

	Cd		**Pb**	
	Stadion 3	Stations 1-4	Stadion 3	Stations 1-4
Min	0.5	0.4	12.6	11.9
Max	1.6	1.6	30.8	19.6
Mean	1.2	0.9	19.8	15.3
SD	0.5	0.4	8.0	2.5

The binding forms of Cd and Pb in the sediment are presented in figure 4. In May, Cd was distributed in a similar manner at each sampling station. Similar quantities of Cd were bound in three fractions: exchangeable, carbonates and easily reducible. In total, ca. 50% of Cd was associated with these fractions. The largest percentage of Cd was bound in the organic/sulphidic phase (31-37%).

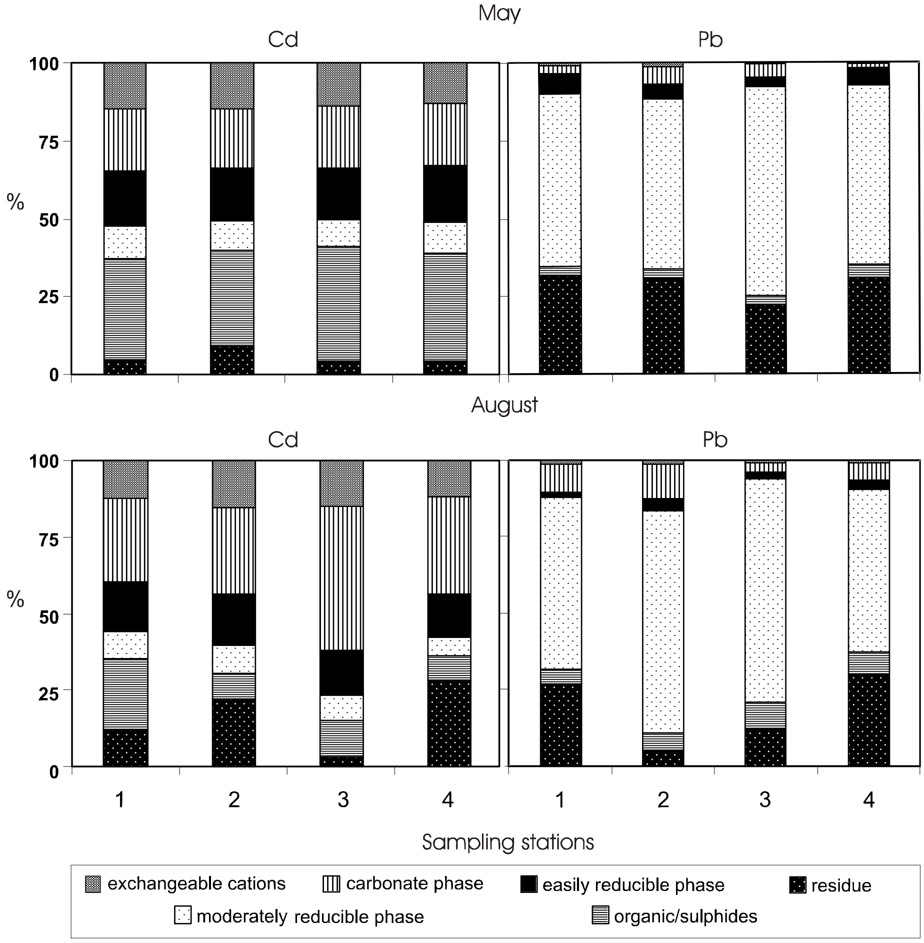

Fig. 4. The phase-specific binding form of Cd and Pb in the upper layer (0-3 cm) of the bottom sediment (Station 1, 2, 3, and 4) of the Dobczyce Reservoir in May and August 1998.

Residual cadmium ranged from 4.3 to 9.2%. In August, greater differences were found between sampling stations. Cadmium was present predominantly as carbonate. An increase in the residual Cd content (to 28.1%) and a decrease in the organic/sulphidic fraction was found in August compared to May. An increase in the Cd content in carbonates at Station 3 was found compared to the remaining stations.

Lead behaves differently than Cd (Fig. 4), and was distributed primarily in the moderate reducible phase of Fe/Mn oxides and the residual in the sediment both in

May and August. 77-89% of the total Pb was bound in these fractions. A minor proportion of Pb was associated with the exchangeable fraction (up to 2%). Lead partitioning in the sediment showed small differences between sampling stations in May, and greater differences in August. Generally, increases in the Pb carbonate fraction (with the exception the Station 4) and organic/sulphide fraction were found in August compared to May. At stations 2 and 3, an increase of Pb in the moderate reducible phase of Fe/Mn oxides, accompanied by a decrease in the residual (compared to May) was also recorded.

The cumulation coefficient (K) of trace elements in the sediment of the Dobczyce Basin was found to be the following: Cd (K=8400) and Pb (K=33000).

DISSCUSION

Water

Cadmium and lead concentrations showed considerable vertical differentiation during the summer, which was connected with the dimictic character of the lower part of the Dobczyce Reservoir. Elevated concentrations of Cd and Pb in the near-bottom water can be attributed to element precipitation from the water column, elements diffusing from the sediments into the overlying water, resuspension, and typical dam reservoir water movement. Precipitation was high during the summer of 2005, and discharge of the Raba River was elevated (Materek 2000). A sharp increase in the concentration of other elements (Fe, Mn, Cu), as well as in suspended matter in the near-bottom water of the Dobczyce Reservoir was observed during this period (Szarek-Gwiazda and Mazurkiewicz 2002, Szarek-Gwiazda 2005). During the “dry” summer season, Cd and Pb concentrations were lower in the near-bottom water of the Dobczyce Reservoir (Szarek-Gwiazda 1998a). Great vertical differences in the Cd and Pb concentrations were also found during autumn mixing. However, because different processes govern the cycling of Cd and Pb in aquatic environments, their vertical profiles were different.

The results demonstrated differences in Cd and Pb partitioning between the dissolved and particulate phases in the surface and near-bottom water of the Dobczyce Reservoir. Similar results were also found by Quintal et al. (2000) in the Jose Antonio Reservoir, Mexico.

Results indicated that Cd and Pb were present predominantly in the dissolved phase in the epilimnion and upper layer of the hypolimnion of the Dobczyce Reservoir, while a higher fraction was found in the particulate phase in the near-bottom water. The geochemical pathway of dissolved Cd in Dobczyce Reservoir water was mainly related to inorganic (PO_4^{2-}) ligands, organic matter (expressed as COD), carbon cycling, pH, and redox conditions. The relation between dissolved Cd and PO_4 may indicate anthropogenic origins, i.e. discharge from municipal waste compost or input via phosphate fertilizers, which plays a particularly critical role in soil contamination (Förstner 1986, Sager 1995). Transport of dissolved Cd with organic matter (COD) played an important role in the reservoir. The binding strength of Cd (II) with organic ligands is much smaller than

those of Pb (II) (Cao et al. 1995, Abate and Masini 2002). According to Dai et al. (1995), Cd is a complex with low molecular weight –organic material. The relation of Cd with Ca and CO_2 indicated that its cycling was related to carbon cycling (CO_2–H_2CO_3 –HCO_3^-) in the water column. The negative correlation of Cd and Pb with pH and redox conditions may indicate that their cycling was related to redox sensitive elements (Mn/Fe) in the near-bottom water. A positive correlation between the content of particulate Cd and the quantities of Mn and Fe in particulate phase confirmed this suggestion. It is well known that Pb binds preferentially to oxides and other O-donors associated with particles (Taillefert and Gaillard 2002). An elevated amount of Cd in particulate phase at a depth of 1 m was found in April during an algal bloom (Pociecha and Wilk-Woźniak 2005). This indicates an important role for biological particles in Cd removal from the water column. A similar phenomenon was also observed by Sigg (1985) in lake environments.

The correlation coefficients did not show any other significant relationships between dissolved Pb and chemical parameters that would indicate that other parameters govern its distribution in the water column. Lead has a high tendency towards the formation of stable complexes with dissolved and colloidal organic compounds in soft water (Muller 1998). In the eutrophic Dobczyce Reservoir, primary productivity may be a source of largely colloidal and dissolved ligands. Such a phenomenon was found in the Clyde Estuary (England), where the colloidal fraction retains the majority of Pb – binding ligands (Muller 1998). Stability constants of organic Pb complexes are similar to those of Cu with organic ligands, and much higher than those of organic Cd and Zn complexes (Muller 1998).

Mean annual concentrations of Cd (ca. 53% of the total amount) and Pb (ca. 40%) in particulate phase in the water of the Dobczyce Reservoir show that Cd tends to be accumulated in the reservoir bottom to a higher degree then Pb.

Sediment

The sediment concentrations of Cd and Pb were relatively low, and typical for slightly polluted water bodies (Górniak et al. 1993, Klavins et al. 1998). The phase-specific binding form of metals in the sediment of the Dobczyce Reservoir indicated that Cd was a highly mobile element, whereas Pb was combined more strongly with solids. The metals behave differently in the sedimentary and diagenetic environment, and thus have different potentials for re-mobilization and uptake by biota. A considerable amount of Cd (up to 15% of the total) was bound to exchangeable ions, potentially the most mobile fraction (Kersten and Förstner 1989) in the Dobczyce Reservoir sediment. Carbonate played an important role in Cd accumulation in the sediment, especially later in the stagnant period (August; up to 47% of the total). This confirms the results of other studies, such as Helios-Rybicka (1986), Schintu et al. (1991), and Kern and Westrich (1998). Up to 18% of Cd was associated with the easily reducible fraction in the Dobczyce Reservoir. An increase in the reducing conditions at the water-sediment interface may result in dissolution of Mn-Fe (hydr)oxides, promoting release of Cd to the pore water and then into the overlying water column, or its immobilization as long as the sediment remains reducing. Considerable quantities of Cd associated with exchangeable ions, carbonate, and the easily reducible fraction of Fe-Mn oxides, confirmed data from the literature that states that Cd is a relatively mobile element in oxic sediments (Förstner 1986, Dawson and Macklin 1998). Organic matter played an important role in the binding of Cd in the sediment (up to 37% in the organic/sulphide phase) of the Dobczyce Reservoir, primarily in May following an algal bloom in April (E. Wilk-Woźniak – unpubl.observations). Cadmium fixation by organic matter in the sediment is well documented (Schintu et al. 1991, Sobczyński et al. 1997, Van den Berg et al. 1998). The degradation of organic matter may result in post-depositional remobilization of Cd (Sobczyński and Siepak 2001, Van den Berg et al. 1998). Sulphides are recognized as important scavengers for Cd and Pb in anoxic sediments, thus reducing their bioavailability (Van den Berg et al. 1998). In the anoxic sediment of the Neckar River (Germany), which is heavily polluted by industrial and municipal discharge, 64-81% of Cd and 36-67% of Pb was bound in the organic/sulphidic fraction. An increase in the mobility of Cd and Pb bound to sulphides in the sediment of the Dobczyce Reservoir may ensue when redox conditions change from anoxic to oxic (e.g., during autumn mixing).

A large fraction of Pb was present in relatively immobile phases in the sediment of the Dobczyce Reservoir, e.g. the moderately reducible phase of Fe/Mn oxides and the residual. The data from Pb partitioning in different aquatic environments (Głażewski 1991, Dawson and Macklin 1998) indicates that the hydrous oxides of Fe and Mn are important as scavengers of Pb in freshwater sediments. The residual fraction, composed of detrital silicate minerals and resistant sulphides (Tessier et al. 1979), was also an important carrier of Pb. Lead bound in the residual phase is unlikely to be reactive during sedimentation and diagenesis, and thus has little potential bioavailability. Similarly, partitioning of Pb in the sediment was also found in other, rather unpolluted water bodies, such as Góreckie Lake (Wielkopolski National Park, Poland) (Sobczyński et al. 1997), Długie Lake (Poland) (Głażewski 1991), and 11 lakes in Latvia (Klavins et al. 1998). However, in highly polluted sediments, Pb may also be combined in more mobile forms, i.e. ion exchangeable, carbonate and oxy-hydroxy fractions, because the surplus of metal contaminants introduced into the aquatic system from anthropogenic activities usually exists in relatively unstable chemical forms, and should, therefore, be more accessible to short- and mid-term geochemical processes (Calmano and Förstner 1983). In the extremely polluted Rio Sarraxinus River, which drains the mine area of Funtana Raminosa (Italy), 53% of the total Pb was bound in the exchangeable-carbonate phase (Schintu et al. 1991). In the Aire River (England), heavily contaminated by industrial and domestic pollution, up to 50% of the total Pb was found in the exchangeable phase (Dawson and Macklin 1998).

Obtained results showed that Cd was a ‘mobile’ element, and therefore, a large portion may be released from the sediment of the Dobczyce Reservoir into the overlying water. In contrast, Pb was rather ‘immobile’ and thus had little potential for remobilization. Lead, which was an immobile element, had accumulated in a considerably higher amount than Cd (K=33000 and K=8400, respectively) in the sediment of the Dobczyce Basin. Therefore, it seems that the most important factor influencing the level of metal deposition in the sediment was the strength of their binding form. Lead, which has little potential for remobilization, was deposited in the sediment to a considerably higher degree than “mobile” Cd.

CONCLUSION

This study documented cadmium and lead partitioning in the water and sediment of the submontane and eutrophic Dobczyce Reservoir (southern Poland). Cadmium and lead were present predominantly in the dissolved phase at depths of 1 and 15 m, and in the particulate phase in the near-bottom water. Parameters such as inorganic (PO_4^{2-}) ligands, organic matter (expressed as COD), carbon cycling, pH, redox conditions, and particulate Fe and Mn concentrations influenced Cd transport in the water column. Transport of Pb was probably primarily related to Fe concentrations. The binding form of Cd and Pb in the sediment indicated that Cd was a potentially more ‘mobile’ element then Pb; thus, a greater part of Cd may be released from the sediment. Cadmium was accumulated in the sediment in considerably lower amounts than Pb (K=8400 and K=33000, respectively). The element that showed higher ‘mobility’ had lower levels of accumulation in the sediment. This conclusion may explain differences in the level of metal accumulation in the sediment.

REFERENCES

Abate G., Masini J.C., 2002, *Complexation of Cd(II) and Pb(II) with humic acids studied by anodic stripping voltammetry using differential equilibrium functions and discrete site models*, Organic Geochemistry, 33(10): 1171-82

Amirowicz A., 1998, *Consequence of the basin morphology for fish community in a deep-storage submontane reservoir*, Acta Hydrobiol., 39: 35-56

Audry S., Shafer J., Blanc G., Bossy C., Lavaux G., 2004, *Anthropogenic components of heavy metal (Cd, Zn, Cu, Pb) budgets in the Lot-Garonne fluvial system (France)*, Applied Geochemistry, 19: 769–86

Calmano W., Förstner U., 1983, *Chemical extraction of heavy metals in polluted river sediments in Central Europe*, The Science of the Total Environment, 28: 77-90

Cao Y., Conklin M., Betterton E., 1995, *Competitive Complexation of Trace Metals With Dissolved Humic Acid*, Environmental Health Perspective, 103: 29-32

Dai M., Martin J-M., Cauwet G., 1995, *The significant role of colloids in the transport and transformation of organic carbon and associated trace metals (Cd, Cu and Ni) in the Rhône delta (France)*, Marine Chemistry, 51: 159-75

Dawson E.J., Macklin M.G., 1998, *Speciation of Heavy Metals in Floodplain and Flood Sediments: A Reconnaissance Survey of the Aires Valley, West Yorkshire, Great Britain*, Environmental Geochemistry and Health, 20: 67-76

Helios Rybicka E., 1986, *The role of clay minerals in the fixation of heavy metals in bottom sediments of the upper Wisła River system*, Kraków, Wyd. AGH, Geologia, Zesz. Nauk. 32, pp. 121

Förstner U., Calmano W., 1982, *Chemical forms of heavy metals in dredged material [Bindungsfirmen von Schwermetallen in Baggerschlämmen]*, Vom Wasser, 59: 83-93

Förstner U., 1986, *Metal speciation in solid wastes - factors affecting mobility*, [in:] *Speciation of Metals in Water, Sediment and Soil Systems*, Landner W. (ed.), Springer-Verlag, Berlin-Hiedelberg-New York-London-Paris-Tokyo, pp. 13-40

Foster I.D.L., Charlesworth S.M., 1996, *Heavy metals in the hydrological cycle: trends and explanation*, Hydrological Processes, 10: 227-61

Fytianos K., Lourantou A., 2004, *Speciation of elements in sediment samples collected at lakes Volvi and Koronia, N. Greece*, Environment International, 30: 11-17

Gouvea S.P., Vieira A.A.H., Lombardi A.T., 2005, *Copper and cadmium complexation by high molecular weight materials of dominant microalgae and of water from a eutrophic reservoir*, Chemosphere, 60(9): 1332-39

Głażewski R., 1991, *Chemical forms of Zn, Pb and Cu in the surface layer of the sediment of Gługie Lake in Olsztyn, [Formy chemiczne Zn, Pb i Cu w osadach powierzchniowych Jeziora Długiego w Olsztynie]*, Substancje toksyczne w środowisku, 1: 11-17

Golimowski J., Merks A.G.A., Valenta P.,1990, *Trends in heavy metal in the dissolved and particulate phase in the Dutch Rhine-Meuse (Maas) Delta*, Sci. Total Environ., 92: 113-27

Górniak A., Misztal M., Magierski J., 1993, *Differentiation of the chemical composition of near-bottom waters and bottom sediments of the mesotrophic Lake Piaseczno (Łęczyńsko-Włodawskie Lake District, Poland)*. Acta Hydrobiol., 35: 193-202

Kern U., Li C.C., Westrich B., 1998, *Assessment of sediment contamination from pollutant discharge in surface waters*, Water Science and Technology, 37(6-7): 1-8

Kersten M., Förstner U., 1989, *Speciation of trace elements in sediment*, [in:] *Trace Element Speciation: Analytical Methods and Problems*, Batley, G. (ed.), Boca Raton, CRC Press, pp. 245

Kleeberg A., Schubert H., 2000, *Vertical gradients in particle distribution and its elemental composition under oxic and anoxic conditions in a eutrophic lake, Scharmützelsee, NE Germany*, Arch. Hydrobiol., 148(2): 187-207

Klavins M., Briede A., Parele E., Rodinov V., Klavin I., 1998, *Metal Accumulation in Sediments and Benthic Invertebrates in Lakes of Latvia*, Chemosphere, 36: 3043-53

Laureano J.S.F., Navar J., 2002, *An assessment of stream water quality of the Rio San Juan, Nuevo Leon, Mexico, 1995-1996*, Journal of Environmental Quality, 31(4): 1256-65

Loska K., Wiechula D., Cebula J., 2000, *Changes in the forms of metal occurrence in bottom sediment under conditions of artificial hypolimnetic aeration of Rybnik Reservoir, southern Poland*, Polish Journal of Environmental Studies, 9(6): 523-30

Mazurkiewicz-Boroń G., 2002, *Factors of eutrophication processes in sub-mountain dam reservoirs*, Supplementa ad Acta Hydrobiologica, 2: 1-68

Materek A., 2000. *Hydrology of tributaries and reservoir [Hydrologia dopływów i zbiornika],* [in:] *Dobczyce Reservoir - ecology - eutrophication - protection [Zbiornik Dobczycki – ekologia - eutrofizacja – ochrona],* Starmach J., Mazurkiewicz-Boroń G. (eds) ZBW, PAN, Kraków, 15-35

Muller F.L.L., 1998, *Colloidal/solution partitioning of metal-selective organic ligands, and its relevance to Cu, b and Cd cycling in the Firth of Clyde,* Estuarine, Coastal and Shelf Science 46: 419-37

Nguyen H.L., Leermakers M., Elskens M., De Ridder F., Doan T.H., Baeyens W., 2005, *Correlations, partitioning and bioaccumulation of heavy metals between different compartments of Lake Balaton*, Science of The Total Environment, 341(1-3): 211-26

Petersen W., Willer E., Williamowski C., 1997, *Remobilization of trace elements from polluted anoxic sediment after resuspension in oxic water*, Water, Air and Soil Pollut., 99: 515-22

Polukhina N.I., Dvurechenskaya S.Ya., Sokolovskaya I.P., Baryshev V.B., Anshin G.N., Vorotnikov B.A., 1998, *Some toxic microelements in Novosibirsk reservoir's ecosystem (data XRF SR and AAS techniques).* Nuclear Instruments and Methods in Physics Research A 405, pp. 423-27

Pociecha A., Wilk-Woźniak E., 2005, *Dynamice of phyto- and zooplankton In the submonuntane dam reservoirs with different trophic status,* Limnological Review, 5: 215-21

Rondeau B., Cossa D., Gagnon P., Pham T.T., Surette C., 2005, *Hydrological and biogeochemical dynamics of the minor and trace elements in the St. Lawrence* River, Applied Geochemistry, 20(7): 1391-1408

Sager M., 1995, *Possible trace metal load from fertilizers,* [in:] Proc. of the DIFusePOL'95 Conf., Brno-Prague, Cr, Part I, 117-124

Samanidou V.F., Papadoyannis I.N., 1992, *Study of heavy metal pollution in the waters of Axios and Aliakmon Rivers in northern Greece*, J. Environ. Sci. Health., A27(3): 587-601

Schintu M., Kudo A., Sarritzu G., Contu A., 1991, *Heavy metal distribution and mobilization in sediments from a drinking water reservoir near a mining area,* Water, Air and Soil Pollut., 57/58: 339-49

Sigg L., 1985, *Metal transfer mechanisms in lakes, the role of settling particles*, [in:] *Chemical processes in lakes*, Stumm W. (ed.), John Wiley and Sons, New York-Chichester-Brisbane-Toronto-Singapore, pp. 283-289

Sigg L., Johnson A., Kuhn A., 1991, *Redox conditions and alkalinity generation in a seasonally anoxic lake (Lake Greifen)*, Marine Chemistry, 36: 9-26

Skwarczek M., Helios-Rybicka E., 2004, *Badania hydro-geochemiczne systemu wodnego Jeziora Rożnowskiego [Hydrological and geochemical studies of the water system in Rożnowski lake],* Geologia, 30(2): 207-14

Sobczynski T., Siepak J., 2001, *Speciation of heavy metals in bottom sediments of lakes in the area of Wielkopolski National Park*, Polish Journal of Environmental Studies, 10(6): 463-74

Sobczyński T., Zerbe J., Elbanowska H., Siepak J., 1997, *Chemical Studies of Sediments of the Góreckie Lake*, Archiwum Ochrony Środowiska, 23: 125-36

Szarek-Gwiazda E., 1998a, *Horizontal, vertical and seasonal distribution of heavy metals in the water of a stratified dam reservoir (Dobczyce Reservoir, southern Poland),* Acta Hydrobiol., 40(2): 113-20

Szarek-Gwiazda E., 1998b, *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),* Acta Hydrobiol., 40(2): 121-29

Szarek-Gwiazda E., Mazurkiewicz-Boroń G., 2002, *Deposition of copper in the eutrophic, Submontane Dobczyce Dam reservoir (Southern Poland)- role of speciation*, Water, Air and Soil Pollut., 140(1-4): 203-18

Szarek-Gwiazda E., 2005, *Deposition of Mn and Fe in the eutrophic, submontane dam reservoir – role of speciation,* Oceanological and Hydrobiological Studies, 34(3): 135-39

Taillefert M., Lienemann Ch-P., Gaillard J-F., Perret D., 2000, *Speciation, reactivity, and cycling of Fe and Pb in a meromictic lake,* Geochim. Cosmochim. Acta 64(2): 169-83

Taillefert M., Gaillard J-F., 2002, *Reactive transport modeling of trace elements in the water column of a stratified lake: iron cycling and metal scavenging,* J. Hydrol., 256(1-2): 16-34

Tessier A., Campbell P.G.C., Bisson M., 1979, *Sequential extraction procedure for the speciation of particulate trace metals,* Anal. Chem., 51: 844-51

Van der Berg G.A., Loch J.P.G., van der Heijdt L.M., Zwolsman J.J.G., 1998, *Mobilisation of heavy metals in contaminated sediments in the river Meuse, the Netherlands,* Water Science and Technology, 37: 39-46

Van Ryssen R., Alam M., Goeyens L., Baeyens W., 1998, *The use of flux-corer experiments in the determination of heavy metal re-distribution in and of potential leaching from the sediment*, Wat. Sci. Tech., 37: 283-90

Webster J.G., Swedlung P.J., Webster K.S., 1998, *Trace element adsorption onto an acid , mine drainage iron (III) oxy hydroxy sulfate,* Environmental Science and Technology, 32(10): 1361-67

Quintal I.D.B., Correa H.E.S., Cortés C.G., Pérez P.A., Garcia J.A., 2000, *Determination of cadmium and lead species in the water column of the Jose Antonio Alzate Reservoir, Mexico*, Water Environmental Research, 72: 132-40