

Potential effect of pH on the leaching of heavy metals from sediments of the Carpathian dam reservoirs

Ewa Szarek-Gwiazda

Polish Academy of Sciences, Institute of Nature Conservation, K. Starmach Department of Freshwater Biology;
al. Mickiewicza 33, 31-120 Krakow, Poland; e-mail: szarek@iop.krakow.pl

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Abstract: Eutrophication processes occurring in the Carpathian dam reservoirs (southern Poland) have resulted in a drastic increase of incidences of decrease of pH and oxygen content in near-bottom water, which may affect metal remobilization from the sediment. The study is aimed to determine the buffer capacity and effects of decreasing pH on the remobilization of heavy metals (Cd, Pb, Cu, Zn, Mn and Fe) from sediments of the Dobczycki Reservoir (DR), the Czorsztyński Reservoir (CR), and the Rożnowski Reservoir (RR), the right side tributary of the Vistula River. Buffering capacity and the leaching of heavy metals from sediments accompanied with an increase in acidity were analyzed in 0.00–0.24 M HNO₃ solutions. Studied sediments had a high buffer capacity. Buffer capacity of sediments at studied sites of the DR and CR was different due to differences in the composition of sediments. The reservoir sediments had a variable ability to release heavy metals with increasing acidity. At pH ~5 and pH ~3, a considerable leaching of Mn (up to 60% and 85% of the total amount, respectively), Cd (up to 35% and 56% respectively), Pb (up to 25% and 39%), the lower leaching of Cu (up to 18% and 30%) and Zn (up to 14% and 20%), and the lowest leaching of Fe (below 5%) were found. The decrease of pH of the water-sediment system caused by eutrophication processes may affect the mobilization of certain heavy metals (mainly Mn, Cd and Pb) from sediment into the water column of the studied Carpathian reservoirs.

Keywords: Carpathian reservoir, sediments, heavy metals, buffer capacity, pH

INTRODUCTION

Remobilization of contaminants from bottom sediments is crucial to the secondary pollution of water reservoirs, metal distribution in the aquatic ecosystem and environmental risk assessment. Therefore, it is important to define the parameters conducive to this process in various bodies of water. It is well known that pH and redox conditions affect the mobility of heavy metals in aquatic ecosystems (Munk & Faure 2004, Calmano et al. 2005, Cappuyens & Swennen 2005). Relatively small changes in pH in water-sediment systems with pH values of 7.0–9.5 can result in a considerable increase in concentrations of metals in solutions (Salomons & Baccini 1986). The effect of decreasing

pH on the release of some heavy metals from the sediment was found in dam reservoirs (Buykx et al. 2000, Munk & Faure 2004, López et al. 2010). Munk & Faure (2004) observed a marked release of certain metals from the sediment of the Dillon Reservoir (US), even under small changes in pH (0.2 units).

Eutrophication processes in the Carpathian dam reservoirs (southern Poland) occur with various intensities. They result in a number of adverse effects, such as the mass development and blooms of algae, including cyanobacteria, or summer oxygen depletion and lowering the pH in the bottom water (Mazurkiewicz-Boroń 2002, Wilk-Woźniak & Mazurkiewicz-Boroń 2003). Changes in the pH and redox conditions in the water-sediment system

may enhance the release of metals associated with exchangeable, carbonate and easily reducible phases in the sediment (Calmano et al. 2005). It is known, that primary diagenetic redox reactions result in a redox gradient within the sediments and the remobilization of elements bound to easily-reducible fractions (Calmano & Förstner 1983). During summer stagnation “internal loading” by Mn and Fe (redox sensitive element), and to a lesser extent by other metals of Carpathian dam reservoirs was observed. This process was supported by the dissolved oxygen content below $4.5 \text{ mg} \cdot \text{dm}^{-3}$ for Mn and below $3 \text{ mg} \cdot \text{dm}^{-3}$ for Fe and neutral pH in bottom waters (Szarek-Gwiazda 2013). “Internal loading” occurred regardless of the trophy (mesotrophic – eutrophic) and type (limnetic – reolimnetic) of the Carpathian reservoirs (Szarek-Gwiazda 2013).

The aim of the study was to determine the buffer capacity and potential effects of decreasing pH on the remobilization of heavy metals from sediments of the selected Carpathian reservoirs varying in terms of the type (limnetic – reolimnetic) and trophy (mesotrophic – eutrophic).

MATERIALS AND METHODS

Study area

Research was carried out in the Dobczycki Reservoir (DR) located on the Raba River, in the Czorsztyński Reservoir (CR) and the Rożnowski Reservoir (RR) located on the Dunajec River (southern

Poland) – the Carpathian tributaries of the Vistula River. Many factors such as morphometric features, age, water residence time, trophic state, the size of the catchment basin, anthropogenic land use differentiate the reservoirs (Tab. 1) (Mazurkiewicz-Boroń 2002). The DR and CR are limnetic, while the RR is reolimnetic. Temperature, dissolved oxygen content and pH show summer stratification in the water column of the reservoirs, which have been affected by hydrological regime of supplying Carpathian rivers. The content of dissolved oxygen in bottom waters during the summer stagnation usually decreases below 4 mg dm^{-3} and pH is near neutral (Mazurkiewicz-Boroń 2002, Szarek-Gwiazda et al. 2013).

Sediment samples were collected from two sites located in the upper and lower parts of each reservoir (DR – sites 1 and 2, the depth of 5 and 25 m, respectively; RR and CR – sites 1 and 2, the depth of 5 and 20 m, respectively) in May 2005 (Fig. 1).

Methods

Samples of the upper sediment layer (0–5 cm) were collected using a polyethylene corer with an area of 12.56 cm^2 ; one sediment sample contained 4–5 subsamples. In the laboratory, they were dried at 105°C for 48 h, and then a fraction of 0.2 mm was dry-separated. To study total concentrations of Cd, Pb, Cu, Zn, Mn, Fe and Ca, three subsamples from each site were digested with 15 mL concentrated HNO_3 in tubes on the heated block of the Tecator Digestion System 12, combined with Autostep 2000 controller set to 120°C for 2 h.

Table 1

The characteristics of the studied dam reservoirs (acc. Mazurkiewicz-Boroń 2002)

| Parameter | Reservoir | | |
|--|-----------|--------------|-----------|
| | Dobczycki | Czorsztyński | Rożnowski |
| Start exploitation | 1987 | 1997 | 1942 |
| Standart damming ordinate [m n.p.m.] – n PP | 269.9 | 529.0 | 264.0** |
| Capacity – n PP [mln m ³] | 125.0 | 231.9 | 228.7 |
| Surface area – n PP [ha] | 950 | 1051 | 950 |
| Mean depth – max PP [m] | 11.7 | 19.0 | 10.0(13)* |
| Max depth [m] | 28 | 46 | 31 |
| Reservoirs length [km] | 10 | 11 | 22 |
| Reservoirs width [km] | ca. 1.0 | ca. 1.0 | ca. 0.7 |
| Water exchange [times · year ⁻¹] | 3.4 | 3.3 | 11.1 |
| Time of water exchange [days] | 107 | 111 | 33 |

* initial 1942, ** ordinate sill of weir

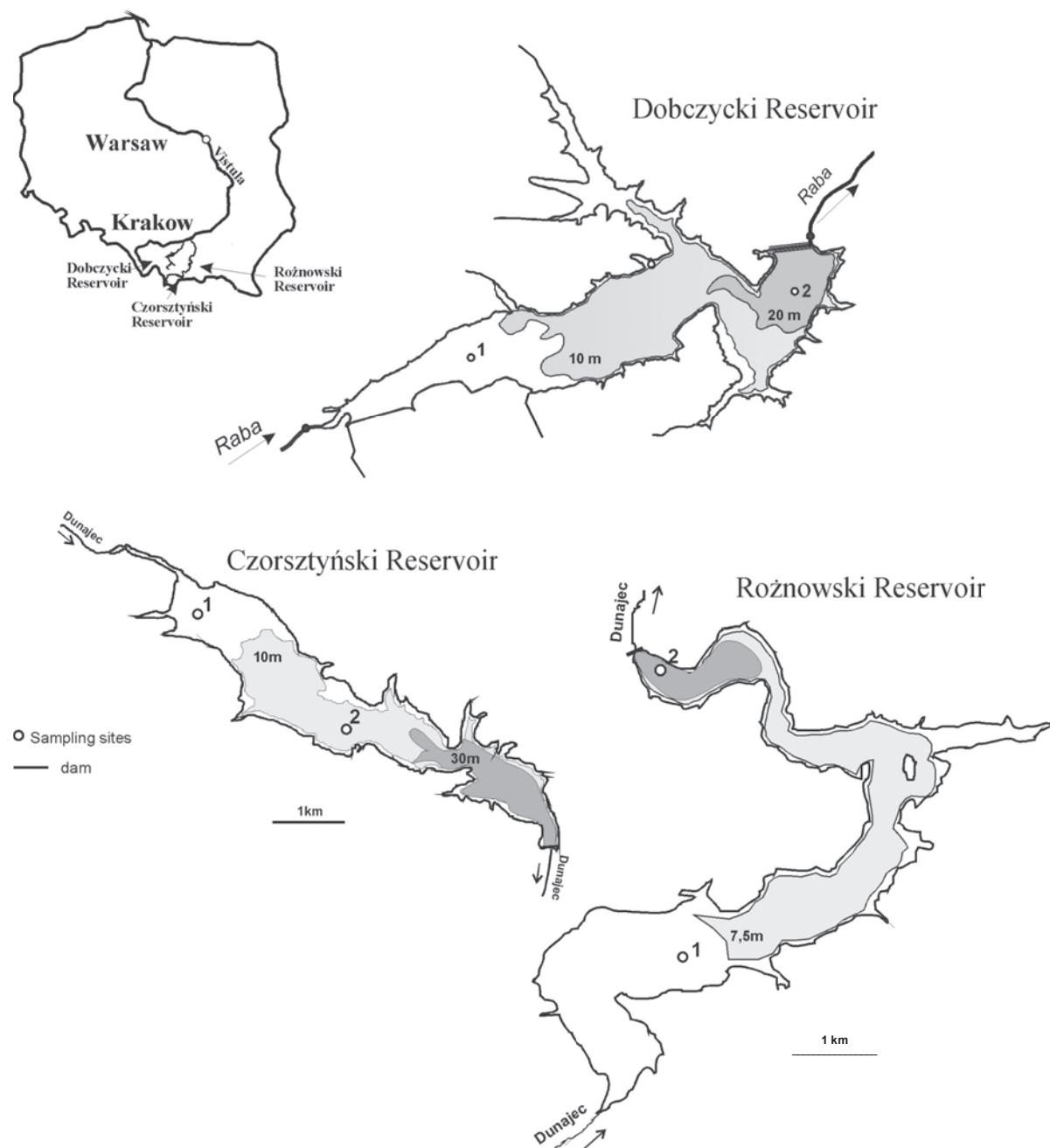


Fig. 1. Dobczycki Reservoir, Czorsztyński Reservoir and Rożnowski Reservoir – sampling sites in 2005

Buffering capacity of sediments and the leaching of heavy metals with an increase in acidity were determined in solutions of HNO_3 having a concentration of 0.00–0.24 M at a solid phase/solution ratio of 1:10. After 24 h of shaking, pH was measured and the concentrations of heavy metals in the solution were determined after filtering it through a $0.45 \mu\text{m}$ filter (Helios-Rybicka et al. 2000). Concentrations of Cd, Pb, Cu, Zn, Fe and Mn in obtained solutions and sediment samples were measured using the atomic absorption

spectrometer Varian (Spektr AA-20) with graphite furnace. Standard reference materials for water (SPS-SW1 Batch 112, Norway) and sediment (NCS DC 73308) were used for the determination of metal concentration. Comparison of the heavy metal contents in the reference material (declared value and measured one) is shown in Table 2. Concentration of Ca was determined using inductively coupled plasma mass spectrometry (ICP-MS, Elan 6100, Perkin Elmer). Values of pH were determined by means of WTW apparatus.

Table 2

Heavy metal concentrations (measured and certified) in the Certified Reference Materials for the samples of sediment (NCS DC 73308) and water (SPS-SW1 Batch 112)

| Reference materials | Cd | Pb | Cu | Zn | Mn | Fe |
|--|-------------|-------------|-------------|-------------|------------|------------|
| Sediment [$\mu\text{g} \cdot \text{g}^{-1}$] | | | | | | |
| Certified value | 1.21 ± 0.05 | 28.2 ± 0.20 | 21.2 ± 1.2 | 45 ± 1.6 | 990 ± 8.2 | – |
| Measured value | 1.12 ± 0.08 | 27 ± 2 | 22.6 ± 1.3 | 46 ± 4 | 1010 ± 29 | – |
| Water [$\mu\text{g} \cdot \text{dm}^{-3}$] | | | | | | |
| Certified value | 0.48 ± 0.01 | 4.9 ± 0.1 | 19.5 ± 0.05 | 20.1 ± 0.22 | 10.4 ± 0.3 | 20.2 ± 0.3 |
| Measured value | 0.50 ± 0.01 | 5.0 ± 0.1 | 20.0 ± 1.00 | 20.0 ± 1.00 | 10.1 ± 0.1 | 20.0 ± 1.0 |

Organic matter content was determined by the ignition of a sediment sample at 550°C for 2 h and it was expressed as loss on ignition (LOI). The grain size fractions (sand: 1.00–0.05 mm, silty clay: 0.05–0.002 mm, and clay: <0.002 mm) were analyzed by the aerometric method (Ostrowska et al. 1991).

RESULTS

The main physicochemical properties of sediment samples and concentrations of heavy metals in the sediments of the Carpathian reservoirs are presented in Table 3.

The sediments of DR, CR and RR were characterized as neutral and slightly alkaline (pH

between 7.3–7.7). At most sites, silty fraction dominated. Silty and clay fractions accounted for more than 90% (of the total amount) at both sites in the RR and at site 2 in the DR and CR. The lowest proportion of silty and clay fractions (52%) was found at site 1 in CR, where a high proportion of sand fraction was found (Tab. 3). Contents of Ca in the reservoir sediments were within the range between 0.7–2.4%, however, Ca content was from 1.5 to 3.4 times higher in sediments of RR compared to CR and DR. Content of Ca was similar at studied sites of the RR but showed a variability in the CR and DR. Its higher content was found in the upper part (site 1) of the DR and middle part (site 2) of the CR. Contents of organic matter in sediments of the reservoirs were low (5.6–8.5%).

Table 3

The values of environmental parameters and concentrations of heavy metals in the sediments in the central part of the Dobczycki Reservoir, Czorsztyński Reservoir and Rożnowski Reservoir

| Parameter | Unit | Reservoirs | | | | | |
|-----------------------|-----------------------------------|------------|--------|--------------|--------|-----------|--------|
| | | Dobczycki | | Czorsztyński | | Rożnowski | |
| | | Site 1 | Site 2 | Site 1 | Site 2 | Site 1 | Site 2 |
| Cd | $\mu\text{g} \cdot \text{g}^{-1}$ | 1.2 | 1.6 | 1.5 | 1.9 | 1.8 | 1.9 |
| Pb | $\mu\text{g} \cdot \text{g}^{-1}$ | 18.1 | 27.7 | 13.5 | 20.1 | 16.9 | 26.3 |
| Cu | $\mu\text{g} \cdot \text{g}^{-1}$ | 31.2 | 43.5 | 25.2 | 33.2 | 30 | 38.4 |
| Zn | $\mu\text{g} \cdot \text{g}^{-1}$ | 101.0 | 215.2 | 93.6 | 113.7 | 108.9 | 167.4 |
| Mn | $\mu\text{g} \cdot \text{g}^{-1}$ | 773 | 1890 | 508 | 843 | 813 | 1109 |
| Fe | % | 2.9 | 4.0 | 2.8 | 3.9 | 3.0 | 3.8 |
| pH | – | 7.6 | 7.7 | 7.5 | 7.3 | 7.6 | 7.2 |
| Ca | % | 1.1 | 0.7 | 0.9 | 1.6 | 2.4 | 2.4 |
| Organic matter | % | 5.6 | 7.7 | 7.0 | 7.3 | 5.8 | 8.5 |
| Grain fractions [mm]: | | | | | | | |
| 1.0-0.05 | % | 18 | 1 | 48 | 17 | 8 | 2 |
| 0.05-0.002 | % | 72 | 51 | 46 | 60 | 75 | 60 |
| <0.002 | % | 10 | 48 | 6 | 23 | 17 | 38 |

Concentrations of heavy metals in the studied Carpathian reservoir sediments ranged as followed (Tab. 3):

- Cd 1.2–1.9 $\mu\text{g}\cdot\text{g}^{-1}$,
- Pb 13.5–27.7 $\mu\text{g}\cdot\text{g}^{-1}$,
- Cu 25.2–43.5 $\mu\text{g}\cdot\text{g}^{-1}$,
- Zn 93.6–215.2 $\mu\text{g}\cdot\text{g}^{-1}$,
- Mn 508–1890 $\mu\text{g}\cdot\text{g}^{-1}$,
- Fe 2.8–4.0%.

Higher concentrations of heavy metals were found at site 2 in each reservoir.

The buffer capacity of the sediments showed variability among studied reservoirs and sites in each reservoir (except RR) in 2005. Sediments from the RR (sites 1 and 2), DR (site 1) and CR (site 2) were characterized by better buffer capacity than those from the DR (site 2) and CR (site 1) (Fig. 2).

At a concentration of 0.02 M HNO_3 , sediments of the first group showed less decrease of pH ($\Delta\text{pH} = 0.06\text{--}0.08$) than the sediments of the second group ($\Delta\text{pH} = 1.3\text{--}1.5$). At a concentration of 0.08 M HNO_3 , a smaller decrease in pH was observed in sediments at both sites from the RR (to pH ~ 6), at site 1 from the DR and at site 2 from the CR (to pH ~ 5), while higher decrease of pH was in sediments at site 2 from the DR (to pH ~ 2) and at site 1 from the CR (to pH ~ 3).

The studied heavy metals were leached in varied amounts from sediments of the DR, CR and RR at a given pH. At pH 6.7–6.9, which was previously found in the reservoir sediments, considerable fractions of Cd and Pb (17.4% of the total amounts), and Mn (up to 13%), and low fractions of Cu, Zn and Fe (below 2%) were released from the reservoir sediments (Fig. 3). At pH 5, the fractions of metals released from the reservoir sediments were considerable higher:

Mn – up to 60% of the total amounts, Cd – up to 35%, Pb – up to 25%, Cu – up to 18%, Zn – 14%, and Fe (up to 1.5%) (Fig. 3). With a decrease of pH to ~ 3 of the sediment suspension, considerable releases of Mn – up to 85% of the total amounts, Cd – 56%, Pb – 39%, Cu – 30%, lower release of Zn – 20%, and very small of Fe – 4% were found.

The sediments of DR, CR and RR showed different ability to release heavy metals with the

increase of acidity. At the lowest pH, the greatest fractions of Cd and Fe were released from the sediments of DR, Cu and Zn from sediment of CR, while Mn and Pb (similar amounts) from the DR, CR and RR.

In most cases, the shape of the curves of metal leaching from sediments was similar at both sites in each reservoir (Fig. 3). The exception was the release of somewhat larger fractions of Cd, Zn and Mn from sediments at site 1 than site 2 in the DR and Mn at site 2 than site 1 in the CR and RR.

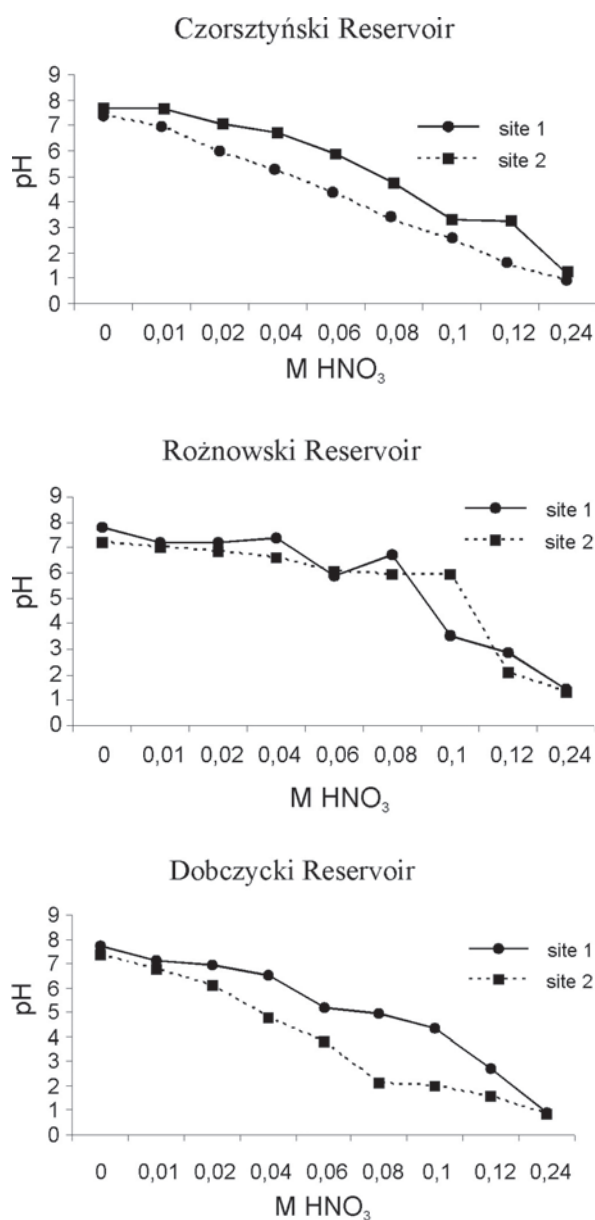


Fig. 2. Buffering capacity of the sediments of the Czorsztyński Reservoir, Rożnowski Reservoir and Dobczycki Reservoir in 2005

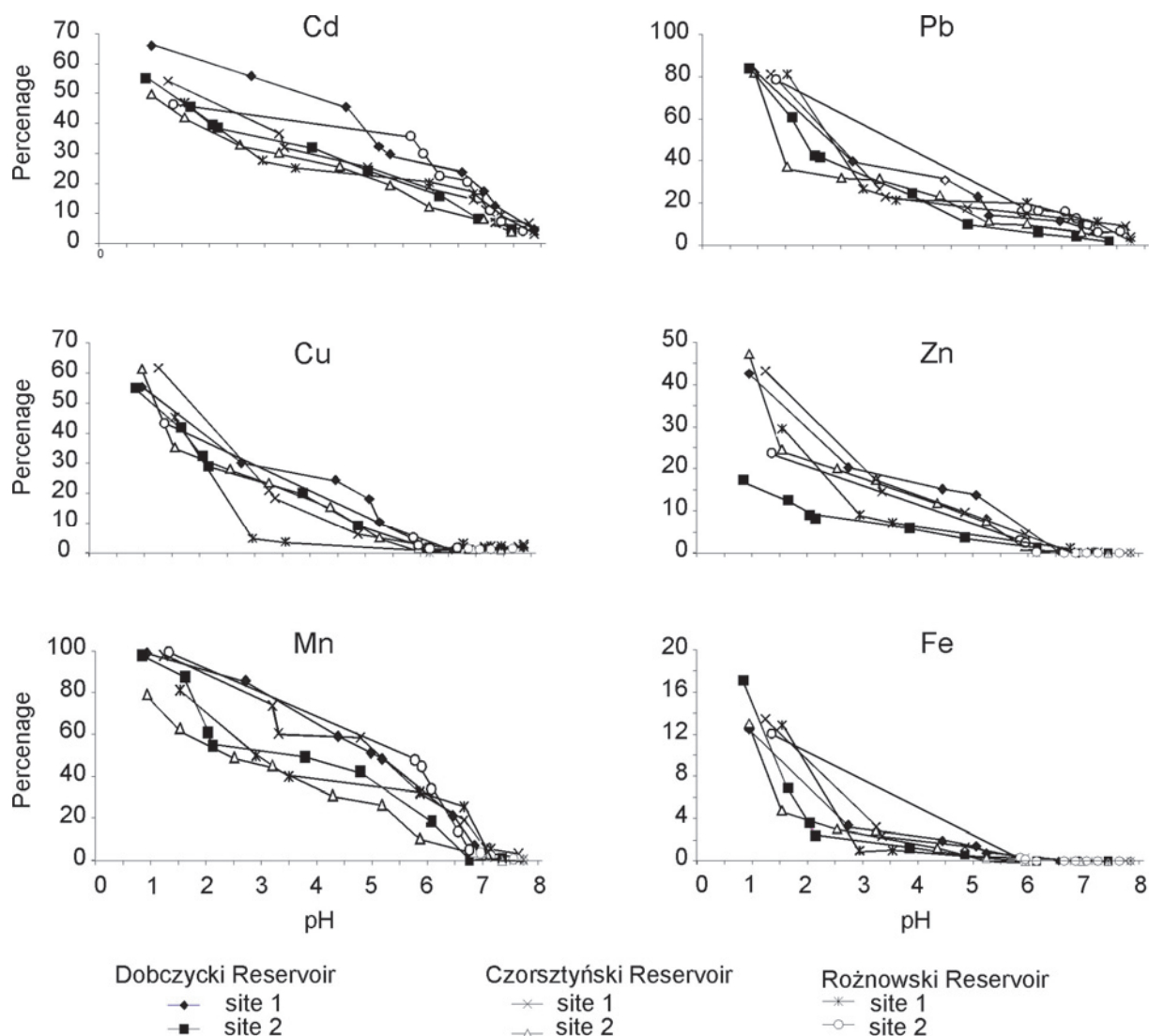


Fig. 3. Leaching of heavy metal from the sediments of the Dobczycki Reservoir, Czorszyński Reservoir and Rożnowski Reservoir under lowering pH

DISCUSSION

The sediments of the Dobczycki Reservoir, Czorszyński Reservoir and Rożnowski Reservoir showed silty-clay character reflecting the geology, soil type, and land use of the catchment area (Kurek et al. 1993, Mrozek et al. 1993). An increase of fine particles at sites located in deeper part of the Carpathian dam reservoirs is typical of deep reservoirs (Thornton 1990, Kroupiene 2007, Szarek-Gwiazda & Sadowska 2010, Szarek-Gwiazda 2013) and it is related to hydrodynamic water flow that affects sedimentary processes. The low content of organic matter and neutral and slightly alkaline pH of the studied sediments were also typical for Carpathian reservoirs. In general, waters of the DR, RR and CR

show the calcium – carbonate type of water (Mazurkiewicz-Boroń 2002, Szarek-Gwiazda 2013). Higher content of Ca in the sediment of RR compared to DR is consistent with the results of study by Mazurkiewicz-Boroń (2002) who measured higher concentrations of HCO_3^- and Ca^{2+} ions in the water of Dunajec River supplying the RR than the Raba River supplying the DR.

Buffer capacities of the sediments of DR, CR and RR, situated on the Carpathian flysch, were shaped by geochemical background and physico-chemical processes proceeding in the reservoirs. In general, the reservoir sediments were characterized by high buffer capacities. Calmano et al. (1986) found that sediment had high buffer capacity if $\Delta\text{pH} < 2$ at the lowest HNO_3 concentration

(0.01 M) in suspended sediment, moderate buffer capacity if ΔpH ranged 2–4, and weak buffer capacity if $\Delta\text{pH} > 4$.

Buffer capacity of the reservoir sediments was associated with the sediment composition. Sediments of the reolimnetic RR had similar composition (contents of silty clay fraction and Ca) and buffer capacity at both stations. In the limnetic CR, higher buffer capacity exhibits the sediment collected in the middle part (site 2) with higher content of Ca (carbonate outcrops located on the bank) and silty clay fraction compared to the upper part (site 1). In the limnetic DR, better buffer capacity had the sediment in the upper part (site 1) with higher amount of Ca in comparison to the lower part (site 2) with lower amount of Ca but higher one of silty clay fraction and organic matter. Thus, the type of reservoir limnetic – reolimnetic that shaped texture and chemical composition of sediments influenced also their buffer capacity. The waters of the three rivers: Biały Dunajec River, Czarny Dunajec River and Białka River supplying the CR are rich in minerals containing Ca. These are derived from the areas of occurrence of carbonate rocks: Tatra Mts (Inner Carpathians) with High-Tatric and Sub-Tatric geological units (nappes) formed of the Triassic-Cretaceous limestones, dolomites and marls as well as the Pieniny Klippen Belt also formed of limestones and marls of Jurassic and Cretaceous age. The last ones are situated in the direct catchment basin, surrounding the CR. The carbonate material is supplied in the detrital form, i.e. as clasts of carbonate rocks (coarse-grained material, e.g. gravels and fine-grained suspended material). To a lesser extent, Ca originates from the decomposition of aluminosilicate minerals (feldspars: plagioclases) contained in the magmatic and metamorphic rocks of the Tatra Mts crystalline massif (Birkenmajer 1977, Birkenmajer & Oszczytko 1989, Poprawa & Nemčok 1989, Alexandrowicz & Poprawa 2000, Lexa et al. 2000, Malata 2008). To the RR carbonate detrital material is delivered in a small extent with the water of the Dunajec River, for instance in the form of calcite veins in siliciclastic detrital flysch rocks of the Outer Carpathians. In a higher amount Ca is delivered in dissolved form and periodically as suspension of fine-grained carbonate material, which sourced from outcrops of carbonate rocks in the Tatra Mts and the Pieniny Pieniny Klippen

Belt mentioned above. Considerable amounts of dissolved Ca may originate also from springs situated in the Beskid Sądecki (Outer Carpathians), where many springs with increased mineralization occur (Birkenmajer & Oszczytko 1989, Poprawa & Nemcok 1989, Alexandrowicz & Poprawa 2000, Lexa et al. 2000, Rajchel & Rajchel 2004, Malata 2008). The rocks forming the catchment basin of the DR are poorer in Ca content. They represent Flysch successions of the Magura and Silesian units (nappes) of the Outer Carpathians developed as siliciclastic-clayey rocks of the Cretaceous-Palaeogene age with minor contribution of marl interbeds as well as carbonate cements (in sandstones) and occasional occurrence of calcite veins. Similarly, as in the case of the RR, dissolved Ca may be supplied with the water of the Raba River to the DR from springs with increased mineralization situated in the catchment basin of this reservoir (Poprawa & Nemčok 1989, Alexandrowicz & Poprawa 2000, Lexa et al. 2000, Rajchel & Rajchel 2004, Malata 2008). In the studied reservoirs, pH and appropriate oxygenation of the epilimnetic water favoured the precipitation of calcium carbonate to the sediments. Also a reduction of the water flow in the reservoirs favoured precipitation of suspended material. Therefore, silty clay fraction but also carbonates were probably an important factor influencing the differentiation of buffer capacity of the sediments among the reservoirs and between the sites.

In general, sediments of the DR, CR and RR were characterized by low concentrations of heavy metals, that is typical for Carpathian reservoirs (Baran et al. 2001, Gruca-Rokosz et al. 2004). The ability of the sediments of Carpathian reservoirs to leach metals with decreasing pH was dependent on the element, pH and buffer capacity of the sediments. Decrease of pH to ~5.0 resulted in significant release of Cd, Pb, Mn (25–34%) i.e. the elements present in larger amounts in exchangeable and carbonate forms in the sediments (Szarek-Gwiazda 2013). Amounts of Cu, Zn and Fe bound to these phases in the DR, CR and RR were considerable lower (Szarek-Gwiazda 2013). It is known that acidification of the sediment affects mainly dissolution of carbonates and results in release of associated metals (Buykx et al. 2000). Therefore, if higher amount of metal is associated with carbonates, the effect of reduced pH on

its release is more evident. Carbonates formed by calcium carbonate and dolomite usually contain small amounts of metals and dilute metal content in the sediment (Horowitz 1985). Cadmium is usually associated with carbonate in sediments in higher amount, for instance up to 30% (of total amount) in the Kozłowa Góra Reservoir in Poland (Rybosz-Masłowska et al. 2000), ca. 35% in the Koronia Lake in Greece (Fytianos & Lourantou 2004), 19–40% in the upper and middle part of the Odra River (Aleksander-Kwaterczak 2007). Carbonate content shaped the concentration of some metals in dam reservoirs (Todorović et al. 2001, Korfali et al. 2006). Differences in leaching of heavy metals from sediment with decreasing pH were also found in river systems, where Zn and Cd were leached more extensively than Pb and Cu at pH 5 (Adamiec & Helios-Rybicka 2002).

In general, similar shape of the curves of metal leaching from the sediments of the Carpathian reservoirs was found. However, curves of metal leaching from the sediment at selected site in the reservoirs depended on the buffer capacity. The acidification of the sediments with better buffer capacity (DR – site 1, CR – site 2) caused smaller drop in the pH and the lower leaching of metals in comparison to the sediments (DR – site 2, CR – site 1) with weaker buffer capacity.

As mentioned above, the adverse effects of eutrophication processes are summer oxygen depletion and lowering the pH in the near-bottom water of the Carpathian reservoirs (Mazurkiewicz-Boroń 2002, Wilk-Woźniak & Mazurkiewicz-Boroń 2003). The obtained results indicated that a decrease of pH (in addition to changes in redox conditions) in water-sediment system of the Carpathian reservoirs might potentially influence the remobilization of some metals (mainly Mn, Cd and Pb) to a certain extent. This confirms the result of previous studies of Szarek-Gwiazda (2013), which show that the total Mn content was negatively correlated with pH in the near-bottom water of the Dobczycki Reservoir.

CONCLUSIONS

The sediments of the Dobczycki Reservoir, the Czorszyński Reservoir and the Rożnowski Reservoir situated on the Carpathian flysch in southern Poland are characterized by high buffer capacities shaped by geochemical background and

physicochemical processes proceeded in the reservoirs. The differences in buffer capacity of the limnetic DR and CR sediments between the studied sites were influenced by spatial distribution of sediment components. The sediments of DR, CR and RR have low concentrations of heavy metals, which is typical of the Carpathian reservoirs. Decrease of the sediment pH to ~5.0 resulted in a significant release of Cd, Pb, Mn and a lower release of Cu, Zn and Fe. Differences in leachability among metals were due to their geochemical associations with individual sediment components (portion in exchangeable and carbonate phase). The results show that decrease of pH (in addition to changes in redox conditions) in water-sediment system of the Carpathian reservoirs caused by eutrophication processes may potentially influence the remobilization of some metals to a certain extent from the sediment.

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