

SEDIMENT SAMPLES FROM THE DOBCZYCE DAM RESERVOIR
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Science and Technology, al. Mickiewicza 30, 30-059 Kraków, Poland^(c)Krakow Water Treatment and Sewage Company (MPWiK distribution of Cr, As, Pb, Cl⁻, NO₃⁻ and SO₄²⁻ in
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Abstract: In the study we have focused on the distribution of several metals (Cr, As, Pb) and anions (Cl⁻, NO₃⁻, SO₄²⁻) and their partition between pore (interstitial) waters and sediments sampled at three stations at the Dobczyce Reservoir which supplies the drinking water to inhabitants from the city of Kraków and its agglomeration. The results show considerable increase in concentrations of Pb and As in pore water samples, when compared to the bottom waters. Meaningful alternations in concentration were observed in case of pore water samples (Pb, As) and sediments (Cr, Pb, As), coming from three stations and their lateral sections. The possible relations between this phenomenon and the sediment characteristic as well as the Fe and Ca content, has been studied. Some comments on the seasonal variations of anion contents in water and pore water samples, are also provided. It was found that nitrates and sulphates show considerable variations.

Keywords: accumulation, dam reservoir, pore (interstitial) water, sediment.

INTRODUCTION

Dobczyce Reservoir (127 Mm³) was completed in 1987. Its 1065 ha area, situated 30 km south of Kraków, is fed with water from the Raba River and several small streams. The Raba River supplies almost 90 % of the total inflow (Mazurkiewicz-Boroń, 2002). Dobczyce Reservoir consists of three main parts: Myślenice Basin, Wolnica Bay and Dobczyce Basin. It supplies about 60 % of the drinking water to the more than 1 million inhabitants from the city and environs of Kraków. The Myślenice Basin plays a role as the initial settling trap for suspension coming from the Raba River. The Wolnica (Zakliczyńska) Bay is supplied by the Wolnica stream. Its depth is maximum 10 m. Waters from this bay mix with the others in a limited way. Both aforementioned basins are polymictic. The Dobczyce Basin is more than 20 m deep, dimictic and is characterised by a distinct thermal and oxygen stratification. The mean water residence time in Dobczyce Reservoir is 4 months - 0.34 year (Mazurkiewicz, 1988).

Various processes in sediments, e.g. adsorption-desorption, oxidation-reduction, ion exchange or biological activity cause important chemical and geological changes at the bottom of reservoirs (Helios-Rybicka, 1991; Kabata-Pendias, 1993; Bojakowska, 1995; PAS, 2005). The accumulation, mobility, release and speciation of metals in Dobczyce Reservoir has been under investigation for the last 10 years (Szarek-Gwiazda, 1998a,b, 2000, 2002 and 2006).

The results presented in this paper are a part of a long-term project concerning the Dobczyce Reservoir (Gofaś, 2005). The project led by the groups from AGH University of Science and Technology, Institute of Nuclear Physics of the Polish Academy of Sciences (PAS), Jagiellonian University and Krakow Water and Sewage Company is aimed at the sediments in the reservoir (Reczyński, 2004 and 2006; Macherzyński, 2005; Jakubowska, 2006) and utility of satellite remote sensing methods (Mularz, 2006; Hejmanowska 2006). Particularly, the group works in the field of

distribution and accumulation of metals, bioactive elements, ions and chosen organics in sediments and water from the reservoir. The fate and adsorption of these components - including toxic and radioactive - is also under investigation.

In this study the distribution of several metals (total Cr, As and Pb) and anions (Cl^- , NO_3^- , SO_4^{2-}) and their partition between bottom water, pore (interstitial) water and sediments (metals only), is presented.

There are only small industries in the catchment basin of the Raba River: dairying, tanning, wood processing, machinery and cable production. Potential contamination of the reservoir with heavy metals occurs mainly from municipal sewage, waste water from villages situated around the reservoir as well as from atmospheric precipitation and incidental impurities of soils (Szarek-Gwiazda E. 2000). Several km up the reservoir, there is the town of Myślenice with about 20, 000 citizens and a not very efficient sewage-treatment plant. Additionally, a road construction as well as an aggregate excavation and dredging works was recently initiated up the reservoir.

In order to define the weakly-bound portion of As, Cr, Pb and several anions in equilibrium with sediments, pore water samples were examined. If the equilibrium is disturbed in certain conditions (flood events, dredging, excavation), weakly-bound polluting phases, can be readily released into water (Echerria, 1998; Sahuquillo, 2003). As far as we know this kind of investigation has not been carried out at Dobczyce Reservoir.

The concentration and distribution of the two elements Ca and Fe, known to play a role in ionic exchange within suspensions and sediments, have been monitored in pore water and sediment samples, in order to find possible correlations between Cr, As and Pb and these elements. Accompanying analyses of physical and chemical properties of water, and sediment samples are also presented.

MATERIALS AND METHODS

All chemicals used were analytical-grade. Solutions were prepared from double-distilled, finally deionized water. Bottom water (P) and sediment samples (PS)- layers A: 1-6 cm (direct contact with bottom water), B: 7-12 cm (moderate contact), and C:12+ cm (inactive layer) were collected from three stations representing three different types of hydrological conditions along the Dobczyce Reservoir – Fig. 1.

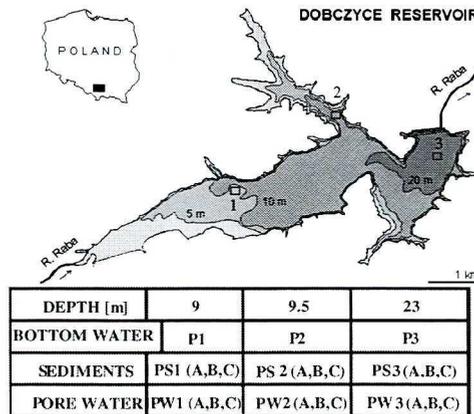


Fig. 1 Dobczyce Reservoir, stations and sample nomenclature.

Station 1 is situated about 3 km down the estuary of the Raba River, at the end of the shallower part of the Myślenice Basin. Station 2 is situated in the narrowing, at the end of the Wolnica stream bay. Station 3 is set up in the middle of the deep dam Dobczyce Basin. A bathometer (Limnos) was used to collect water samples. A sediment sampler (Limnos) was used to collect and partition sediment samples.

Samples were placed in polypropylene boxes (sediments) and high-density polyethylene bottles and vials (waters). They were kept in portable freezers, until transported to our laboratories and stored in refrigerators, before being used in the analyses. The pore water samples (PW) were extracted from fresh sediments (about 400 g) by centrifugation (4000 rpm, 300 s). Water and pore water samples for metal analyses were immediately acidified with HNO_3 to obtain 2.5 % (w/w) solutions. Finally, all liquid samples were filtered using nitrocellulose membranes (450 nm). Sediment samples (PS) were carefully mixed, dried in air (40 °C), carefully crumbled, sieved at 2 mm and wet-digested (two repetitions for each sample) with the use of the microwave system Uniclever II.

Atomic absorption spectrometry (AAS) - a Perkin-Elmer spectrometer model 3110 - was used for flame analyses of Ca and Fe. A Perkin-Elmer graphite furnace - model HGA-600 - was used for electrothermal analyses of Pb and As. In order to determine concentration of Cr, a Zeeman ZL 4100 Perkin-Elmer spectrometer was used. Sediment - pore water equilibrium coefficients (K) were calculated as the ratio of the concentration of As, Pb and Cr in each sediment and its pore water.

Ionic chromatography (IC) - Knauer/Alltech was performed using external anionic standards to determine and compare the concentration of selected anions.

Analyses of water (pH, Eh, χ , temperature) were performed directly on the boat, during collection of samples. Temperature was read from the thermometer located inside the 3.5 l volume bathometer, immediately after sampling. Water from the bathometer was carefully transported to a 1 l polypropylene beaker equipped with a set of sensors. To measure pH, the combined ERH-11 electrode (Hydromet) linked to a millivoltmeter equipped with a Pt - 100 thermometer, was used. Eh was measured with the use of a Pt-Ag/AgCl cell, linked to a millivoltmeter. The conductivity was measured using a Pt conductometric cell EPS-2 ZM (Eurosensor) linked to the conductometer CC-315 (Elmetron) equipped with a Pt -100 thermometer. Water samples for O_2 analyses were carefully collected in hermetic glass bottles. The oxygen concentration CO_2 was analysed with the Stirr Ox-G electrode linked to the Oxi 538 gauge.

Organic matter was determined by the ignition loss at 550 °C (2 h). Grain size analysis was performed using a Coulter LS particle size analyzer.

The standard deviation for each metal analysis in water ($n = 4$; one sample) and sediment ($n = 4$; two separately digested samples, two repetitions) was calculated. In ionic chromatography, each result is the average of two measurements. To identify possible correlations between the concentrations of Cr, As and Pb versus Fe or Ca content at the three stations and within the three layers, the correlation matrix at the significance level of 0.05 was calculated for $n = 9$ (Statistica 7). Each significant correlation is indicated in the discussion by the correlation coefficient "r".

RESULTS AND DISCUSSION

Physical and chemical properties of water at the stations

Samples were taken by the end of the warm June of 2006 (temp. of surface water 23.4-25.3 °C), during thermal and moderate oxygen stratifications. Some important physical and chemical properties of bottom waters and sediments are presented in Table I.

Table 1. Physical and chemical properties of bottom water and top sediment samples. Dobczyce Reservoir - summer 2006.

Bottom water parameters	t [°C]	pH	χ [$\mu\text{S}\cdot\text{cm}^{-1}$]	Eh vs. SHE	CO_2 [$\text{mg O}_2\cdot\text{dm}^{-3}$] (Saturation)
P1 (9 m)	13.9	7.70	253	+0.228 V at 18.3 °C	6.2 (62%)
P2 (9.5 m)	13.3	7.70	239	+0.252 V at 17.1°C	6.1 (60%)
P3 (23 m)	9.0	7.54	219	+0.246 V at 13.5 °C	5.0 (45%)
Top sediment (A: 1-6 cm) parameters	t [°C]	Organic matter [%]	Clay < 2 μm volume [%]	Medium & fine silt < 15.6 μm volume [%]	Content of pore water [%]
PS1A (9 m)	13.9	6.27	9.0	35.4	48
PS2A (9.5 m)	13.3	8.99	13.4	48.1	60.5
PS3A (23 m)	9.0	8.91	16.8	51.9	68

Bottom water samples (P1, P2, P3) are characterized by lower concentrations of O_2 with saturation values: 62, 60 and 45%, respectively. rH, defined as $[\text{Eh} + 0,06 \cdot \text{pH}] / 0.03$ is equal to 23 - 23.8 (weakly oxidising conditions). pH of the surface water samples in these three points was 1.1 - 1.15 higher than the pH of bottom water samples (intensive photosynthesis). The conductivity of bottom waters at P1 to P3 decreased from 253 through 239 to 219 $\mu\text{S} \cdot \text{cm}^{-1}$, respectively. This dependence is related to several factors varying along the Dobczyce Reservoir: (1) lower temperature of the bottom water, (2) higher sorption capacity of sediment (finer graining, more organics), (3) more Fe and Mn colloids in the bottom water suspension in the deep Dobczyce Basin (Szarek-Gwiazda, 2005). The conductivity of surface water at the points P1-P3 was at a stable level of 270-255 $\mu\text{S} \cdot \text{cm}^{-1}$, however near the estuary it rose to 340 $\mu\text{S} \cdot \text{cm}^{-1}$.

Distribution of total Cr, As and Pb in bottom and pore water samples

The concentration of Cr in bottom water was determined to be 0.5 – 1 ppb (w/w) and concentrations of As and Pb in the same samples did not exceed the blank sample level (acidified deionised water), thus they must be lower than 1 ppb. In earlier work by (Szarek-Gwiazda 2006) in June 1998, the concentration of Pb in bottom water was about 0.7 ppb and in our previous investigations (Macherzyński, 2005) did not exceed 1 ppb. Therefore, the concentration of total Cr and As but especially Pb, in pore water samples is considerably high – Fig. 2 and 3.

Cr occurs in all points and layers at the stable level of 5.2 ± 1.0 ppb (except PW1C). Relatively higher concentrations of As (12 – 38 ppb) in the same samples were determined. The concentration of this element increases with the depth of each core from a layer A to C and is similar in each layer (average: A- 15.0 ± 3.6 ppb, B- 20.7 ± 7.4 ppb, C- 33.0 ± 4.6 ppb) at all 3 stations. Nevertheless, the total amounts of weakly-bound As in each layer do not differ from each other as much, because every deeper layer contains a lower volume of pore water.

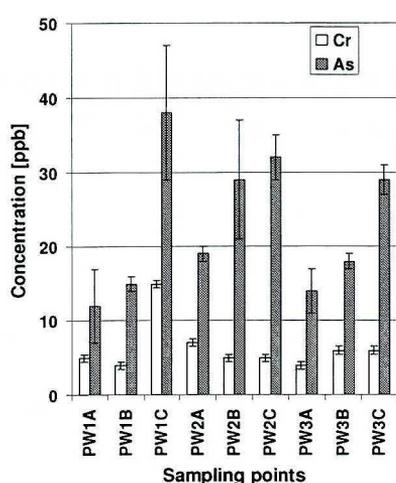


Fig. 2 Concentration of As and Cr in pore waters. Standard deviation bars, $n=4$. Dobczyce Reservoir - summer 2006.

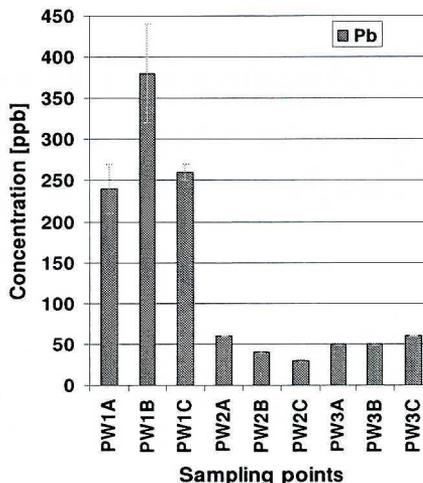


Fig. 3 Concentration of Pb in pore water. Standard deviation bars, $n=4$. Dobczyce Reservoir - summer 2006.

Abnormally high concentrations of Pb in pore water samples (240–380 ppb) in PW1 were found. The standard value of Pb for classified water is 50 ppb (MOŚZNIŁ, 1991; MZ, 2002) and 10 ppb (EU Directive, 1998). This contamination may have resulted from the road construction works along the Raba River or dredging sediments and excavation of aggregate, due to the ground works on the very busy and heavily exploited road and sediment removal. The works began in 2005 and continued into 2006, in the area close to the river estuary to the reservoir. The smaller sorption capacity of sediments (smaller amount of organic matter and smaller volume of clays and finer silts – Table I) might cause the elevated amounts of weakly-bound Pb present in the pore water at PW1.

Table 2. Concentration of Fe and Ca and standard deviation (SD) in bottom water (P1-P3), pore water (PW1-PW3) and sediment (PS1-PS3) samples. Dobczyce Reservoir - summer 2006.

SAMPLE	P1	PW1A	PW1B	PW1C	P2	PW2A	PW2B	PW2C	P3	PW3A	PW3B	PW3C
C_{Fe} [ppm]	0.52	22.4	26.5	12.9	0.33	16.5	26.3	22.1	0.43	5.4	8.7	19.2
<i>SD, n=4</i>	0.03	0.14	0.01	0.16	0.03	0.02	0.06	0.35	0.03	0.18	0.08	0.23
C_{Ca} [ppm]	47.1	32.0	27.0	40.4	36.7	33.6	47.1	81.9	33.8	27.9	37.9	82.4
<i>SD, n=4</i>	0.23	0.04	0.20	0.61	0.05	0.04	0.08	0.37	0.04	0.02	0.28	0.35
SAMPLE	-	PS1A	PS1B	PS1C	-	PS2A	PS2B	PS2C	-	PS3A	PS3B	PS3C
C_{Fe} [ppm]	-	24182	23253	24543	-	23792	23455	26913	-	30575	32950	32058
<i>SD, n=4</i>	-	799	1835	1106	-	1222	1651	41	-	636	2720	1618
C_{Ca} [ppm]	-	9594	10503	8068	-	1870	1503	2031	-	3680	5435	3054
<i>SD, n=4</i>	-	474	274	28	-	62	59	10	-	102	184	107

Nevertheless, the concentration of Pb in all pore water samples from stations PW2 and PW3 were at a stable and much lower level than the PW1 level of 48.3 ± 11.7 ppb. The concentration of Pb in pore water samples is strongly correlated with the concentration of Ca in sediments ($r = 0.925$, $n = 9$). The total Fe and Ca concentration in pore water samples in ppm (w/w) and in sediment samples in mg / kg of dry mass, expressed in this paper as ppm, is presented in Table II. Some comments on the distribution of Fe and Ca are presented in the section 4).

Distribution of total Cr, As and Pb in sediment samples and equilibrium ratio (K) between the concentrations of these metals in sediment and pore water samples

The concentration of total As, Pb and Cr in sediment samples is presented in Fig. 4. The average concentration of each metal is 18.7, 23.7 and 49.8 ppm (w/w), respectively. The concentration of Pb is very well negatively correlated with the concentration of Ca in sediment samples ($r = -0.964$, $n = 9$), which might suggest competition between these divalent metals for available sorption sites within the sediment. It is important to point out that in the summer of 2005, much lower levels of Pb (5–10 ppm) were determined in the sediment samples, collected at the 17 stations from the Dobczyce Reservoir (unpublished data). However, it was noted in (Szarek-Gwiazda, 2000) that Pb was found at a level of 16.1–50.3 ppm in 1994 and 4.1–30.8 ppm in 1998. These data show a considerable annual and site-dependent variability of the lead concentrations in sediments from Dobczyce Reservoir.

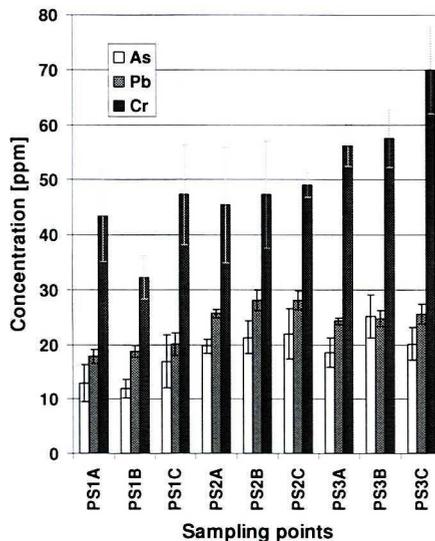


Fig. 4 Concentration of As, Pb and Cr in sediments. Standard deviation bars, $n=4$. Dobczyce Reservoir - summer 2006.

Sediment - pore water equilibrium coefficients (K), calculated as the ratio between the concentration of each metal in a sediment and its pore water are presented in Table III. K indicates the immobilisation of each metal and its affinity to the active compounds within sediments. Cr appears as a contaminant mainly due to the tanning industry further up the Raba River course. Cr is immobilised in the analysed sediments very efficiently (mean $K_{Cr} \approx 9000$). The concentration of Cr in sediments tends to increase from the station 1 to 3, reaching 70.0 ± 7.9 ppm at the PS3C. One possible explanation of this phenomenon is a distinct correlation of these results with the total Fe

concentration in sediments ($r = 0.853$, $n = 9$). The strong affinity of Cr towards sediments explains its low concentrations in pore water samples at all the three stations.

Table 3. Equilibrium ratios (K) between the concentration of metal in sediment and its pore water.

SAMPLE	P1A	P1B	P1C	P2A	P2B	P2C	P3A	P3B	P3C	MEAN
K_{As}	1081	794	445	1036	737	686	1321	1401	695	911
K_{Pb}	74	49	77	427	702	936	485	495	426	408
K_{Cr}	8670	8063	3150	6483	9476	9816	14063	9583	11662	8996

The high concentrations of Pb in the pore water samples (PW1A-PW1C) influence the abnormal low equilibrium coefficients of this element in this sediments (mean $K_{Pb} = 67$).

As is immobilised in the sediment at the moderate level (mean $K_{As} \approx 900$) and its concentration is well negatively correlated with the concentration of Ca in sediments ($r = -0.765$, $n = 9$), as it is in case of Pb.

Distribution of total Fe and Ca in water and sediment samples – Table II

The concentration of total Fe in bottom water at P1 to P3 is less than 1 ppm, although in pore water samples, it is between 5 and 27 ppm. This excess can be caused by the higher mobility of iron ions within the sediment, which might be explained by the prevalence of the more soluble Fe^{2+} ion. The acute drop of Eh usually take place in sediments (Lampert, 1999). Since the Eh of the bottom water samples at P1 to P3 was in the range of Fe^{2+}/Fe^{3+} equilibrium (+0.2 - +0.3 V) – Table I, one can predict the existence of some Fe^{2+} ions in the sediments. Szarek-Gwiazda (2000) showed that the concentration of Fe in bottom water samples tends to rise (from 0.3 to 3.5 ppm) from June to September, which confirms the release of the soluble Fe during the summer season.

Ca also takes part in the ionic exchange, crystallisation and precipitation within the sediments or competition with other cations. The highest concentration of Ca in pore water samples is observed in the deepest layers (C) of each core, which might be again related to the fact that every deeper layer contains a lower volume of pore water, as the total amount of a soluble form within the sediment remains similar in the whole core. The concentration of Ca in sediments tends to be independent of depth of each core, but is highest at the PS1 (coarse silt sediment).

Distribution of selected anions in water and sediment samples

The concentrations of several anions in water and pore water samples, in the course of three seasons (15.04, 27.06 and 19.10) in 2006, were determined. In each season the samples were taken from the same three stations, but without P2 in spring.

NO_3^- ions are present in bottom water samples at the level of 2.5 - 6.5 ppm. With a few exceptions in P1, nitrates do not exist in the pore water at levels higher than 0.1 - 0.05 ppm (detection limit) – Fig. 5. No nitrites are observed in the chromatograms. These results indicate a denitrification within the sediments. This result is contrary to measurements performed in the summer of 2004 (Macherzynski, 2005), when a moderate accumulation of nitrates within the sediments was observed.

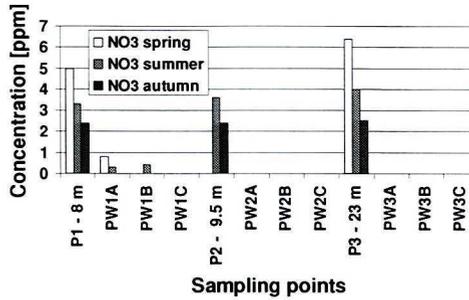


Fig. 5 Concentration of NO₃⁻ in bottom and pore water samples, n=2. Dobczyce Reservoir – spring (except P2), summer and autumn 2006.

The concentrations of Cl⁻ and SO₄²⁻ are shown in Fig. 6 and 7. The steady concentration of chlorides in bottom water is ca. 6 ppm in spring and summer, but increases to 10 ppm in autumn (possible reasons: lower water flow, road building and excavation works up the reservoir). Chlorides accumulate moderately in pore water, except in autumn. Small amounts of F⁻ ion in bottom water (up to 0.1 ppm), with a possible accumulation in pore waters (0.1 - 0.2 ppm) are also observed.

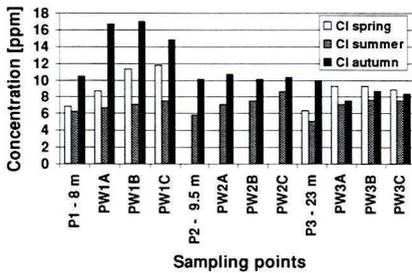


Fig. 6 Concentration of Cl⁻ in bottom and pore water samples, n=2. Dobczyce Reservoir – spring (except P2), summer and autumn 2006.

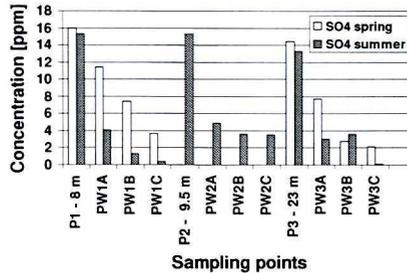


Fig. 7. Concentration of As, Pb and Cr in sediments. Standard deviation bars, n=4. Dobczyce Reservoir – summer 2006.

The steady concentration of sulphates in bottom water samples is between 15 and 20 ppm. The concentration of this ion is up to 38 (130 – in one special case) times higher in bottom waters than in pore water samples, and this ratio increases with the depth of each core. The prime reason for this phenomenon might be that with increasing depth of each core, the Eh potential decreases resulting in some biological reduction of sulphates. In recent work (Macherzynski, in preparation), SEM-BSE-EDS (scanning electron microscopy with back scattering and microanalysis) observations on sediments from the Dobczyce Reservoir, has shown numerous, small authigenic framboidal aggregates of iron sulphides. Precipitation of barite can be an other process responsible for the sulphate uptake within the sediment cores. Taking into consideration the relatively high concentration of total Ba in bottom and pore water samples, barium cations seem to control the concentration of SO₄²⁻ ions in the bottom and pore water samples by the barite solubility product constant (Macherzynski, 2005; Macherzyński in preparation). IC analyses of sulphates in autumn 2006 showed abnormal concentrations of this anion in pore water samples, especially at the deepest

PW3. The observations were repeated in 2007, in order to find a reasonable explanation for this phenomenon. The results, after appropriate reduction, will be reported elsewhere.

CONCLUSIONS

1) The concentration of total As, Cr and Pb in the bottom water and sediment samples from the sampling points (P1 – P3) of the Dobczyce Reservoir is low and does not exceed the acceptable limit values (EU Directive, 1998; MOŚZNiL, 2002; Bojakowska, 2001).

2) The concentration of total Cr and As, but especially Pb, in pore water samples is considerably high. Some discharge of Pb from the Raba River must have taken place before the measurements resulting in the abnormally high concentration of Pb in pore water samples from the station situated near the estuary of the river (PW1).

A significant variation of As and Pb concentrations in pore water samples has been found, since the chosen three sampling points represent the three different types of hydrological conditions along the Dobczyce Reservoir.

3) The immobilisation of Cr, As and Pb in the sediments is expressed by the K ratio between the concentration of each metal in sediment and pore water samples. The mean K values were about 9000, 900, 400 for Cr, As and Pb, respectively.

4) A significant variation of NO_3^- and SO_4^{2-} concentrations in bottom and pore water samples was observed. An advanced level of denitrification within the sediments takes place (especially in P2 and P3). The concentration of sulphates is up to 38 (130 – in one special case) times higher in bottom waters than in pore waters (spring, summer), and this ratio increases with the depth of each core. Some possible explanations of this phenomenon are presented.

Hydrological conditions, including the sedimentation process, and the composition of sediment at each station (P1-P3) influenced the distribution of Cr, As and Pb in the pore water and sediment samples. Higher amounts of heavy metals in the appropriate sediments in the Dobczyce Reservoir are related to their sorption on clay minerals, organic matter and Mn or Fe oxides and hydroxides. From this point of view, the sample PS1 differs from the others. It is a coarse silt sediment with higher amounts of Ca (0.1 %), smaller quantities of clays (9 %) and organic matter (6.3 %). On the other hand, there is a fine silt and clay sediment in the dam Dobczyce Basin (PS3), and the aforementioned values are 0.04 %, 16.9 % and 8.9 %, respectively. Additionally, the AAS analyses indicate a higher total Fe concentration at this location. The aforementioned observations and results provide a possible explanation of why the concentrations of Cr, As and Pb in sediments tend to increase from P1 to P3 and provide a possible origin for the observed correlations between the concentration of Cr, As and Pb versus the concentrations of Ca and Fe.

The same approach and measurements as presented in this paper, however comprising more components and sorption studies, will be continued in the future.

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