DEPOSITION OF COPPER IN THE EUTROPHIC, SUBMONTANE DOBCZYCE DAM RESERVOIR (SOUTHERN POLAND) – ROLE OF SPECIATION

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Abstract. In order to better understand Cu behaviour in the submontane, eutrophic Dobczyce dam Reservoir (southern Poland), speciation measurements of Cu in the water and the sediment were conducted. To investigate the partitioning of Cu in the main components of the sediment, a scheme of VI-step sequential extraction was used. In addition, other physical and chemical parameters of the water, such as temperature, pH, dissolved O_2, nutrients, and suspended particulate matter were determined. Copper content in the water and the sediment was low (1.1–7.4 μg L^{-1} and 5.5–45.4 μg g^{-1}, respectively). In the water Cu was usually present in the dissolved state (with the exception of the near-bottom water). This was probably the main reason of its small accumulation (cumulation coefficient K = 10687.5) in the sediment of the Dobczyce Reservoir. The seasonal variations in Cu contents in the dissolved and particulate phases as well as observed correlations with the physico-chemical parameters of the water are discussed. In the sediment Cu occurred mainly in a strongly bound form. Most Cu found there was in the moderately reducible phase and residual. Therefore, copper (re-)mobilization from the sediment to the water was probably not of importance.

Keywords: copper, dam reservoir, sediment, speciation, water

1. Introduction

Dam reservoirs interrupt the transportation of trace metals in a fluvial system because of the relatively long water residence time. Several studies have shown that trace elements can accumulate there more easily than in running water (Pita and Hyne, 1975; Harding *et al.*, 1981; Reczyńska-Dutka, 1985). For instance, Dervent Reservoir (northern England) accumulated up to about 70% of Zn, 98% of Cd, and 89% of Pb contained in the inflowing water (Harding *et al.*, 1981). On the other hand, the studies of Reczyńska-Dutka (1985) and Szarek-Gwiazda (1999), among others, showed that not all metals accumulate in a dam reservoir at the same rate. Szarek-Gwiazda (1999) found that the submontane Dobczyce dam Reservoir (southern Poland) was not a good deposition place for Cu, Zn, and Fe.

The degree of trace metal accumulation in the reservoir depends on a number of factors, from which the forms of metal occurrence in the water and sediment are very important. Metals are present in water in a number of different forms or

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species, both in dissolved and particulate phase (Förstner and Whittmann, 1983; Batley, 1990; Sigg *et al.*, 1995). Metals in the particulate phase are generally removed at a higher rate from the water column by sedimentation. Their distribution between particles and solution in the water is regulated mainly by physicochemical parameters of the water (e.g. pH, redox potential), biological activity of algae, and chemical properties of a given metal (Salomons and Förstner, 1984; Sigg, 1985; Revis *et al.*, 1989; Batley, 1990; Sigg *et al.*, 1995; Cao *et al.*, 1995). Also in the sediment, metals accumulate in different forms affecting their mobility, e.g. recycling between solution and sediment (Helios-Rybicka, 1991; Sobczyński *et al.*, 1997; Dawson and Macklin, 1998; Klavins *et al.*, 1998). The speciation measurements of heavy metals in the water and sediment can help in better understanding of their transport and geochemical cycling processes as well as in predicting their biological impact.

The previous studies of Szarek-Gwiazda (1998a, b) pointed to a slight contamination of the water and sediment of the reservoir by heavy metals. In order to better understand the role of speciation in Cu deposition in the eutrophic, submontane Dobczyce Reservoir we studied, the speciation of Cu in the water and sediment.

2. Study Area

The Dobczyce Reservoir (49°52′N, 20°02′E, alt. 270 m), typical of the submontane part of the Polish Carpathians, was built on the River Raba (Wisła basin, southern Poland) in 1986, as a drinking water reservoir for the Cracow's agglomeration. It is 10 km in length, has an area of ca. 1000 ha, a mean depth of 11 m (max. 30 m), and a capacity of 99.2×10^6 m^3. The River Raba supplies 88.6% of the total inflow. The average water exchange is 3.6 times a year (Mazurkiewicz, 1988). The reservoir now is eutrophic. This results in algal blooms, usually dominated by diatoms in spring and by cyanobacteria/diatoms in autumn. Green algae may also occur in large numbers but usually in summer (Wilk-Woźniak, 1996). The reservoir is dimictic in its lower, deeper part – the Dobczyce Basin. There, circulation of the water during spring and autumn takes place while in it is stratified summer stratification forms.

There is no large industrial plant in the catchment basin of the River Raba, which is mainly contaminated by the municipal sewage from three small towns (less than 18 000 of inhabitants) as well as by waste water from villages (with no sewage system) lying in the surroundings of the reservoir (Mazurkiewicz, 1996). In spite of the fairly great distance (40 km) from urban and industrial agglomerations, atmospheric precipitation in the area of the reservoir is threatened by emission from the metallurgical industry in Cracow and two power plants. In the atmospheric precipitation in the area of the neighbouring direct catchment of the reservoir (5 sampling points) ca. 20 μg L^{-1} of Cu were found (Turzański and Bik, 1993). Small differences in Cu contents in the atmospheric dust between the eastern (mean

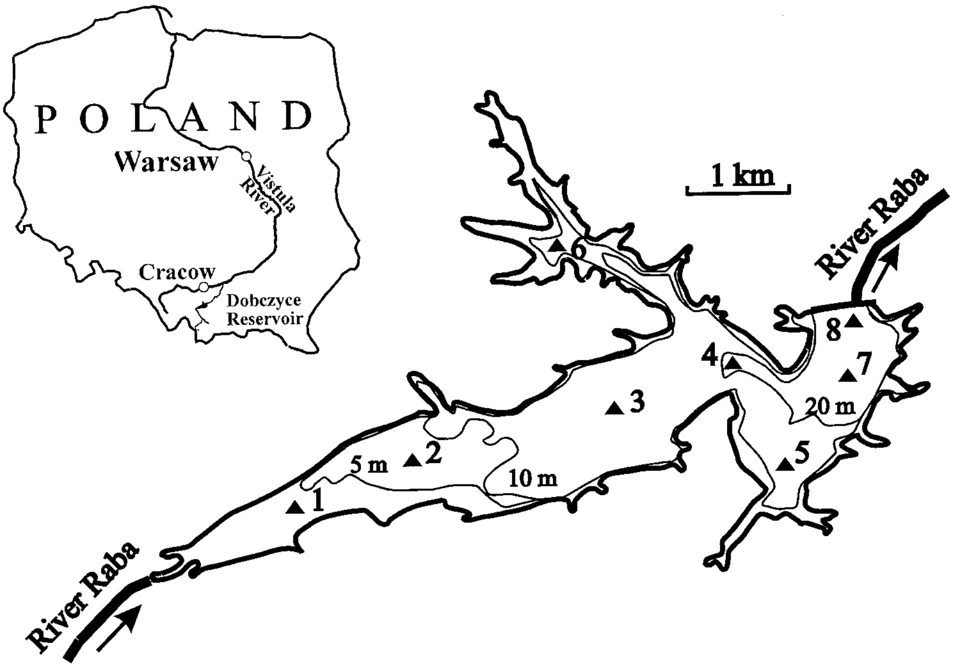

Figure 1. The study area in the Dobczyce Reservoir, 1–8 sampling stations.

8.9 μg L^{-1}; range from 5.4 to 17.6 μg L^{-1}) and the western (mean 8.1 μg L^{-1}; range 4.2–15.1 μg L^{-1}) part of the neighbouring direct catchment of the Dobczyce Reservoir (21 sampling points) were found (Manecki and Tarkowski, 1993).

3. Materials and Methods

3.1. SAMPLE COLLECTION

Samples of water were taken from the water column (depths: 1 m – epilimnion, 15 m – upper layer of the hypolimnion, and 1 m above the bottom – the near-bottom water) from the Station 7 located in the Dobczyce Basin (depth: ca. 26.5 m), about 200 m from the dam, from January to November (except for July) in 1998 (Figure 1). In these samples physico-chemical parameters of the water (temperature, pH, dissolved O_2, NO_3, NH_4, PO_4, suspended matter) as well the partitioning of Cu between the dissolved and particulate phase were determined. The water samples for Cu analyses were stored in 1500 mL polyethylene bottles.

In order to calculate the coefficient of Cu accumulation in the sediment, the samples of sediment (0–3 cm layer) were collected with a polyethylene corer (diameter 4 cm) into plastic cups from Station 7 on the same dates. All polyethylene bottles and plastic cups, used in this study, were cleaned and soaked in 30% HNO_3 for 48 hr and then rinsed twice with double-distilled water.

Sediment samples from the upper layer (0–3 cm) of the sediment were also taken at eight Stations (1–8) in 19 May and 12 August 1998 (Figure 1). Since differences in the deposition rates for Cu in various parts of the reservoir were expected, samples were collected from Stations 1, 2, 3, 4, 7, and 8 located along the main axis of the expected flow direction of the River Raba water across the reservoir, and Stations 5 and 6 located in the more remote part of the reservoir. In each sample total Cu concentration was analysed. In the samples collected from Stations 2, 3, 7, and 8 the phase-specific binding form of Cu in the sediment was determined.

3.2. ANALYTICAL METHODS

3.2.1. *Water*

Water temperature was measured *in situ* with an accuracy of 0.1 °C. The pH was measured with an Orion pH meter (Expandable ion Analyser EA 940). Dissolved oxygen was determined according to the Winkler method (APHA, 1985). In the water samples filtered through GF/F fiberglass filters we analysed nitrates by the hydrozine reduction method, ammonia by the nesslerization method, and phosphorus by the molybdenum blue method. Total suspended solids were obtained by drying the residue retained on the filter to a constant weight at 103–105 °C (APHA, 1992).

To study the Cu partitioning in the water, suspended particulate matter was separated from the water by filtration through a <0.45 μm filter within a few hours after sampling. One L of both nonfiltered and filtered water was acidified to pH 2 with HNO_3 and then 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 analysed in duplicates.

3.2.2. *Sediment*

Samples of sediment used for total Cu determination were dried at 105 °C for $\geq$24 hr, and then homogenized using the Planetary Mill ‘Pulveriset 5’ with teflon grinding balls. Triplicates of approximately 0.5 g of dry sediment samples were 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 content of 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.

Samples of sediment used for the determination of Cu partitioning in the sediment were air-dried. Analyses for a phase-specific binding form of Cu in the sediment were carried out according to the method originally described by Tessier *et al.* (1979) and modified by Förstner and Calmano (1982). Six fractions were obtained. These fractions were operationally defined and obtained as indicated in Table I. The

TABLE I

Sequential extraction scheme for fractionation of Cu in the sediment of the Dobczyce Reservoir (after Förstner and Calmano, 1982). Dry mass of the sediment sample 0.5 g

Step	Metal fraction	Extracting solution	pH	Volume of solution (mL)	Conditions
1[a]	Exchangeable	1 mol L^{-1} CH_3COONH_4	7	10	Shake 2 hr, at room temperature
2[a]	Carbonates	1 mol L^{-1} CH_3COONa + CH_3COOH	5	10	Shake 5 hr, at room temperature
3[a]	Easily reducible phases (Mn oxide, amorphous Fe oxihydroxides)	0.1 mol L^{-1} $NH_2OH{\cdot}HCl$	2	50	Shake 12 hr, at room temperature
4[a]	Moderately reducible phases (mainly poorly crystalline Fe-oxyhydroxides)	0.2 mol L^{-1} $(NH_4)_2C_2O_4$ + 0.2 mol L^{-1} $H_2C_2O_4$	3	50	Shake 24 hr, at room temperature
5[b]	Organic/sulphides	(a) 30% (v/v) H_2O_2	2	15	2 hr, 85 °C
		(b) 1 mol L^{-1} CH_3COONH_4	7	50	Shake 12 hr, at room temperature
6[c]	Residual	65% NHO_3		20	2 hr, 120 °C

[a] – Extractions 1–4: the samples remain in the centrifuges vessels; after extraction the solutions were centrifuged with 3500 rpm; then filtered (mesh 0.45 μm).

[b] – Extraction 5: The residue obtain after step 4 was transferred into a 100 mL beaker; H_2O_2 was added and digested on a sand bath. The procedure (addition of H_2O_2) was repeated three times until the solution finished to bubble. Then the solution was evaporated until nearly dry; ammonium acetate was added and after shaking the solution was centrifuged.

[c] – Digested at 120 °C and centrifuged.

analyses were done in duplicate. All volumetric flasks, were washed and soaked in 30% HNO_3 for 48 hr and then thoroughly rinsed with double-distilled water before analyses. It is known that the acidified hydroxylamine hydrochloride buffer used here can be of advantage for the investigation of processes involved in the diagenetic remobilization and enrichment of metals in Mn/Fe concretions as it indicates the relative availability of metals in the easily-reducible fractions of sediments (Calmano and Förstner, 1983).

Copper concentrations were determined using a Perkin – Elmer 403 atomic absorption spectrophotometer equipped with a Graphite Furnace (HGA – 74). The recommendations mentioned in the graphite furnace manual (Perkin-Elmer, 1977) were taken into consideration for Cu determination using this instrument. The temperature of Cu atomisation was 937 °C. Instrument calibration was performed according to the manufacturer's instructions. Calibration solutions of Cu were prepared from a 1000 mg L^{-1} metal stock solution (purchased from the Central Office of Measures, Warsaw) immediately before analysis. The precision of the instrument and the calibration curve were checked with replicate analyses of calibration solutions at the start and subsequently after every ten samples analysed. Analysis of blank samples was also conducted to check the purity of reagents. All analyses were corrected for blanks. The percentage coefficient of variation of Cu in duplicate water sample analyses ranged from 1.6 to 7.2%, that of total Cu in triplicate sediment sample analyses ranged from 2.4 to 9.4%, and that for Cu extracted from the sediment in duplicate sample analyses (VI-steps extraction) ranged from 2.2 to 7.9% for all analyses. The accuracy and precision of the determination of Cu contents in water samples was validated in a calibration study organised by the Institute of Chemistry, Jagiellonian University (Cracow, Poland). In order to estimate the accuracy of the sequential extraction scheme employed, the sum of single concentrations from the six steps was compared with values obtained for total Cu concentrations. The recovery rates for total Cu concentrations in samples for the six steps were 88–106%.

3.3. STATISTICS

The coefficient of variation (CV) of the content of different Cu fractions at various depths in the water was calculated. Significant differences in Cu contents between the particulate and dissolved phase from various water depths were determined using a nonparametric Wilcoxon's signed-ranks test (Sokal and Rohlf, 1987). The correlation analyses between the Cu content and physico-chemical parameters (NO_3, NH_4, PO_4, suspended matter) in the water were performed using Microsoft Excel software. The accumulation coefficients (K) of Cu in sediment were calculated as a quotient of the mean Cu content in the upper layer (0–3 cm) of the sediment to the mean Cu content in the water. All statistical calculations were performed for the data obtained from the Station 7.

4. Results and Discussion

4.1. PHYSICO-CHEMICAL PARAMETERS OF THE WATER

Figure 2 shows the ranges of physico-chemical parameters of the water in the period January-November 1998. These parameters show the presence of seasonal trends in the water of the Dobczyce Basin (Station 7). In this basin mixing occurred in April and October. Stratification began in May and finished at the end of September.

The pH ranged from 7.6 to 9.0 and was somewhat higher in the epilimnion during summer. It is well known that the pH value in the water of water bodies affects the form in which Cu occurs and the stability of its complexes. Generally, at pH $\leq$ 6 copper occurs as (Cu^{2+}_{aq}), at pH 6–9 as $[CuCO_3]^o_{aq}$, at pH 9–11 Cu is in the form $[Cu(CO_3)_2]^{2-}$, whereas at pH > 13 the form $[Cu(OH)_4]^{2-}$ dominates (Nriagu, 1979). Apparently not all Cu species are equally toxic. Free copper

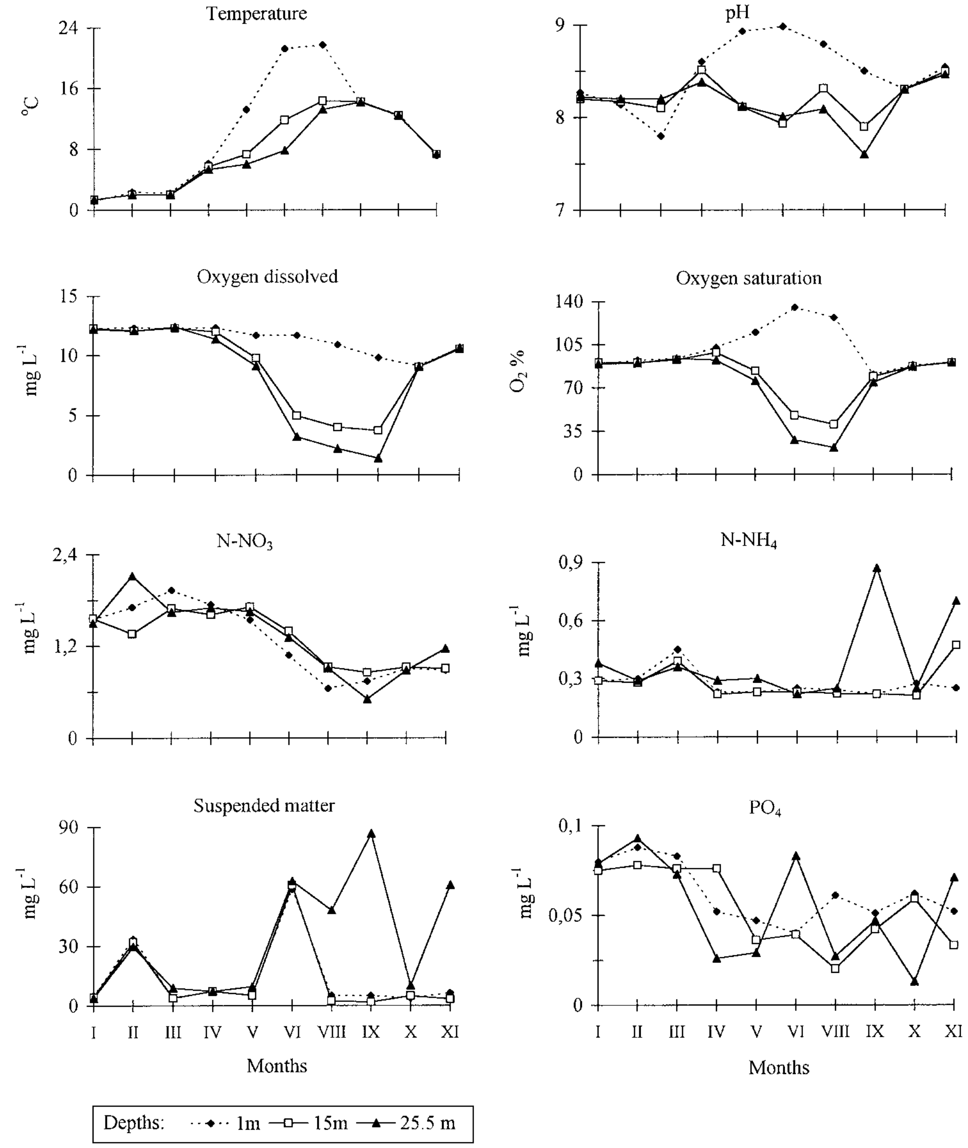

Figure 2. Changes of the physico-chemical parameters of the water (depths: 1 m – epilimnion, 15 m – upper layer of the hypolimnion, and 25.5 m – 1 m above the bottom) at the Station 7 in 1998.

(Cu^{2+}_{aq}) is generally assumed to control the bioavailability and toxicity of copper (Huntsman and Sunda, 1980; Petersen, 1982; Visviki and Rachlin, 1994), although lipid-soluble toxic copper complexes may also be available. Thus, Cu in the water of the Dobczyce Basin occurred mainly in forms which are less toxic for organisms i.e. not in the ionic form.

The oxygen conditions in the Dobczyce Basin were very good in winter and during mixing in spring and autumn, as well as in the epilimnion during the period of summer stagnation. The oxygen saturation of epilimnion was good over the studied year (81–135%). In the near-bottom water oxygen depletion was observed from June to the end of September.

The greatest amount of nutrients (phosphate and nitrate) was found in winter and early spring. This was naturally connected with the development of phytoplankton, the chief consumers of mineral nutrients, which to a greater degree decreases their content in summer than in winter. An increase in phosphate content in June and November can be explained by inputs by the River Raba as well as by redissolution of P from the sediment. The content of $N\text{-}NH_4$ ranged from 0.22 to 0.87 mg L^{-1}. The greatest amount of $N\text{-}NH_4$ was found in the near-bottom water in September, which indicates an increase in reductive conditions of the environment.

In general, the content of suspended matter in the water was low, higher concentrations were found in the near-bottom water in the summer months and in November.

4.2. COPPER IN THE WATER

The content of Cu in the water of the Dobczyce Basin (Station 7) ranged from 1.1 to 7.4 μg L^{-1} (Figure 3). Cu revealed a significant preference for the occurrence in the dissolved phase in the Dobczyce Basin water. Statistical calculations showed that dissolved Cu dominated in the epilimnion ($T = 1$, $p = 0.005$, $N = 10$) and the upper layer of the hypolimnion ($T = 9$, $p = 0.03$, $N = 10$). No significant differences in Cu content between these two phases in the near-bottom water were found. A preference of copper for occurrence in dissolved phase has also been found in other water bodies, such as lake Constance (Sigg *et al.*, 1982) or the eutrophic Lake Greifen (Sigg *et al.*, 1995). Results of studies by Van den Berg *et al.* (1987), Verveij *et al.* (1989), Cao *et al.* (1995), Xue *et al.* (1995), indicate that this preference is mainly caused by a high affinity of Cu for naturally occurring organic ligands and by a great tendency of Cu towards the formation of soluble organic complexes in fresh waters. Such complexes have high stability constants and remain in solution for a long time. According to Van der Berg *et al.* (1987), interaction of Cu with dissolved organic complexing ligands determines the geochemical pathway of Cu. Natural ligands may be either specific ligands released by organisms (e.g. during growth or upon decay of algal material) or degradation products of biological material (Sigg *et al.*, 1995). The presence of high concentrations of ligands in lakes has been linked to the high algal productivity (Bührer and Wasmer, 1992). Therefore, the extent of Cu complexation in a eutrophic lake was higher than that in an oligotrophic one (Sigg *et al.*, 1995). In general, copper has a relatively small affinity towards particles. Hence, a high extent of Cu complexation with organic ligands may also be expected in the eutrophic Dobczyce dam Reservoir, characterised (from 1990) by yearly algal blooms.

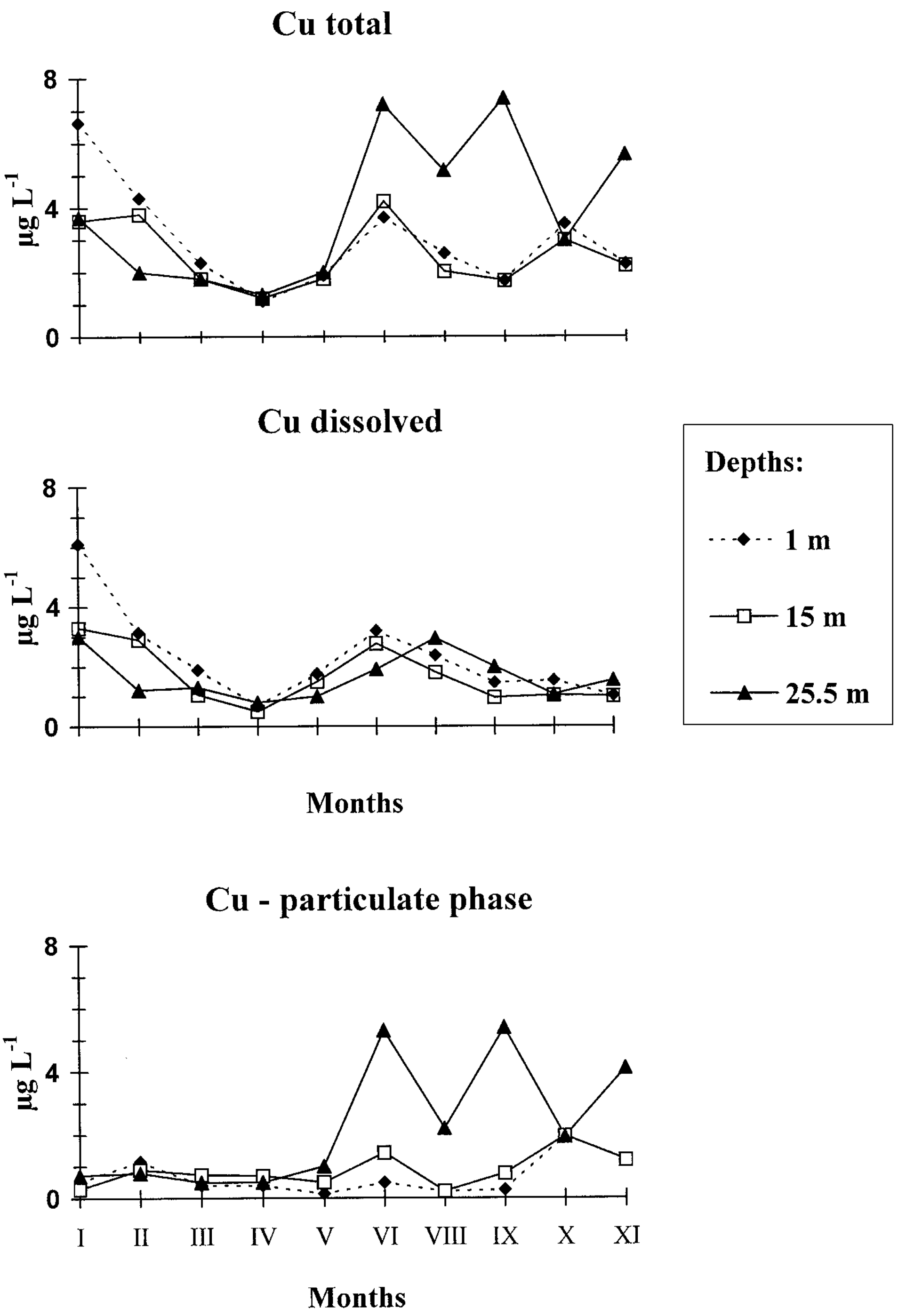

Figure 3. Distribution of different Cu fractions in the water (depths: 1 m – epilimnion, 15 m – upper layer of the hypolimnion, and 25.5 m – 1 m above the bottom) at the Station 7 in 1998.

TABLE II

Mean annual ($\overline{x}$) and coefficients of variation (CV) of Cu contents in the water column at the Station 7 in 1998

Depth	Cu total		Cu dissolved		Cu particulate phase	
	$\overline{x}$ μg L^{-1}	CV %	$\overline{x}$ μg L^{-1}	CV %	$\overline{x}$ μg L^{-1}	CV %
1 m	0.3	53.6	2.3	67.2	0.7	86.0
15 m	2.5	40.7	1.7	57.9	0.9	61.5
25.5 m[a]	3.9	58.3	1.7	46.7	2.2	87.7

[a] 1 m above the bottom.

TABLE III

Correlation coefficients between various Cu fractions and water physico-chemical parameters during the studied year and in the stratification period, calculated for Station 7

Data		N-NO$_3$	N-NH$_4$	PO$_4$	Suspended matter
From January–November (N = 30)	Cu dissolved	0.03	–0.01	0.27	0.26
	Cu – particulate phase	–0.37	0.56	0.05	0.66*
Stratification period; From May–September (N = 12)	Cu dissolved	–0.11	–0.40	0.21	0.23
	Cu – particulate phase	0.05	–0.18	0.61	0.57

* Significant at $p < 0.01$.

The Cu content in the dissolved phase showed smaller vertical and seasonal variations in the water of the Dobczyce Basin than in the particulate phase (Table II). The highest concentrations of Cu in the dissolved phase were found in the epilimnion and higher layer of the hypolimnion in winter (January, February) and summer (the end of July) (Figure 3). It seems that development of algae affected the content of Cu in the dissolved phase in the water of the Dobczyce Basin. In the periods the highest contents of Cu in dissolved phase were found the algae developed very weakly (Wilk-Woźniak, unpublished data). In 1998 an algal bloom occurred from the beginning of April (21 μg L^{-1} chl *a*) to mid July (ca. 30 μg L^{-1} chl *a*). At the end of July, a ‘clear-water’ phase (i.e. the phytoplankton biomass fell to very low levels) was observed (Wilk-Woźniak unpublished data).

The statistical calculations showed a positive correlation between the amount of suspended matter and the content of Cu in the particulate phase of the water mass during the year (Table III). The highest content of Cu in the particulate phase was

TABLE IV

The cumulation coefficient (K) of Cu in the sediment of the reservoir at the Station 7 in 1998, expressed as a ratio of the mean Cu content in the upper layer (0–3 cm) of the sediment to the mean Cu content in the water

Element		Sediment μg kg^{-1}	Water μg L^{-1}	K
Cu	Range	21800–43500	1.1–7.4	
	Mean	34200	3.2	10687.5

found in the near-bottom water in July, August and October, when an increase in the suspended matter was also recorded (Figures 2 and 3). An enhanced load of suspended particulate matter in the near-bottom water was mainly due to the movement of colder water from the River Raba along the reservoir bottom after a very rainy period (June, July, August and October). A similar effect seems to have occurred in Dervent Reservoir (England) (Harding *et al.*, 1981), causing an increase in Zn, Cu and Pb content in the near-bottom water of that reservoir. The higher content of Cu in the particulate phase in the near-bottom water of the Dobczyce Basin (especially during the summer stagnation) could also have been caused by Cu removal from the water column. Some geochemical mechanisms might have been responsible for this phenomenon. For instance, pH 9.0 favours the precipitation of Cu mainly with Fe hydroxides (adsorption, coprecipitation). Ferric oxides may compete with humic acids for metal sorption. At pH 9, the metals are displaced from the humic acids to ferric oxides, and this effect increases with pH (Förstner, 1986). On the other hand, some authors suggest that sedimentation of plankton detritus may be the most efficient method of Cu removal from the water column (Salomons and Mook, 1980; Sigg, 1985). Besides being incorporated into the biological material, Cu can also be bound to the particle surface (Sigg, 1985).

The correlations between the content of Cu in dissolved and particulate phase, and the amount of nutrients in the water were not significant (Table III). Relationships between the content of Cu and NO_3, and P have been observed, for instance, in oceans (Bruland, 1980). The following explanation may be given for the findings in the Dobczyce Basin: (1) pollution input, especially from the River Raba, is too dynamic; (2) the spring and autumn mixing can blur the proportions.

The accumulation of Cu in the sediment of the Dobczyce Reservoir was not high. The accumulation coefficient (K) of Cu in the sediment of the Dobczyce Basin reached the value of 10687.5 (Table IV). Other metals which dominated in the particulate phase of Dobczyce Reservoir water and which were strongly bound to the sediment, had much higher accumulation coefficients (K), e.g. for Fe K = 49000 and for Pb K = 32500 (Szarek-Gwiazda, unpublished data).

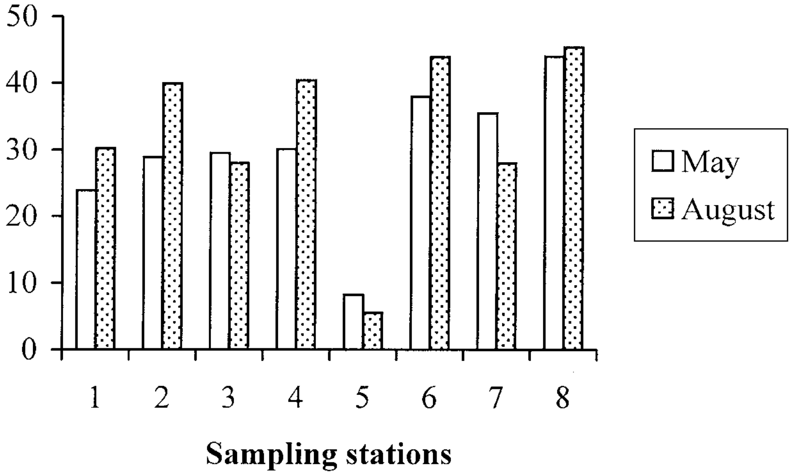

Figure 4. Copper concentrations (μg g^{-1}) in the upper layer (0–3 cm) of the bottom sediment of the Dobczyce Reservoir at the Stations 1–8 in May and August 1998.

4.3. COPPER IN THE SEDIMENT

The total content of Cu in the sediment of the Dobczyce Reservoir was rather low (5.5–45.4 μg g^{-1}) (Figure 4). The expected higher Cu accumulation in the sediment at Stations 5 and 6, which are located in a more remote area of the reservoir compared to Stations 1, 2, 3, 4, 7, and 8 situated along the long axis of the reservoir was not observed. The lowest content of Cu in the sediment was found at Station 5, and was probably caused by the influence of a smaller tributary, which enters the reservoir there. The previous study of Szarek-Gwiazda (1998b) indicated that the Cu distribution in the sediment of the reservoir was mainly related to the distribution of clay silty fraction.

Copper partitioning in the sediment showed a similar pattern in all studied sampling stations (Figure 5). Most of the Cu was found in the moderately reducible phase (40.2–54.1% of total amount) and the residual (26.2–39.3% of total amount), both in May and August. According to the results reported above, Fe oxyhydroxides are suggested to play an important role in the binding of Cu in the sediment of the Dobczyce Reservoir. Fe(III) and Mn(IV)–oxides, occurring as coatings on detrital particles, as cement between particles, and as pure concretions, are important components of both solids and sediments (Batley, 1990). Their ability to adsorb and control the solid/solution partitioning of trace metals is well documented. Only about 10% of the Cu in this study was bound to the organic/sulphidic fraction. Probably, this was connected with the small amount of organic matter in the sediment of the Dobczyce Reservoir (from 1.4 to 3.3% as determined by the COD method) (Szarek-Gwiazda, 1998b), which is typical for submontane dam reservoirs in southern Poland (Wójcik, 1991). High percentages

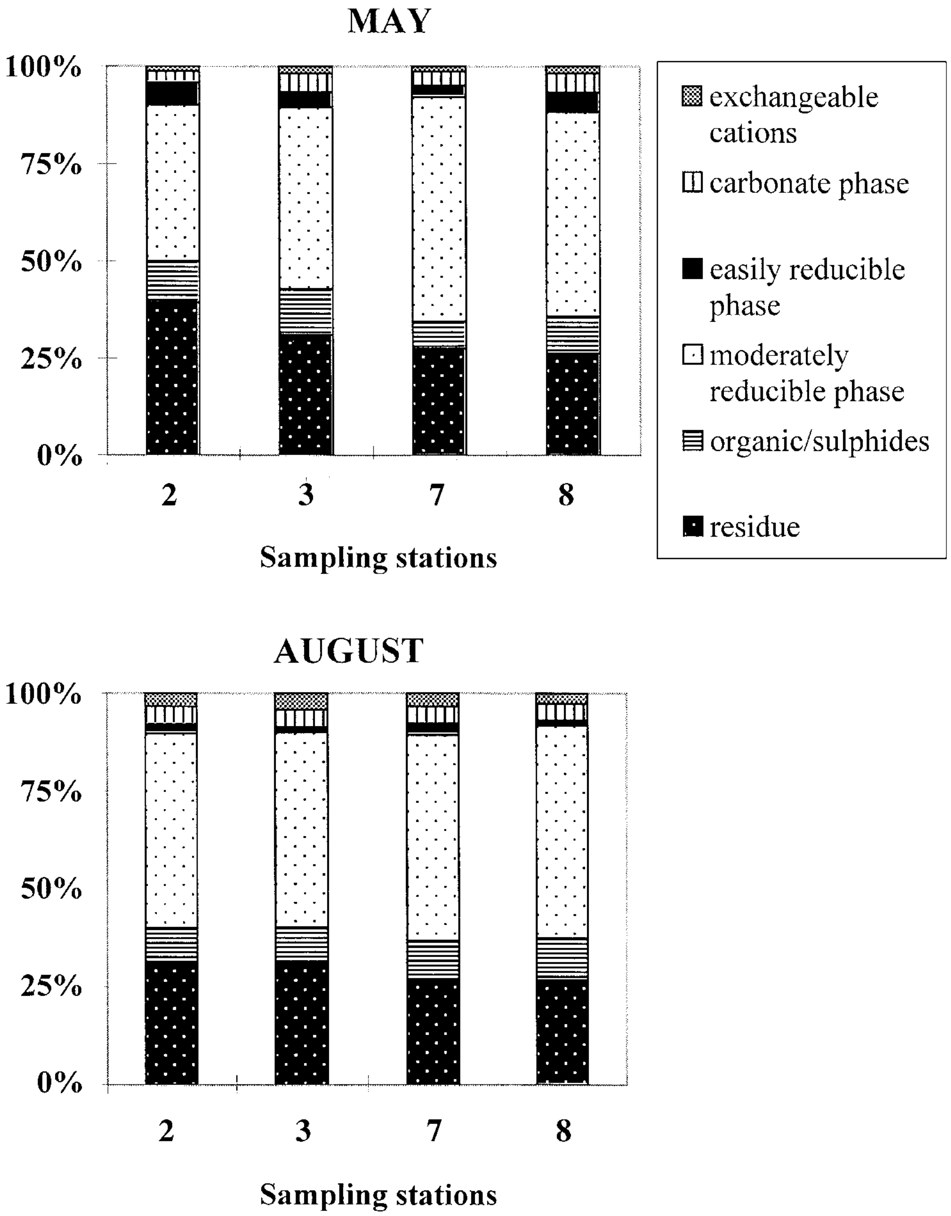

Figure 5. The chemical speciation of Cu in the upper layer (0–3 cm) of the bottom sediment of the Dobczyce Reservoir at the Stations 2, 3, 7, and 8 in May and August 1998.

of Cu associated with organic matter were found for instance by Zachman and Block (1994), Dawson and Macklin (1998) and Klavins *et al.* (1998). This indicates that organic matter can play an important role in the binding of Cu. For example, in the Flumendosa drinking water reservoir located downstream from the Funtana Raminosa mining area in Sardinia (Italy) about 66% of Cu was found in the organic fraction (Schintu *et al.*, 1991). A small part of Cu in the sediment of the Dobczyce Reservoir was bound to exchangeable cations, carbonate fraction and easily reducible phases (together 12% of the total amount). The scheme of Cu partitioning showed that the sediment of the Dobczyce Reservoir was polluted by Cu to a small degree. A great part of Cu was strongly combined with the solids, therefore copper (re-)mobilization from the sediment to the water was probably not very important.

5. Conclusions

Speciation measurements of Cu in the water and sediment of the Dobczyce dam Reservoir (southern Poland) were conducted. Copper migrated in the water mainly in the dissolved phase. This is probably the main reason for its small accumulation in the sediment of the reservoir. It was strongly bound with the sediment, therefore copper (re-)mobilization from the sediment to the water was probably not very important. Present results indicated that the speciation of Cu in the water has an important effect on its small deposition in the sediment of the Dobczyce Reservoir. Since, this reservoir is relatively young, such investigations will be also conducted in a few years time, to check if observed speciation of Cu in the water will have a measurable, decisive effect on its deposition in the sediment.

It seems that the behaviour of Cu found in the abiotic parameters of the eutrophic Dobczyce Reservoir may be typical of other similar eutrophic, submontane, slightly polluted dam reservoirs.

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