Oceanological and Hydrobiological Studies
International Journal of Oceanography and Hydrobiology
Vol. XXXV, No.4

Institute of Oceanography (331-352) University of Gdańsk
2006

ISSN 1730-413X

Received: *June 05, 2006*
Accepted: *August 15, 2006*

Trace element concentrations in fish and bottom sediments of a eutrophic dam reservoir

Ewa Szarek-Gwiazda[1], Antoni Amirowicz, Robert Gwiazda

Institute of Nature Conservation, Polish Academy of Sciences
Karol Starmach Institute of Freshwater Biology
Al. Mickiewicza 33, 31-120 Cracow, Poland

Key words: trace elements, speciation, sediment, fish, reservoir

Abstract

Total trace element concentrations and their binding forms were studied in benthic sediments and in roach (benthivore), bream (planktivore/benthivore), and pikeperch (piscivore) in the upper and lower sections of the Dobczyce Reservoir in southern Poland. The sediment was polluted to a low degree by Cd and relatively unpolluted by Pb, Zn, Mn, and Fe. According to the index of geoaccumulation (I_{geo}), Cd was the most mobile element in the sediment and was bioconcentrated in fish tissues to the highest degree, especially in roach, which feeds by burrowing into the sediment. The trace element distribution in fish tissues (muscle, liver, kidney, and gills), fish species, and in fish from different locations is discussed.

---

[1] Corresponding author: *szarek@iop.krakow.pl*

INTRODUCTION

Contamination by metal pollutants is one of the main contemporary anthropogenic hazards to aquatic environments. Therefore, various fish species are widely used as bio-indicators of metal contamination (Allen-Gil and Martynov 1995, Blanchard et al. 1999, Andres et al. 2000, Rashed 2001, Storelli and Marcotrigiano 2001, Svobodová et al. 2004). Interspecific differences in metal concentrations in fish are related to differing homeostatic control, detoxification, and rejection abilities (Allen-Gill and Martynov 1995), differential induction of the metallothionein (MT) gene (Olsson and Kille 1997, De Boeck et al. 2003), and variations among fish species in the processes of uptake, internal distribution, storage duration, and excretion of metals (Andres et al. 2000). Langevoord et al. (1995), Amundsen et al. (1997), and Andres et al. (2000) reported that diet composition and food quality play an important role in the level of metal bioaccumulation. Individual fish age and size may also influence metal concentrations in fish tissues (Barak and Mason 1990, Carru et al. 1996, Kostecki 2000, Dobicki and Polechoński 2003, Łuczyńska and Brucka-Jastrzębska 2005).

It is well known that trace element accumulation in fish also depends on the abiotic features of the environment (e.g., pH, redox potential, alkalinity, salinity), metal concentration, and the duration of exposure (Protasowicki and Chodyniecki 1988, Cain et al. 2000, Martinez et al. 2002, Jezierska and Witeska 2001, Witeska and Jezierska 2003, Smolders et al. 2003). The transfer of chemicals from bottom sediments to organisms is now considered to be the main contamination route for many species.

Operationally defined, phase-specific binding forms that affect the behavior of an element in sediments have been studied intensively (Tessier et al. 1996, Sobczyński and Siepak 2001, Szarek-Gwiazda and Mazurkiewicz-Boroń 2002, Ikem et al. 2003, Fytianos and Lourantou 2004, Głosińska et al. 2005, Wiechuła et al. 2005). The sequential extraction procedure is commonly applied in the assessment of heavy metal mobility and bioavailability in sediments. Changes in physicochemical environmental characteristics (e.g., pH, redox potential) may cause the mobilization of pollutants (Calmano et al. 1993, Zuomis et al. 2001, Hongve 2003). In an earlier study (Szarek-Gwiazda and Amirowicz 2006), the present authors reported that there is a possible relationship between the strength of the binding form of the element in the sediment and the accumulation of it in fish. They found that the most mobile elements in the sediment were accumulated to the highest degree in roach and white bream, which are benthivorous fishes that burrow in the bottom and feed on benthic macroinvertebrates. This phenomenon was observed in Piaseczno Lake (an inundated, open-cast sulfur mine in southern Poland), which is heavily contaminated by Sr and Mn.

Some authors (Kuznetsova et al. 2002, Farkas 2003) describe high variability in trace element concentrations in selected fish species that inhabit the same water body. Such variability also may be expected in Dobczyce Reservoir, a submontane limnetic dam reservoir in southern Poland. The water entering a reservoir becomes the medium of physical, chemical, and biological processes which differ to some extent from those in reservoir tributaries. If the water residence time is a few months or more, these processes produce pronounced differences in the environmental conditions at the inlet (i.e., the shallow backwater area near the inlet of the main tributary where water is rich in nutrients, turbid, and polymictic) and in the deeper end of the reservoir, which is a relatively low-trophic, transparent, dimictic deep water pool near the dam.

The aim of this study was fourfold: (1) to determine trace element concentration and speciation in the bottom sediments in the upper and lower parts of the reservoir; (2) to identify differences in metal concentrations in the fish tissues of species with different feeding strategies (i.e., roach - benthivore, bream - planktivore/benthivore, pikeperch - piscivore); (3) to determine differences in trace element concentrations in fish from the upper and lower parts of the reservoir; (4) to test the hypothesis that the most mobile elements in the sediment are bioaccumulated to a higher degree in benthivorous fish.

STUDY AREA

The Dobczyce Reservoir (49°52’ N, 20°02’ E) is located between the upper and middle sections of the Raba River (a Carpathian tributary of the Vistula River) about 30 km south of Cracow (Fig. 1). The reservoir is approximately 10-km long, eutrophic, and 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). The annual mean water residence time is four months (0.34 yr).

The fish community of the Dobczyce Reservoir consists of approximately 20 species. The dominants are five cyprinid and percid species (i.e., roach *Rutilus rutilus* (L.), bream *Abramis brama* (L.), bleak *Alburnus alburnus* (L.), perch *Perca fluviatilis* L., and pikeperch *Sander lucioperca* (L.)). White bream *Blicca bjoerkna* (L.), rudd *Scardinius erythrophthalmus* (L.), and chub *Leuciscus cephalus* (L.) are also relatively abundant. The remaining species are considered rare. There are no notable differences in the species composition of the fish communities in particular parts of the reservoir; however, some differences in fish density do occur. In a 2002 study, the median catch per unit effort was

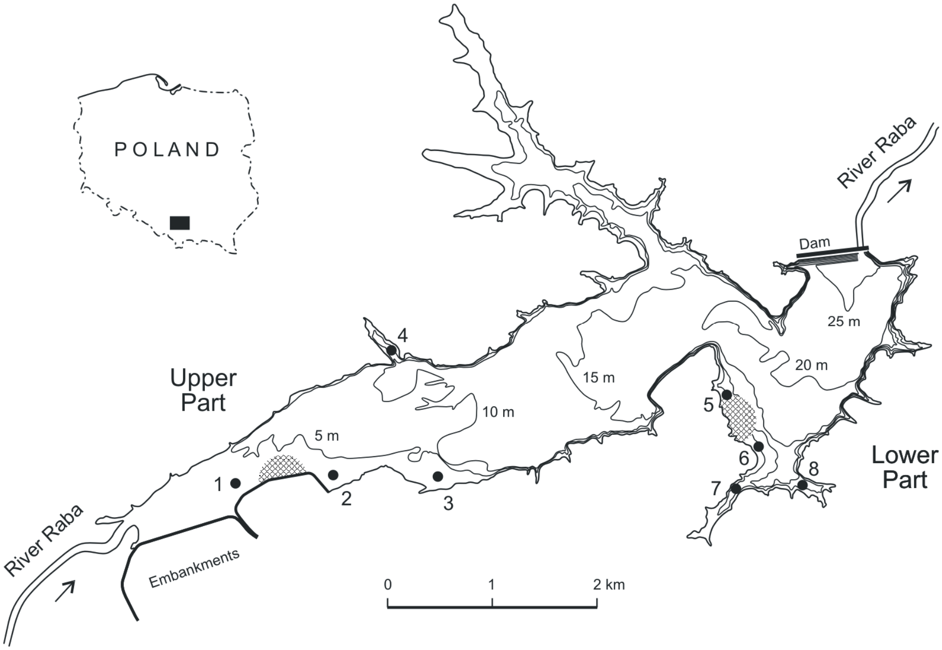

Fig. 1. Location of sampling sites in the Dobczyce Reservoir: cross-hatched area – fishes, circles – bottom sediment.

noted at a ratio of 2:1 in the littoral zone of the upper and lower parts of the reservoir, respectively (Gwiazda and Amirowicz, unpubl.). The most important commercial species were bream, roach, perch, and pikeperch, which constituted 65.9%, 17.9%, 4%, and 10% of the total catch in 2004, respectively (data provided by the Regional Water Management Board in Cracow).

MATERIAL AND METHODS

Sample collection and analytical methods

The fish were sampled with gill nets from the upper and lower parts of the Dobczyce Reservoir (Fig. 1) on August 19, 2003. Ten specimens each of bream, *Abramis brama* (L.), roach, *Rutilus rutilus* (L.), and pikeperch, *Sander lucioperca* (L.), were collected from each location (60 specimens in total). Adult individuals of similar size were selected from both parts of the reservoir (Table 1). The food composition of the species studied within this size range differed. Roach is a benthivore that feeds on benthic invertebrates, filamentous algae and a large amount of detritus, while bream forages on zooplankton and

Table 1

Size of fish collected in two sections of the Dobczyce Reservoir on August 19, 2003 (location of sampling sites in Fig. 1)

Species	Number of specimens	Total length (cm)	Body mass (g)
Bream			
Upper part	10	26.7–43.1	181–754
Lower part	10	25.0–42.5	141–843
Roach			
Upper part	10	22.5–31.0	123–334
Lower part	10	22.8–30.8	129–337
Pikeperch			
Upper part	10	40.7–49.5	596–1132
Lower part	10	32.5–48.9	283–1059

bottom macrofauna, and pikeperch is an exclusive piscivore (Amirowicz, unpubl.).

After they fish were caught, they were placed in individual polyethylene bags and chilled on ice during transport to the laboratory. They were dissected with stainless steel instruments. Samples taken from the dorsal muscle (about 1 g dw), gill filaments, liver, and kidney (about 0.4 g dw each) were analyzed separately. Selected muscle samples were analyzed in duplicate. The samples were dried in an oven at 60°C for 48 h, homogenized and digested with a mixture of pure nitric (MERCK) and perchloric acid (4:1, 15 ml) in the heated block of a Tecator Digestion System 12 with an Autostep 2000 controller according to the method by Frank (1984). Small samples were digested in quartz vessels on a heated plate. Initial digestion was conducted at room temperature for 24 h. This was followed by careful heating at 40°C for 2 h, to prevent frothing, after which the temperature was raised to 225°C for 4 h. The samples were allowed to cool, and final solutions of 10 ml were made with double-distilled water. They were stored at 4°C until analysis.

On the same sampling date, samples of the upper layer (0–4 cm) of the bottom sediment were collected at four sites in both the upper (Stations 1–4) and lower parts of the reservoir (Stations 5–8; Fig 1). Samples were taken using a polyethylene corer (diameter 4 cm). At least three subsamples were taken at each location. The samples were placed in plastic containers. The total element concentrations and their phase-specific binding forms were determined for each sample. The samples used to determine the total trace element concentrations were homogenized using a planetary mill (Pulverisette 5) with Teflon grinding balls. Approximately 0.5 g of dry sediment (three subsamples from each station) was digested with 15 ml conc. HNO_3 in the heated block of a Tecator Digestion System 12 with an Autostep 2000 controller at 120°C for 2 h. After digestion, the contents of each tube were filtered through a 0.45 µm filter (GF/C Whatman) into a calibrated 50-ml volumetric flask. The remaining sediment in each tube was rinsed with double-distilled water to remove all of the acid solution, and the flask was filled with double-distilled water.

Six fractions of the 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 oxyhydroxides), F5 – organic/sulfides, and F6 – residual) were analyzed according to the method by Tessier et al. (1979) following modifications by Förstner and Calmano (1982). The fractions were extracted in the following steps:

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

F2 – The residue from F1 was leached for 5 h shaking time with 1 mol 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 for 12 h shaking time with 0.1 mol 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 for 24 h shaking time with 0.2 mol ammonium oxalate $(NH_4)_2C_2O_4$ and 0.2 mol oxalic acid $H_2C_2O_4$, adjusted to pH 3.0 with HNO_3, at room temperature, and 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 at 3500 rpm and then passed through a 0.45 µm filter.

F5 – The residue from F4 was transferred into a 100-ml beaker, 30% H_2O_2 was added, and the solution was digested at 85°C. The addition of H_2O_2 was repeated until the solution stopped bubbling. Then the solution was evaporated until the sample was nearly dry, and then 50 ml of 1 mol ammonium acetate was added and shaken for 12 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°C, and with a solid/solution ratio of 1:100.

Trace element analyses were performed on all the solutions obtained with a Varian (model 20) atomic absorption spectrophotometer with the graphite furnace atomic absorption technique, as well as by direct flame aspiration with an acetylene/air flame. The optimum analytical conditions and reduction of matrix effects for Pb in fish tissues was achieved through the addition of a modifier (ammonium dihydrogen orthophosphate). All flasks used in analyses were washed and soaked in 30% HNO_3 for 48 h and then thoroughly rinsed with double-distilled water before analyses.

The calibration solutions of trace elements were prepared with 1000 mg l^{-1} metal standard stock solution (purchased from the Central Office of Measures, Warsaw) immediately before analysis. The calibration curves were checked with replicate analyses of calibration solutions at the beginning of the analysis and subsequently at every tenth sample analyzed. Blank analysis was conducted to check the purity of the reagents. The percentage coefficient of the variation of trace element concentrations ranged from 0.8 to 7.9% in duplicate analyses of muscle samples, and from 0.8 to 4.5% in triplicate analyses of sediment. The sum of the concentrations obtained with the six-step selective leaching method was compared with those obtained with the total acid-soluble procedure and good agreement was achieved (Cd 97-108%, Pb 96-106%, Zn 92-103%, Mn 99-106%, Fe 100%). All element concentrations from the fish and the sediment are given as dry weight (µg g^{-1} dw).

Statistics

Average concentrations and standard deviations were calculated for each element, tissue, and fish species. The significance levels of the differences between element concentrations in the studied fish organs and between locations were determined using the Mann–Whitney test (Sokal and Rohlf 1987).

The individual contamination factor (ICF) was calculated using the modified formula given by Ikem et al. (2003). For a particular element, the sum of the four "mobile" fractions (i.e. the exchangeable, carbonate bound, easily reducible, and sulfide/organic) was divided by the two "immobile" fractions (i.e. moderately reducible and residual). The index of geoaccumulation (I_{geo}) was calculated with the Müller (1981) equation:

$$I_{geo} = \log_2 (Cn/1.5\ Bn)$$

where: Cn is the mean concentration of an element in the bottom sediment, and Bn is the geochemical background of the element in the shale (Turiekian and Wedepohl 1961).

According to values of the I_{geo}, Müller (1981) described seven categories of sediment contamination, from unpolluted (category 0; $I_{geo}<0$) to extremely contaminated bottom sediment (category 6; $I_{geo}>5$).

The bioconcentration factor (BCF) was calculated as the ratio of the mean element content in fish tissue (mean from 10 specimens) to its mean content in the sediment (mean from Stations 1-4) in the upper part of the reservoir. Calculations for the lower part of the reservoir were performed in a similar manner. The factor indicates the ability of fish to accumulate trace elements regardless of the way the element is taken up.

RESULTS AND DISCUSSION

Element concentration and speciation in bottom sediment

The ranges of the trace element concentrations in the sediment of the Dobczyce Reservoir were Cd 0.69–1.96, Pb 4.4–44.8, Cu 5.4–35.2, Zn 116–260, Mn 95–773 µg g^{-1} dw, and Fe 4.5–32.6 mg g^{-1} dw. In general, the mean concentrations of all the studied elements were higher in the upper part of the reservoir; however, the differences between the two ends of the reservoir were not significant (Table 2). The standard deviations seemed to be greater in the upper region, which may indicate that there were considerable local differences in the concentrations of trace elements in the sediment. According to I_{geo} values, the reservoir sediment was polluted to a low degree by Cd and relatively unpolluted by Pb, Zn, Mn, and Fe (Table 2).

Table 2

Total concentration (mean and standard deviation), Index of geoaccumulation (I_{geo}), and Individual contamination factor (mean and standard deviation) of trace elements in the bottom sediment in the upper (Stations 1–4) and lower (Stations 5–8) sections of the Dobczyce Reservoir

Parameters	Elements				
	Cd	Pb	Zn	Mn	Fe
Total concentration (µg g^{-1} dry wt.)					
Upper part	1.4 ±0.5	27 ±17	189 ±61	481 ±334	19190 ±12270
Lower part	1.1 ±0.1	23 ±6	156 ±15	221 ±95	15900 ±8050
Index of geoaccumulation (I_{geo})					
Upper part	1.7 (II class)	-0.1 (0 class)	0.4 (I class)	-1.4 (0 class)	-1.9 (0 class)
Lower part	1.3 (II class)	-0.4 (0 class)	0.1 (I class)	-2.5 (0 class)	-2.2 (0 class)
Individual contamination factor (ICF)					
Upper part	12.2 ±5.8	1.5 ±0.1	0.50 ±0.39	11.2 ±4.9	0.16 ±0.10
Lower part	13.3 ±1.8	1.4 ±1.2	0.44 ±0.15	0.7 ±0.3	0.29 ±0.20

The exchangeable phase (F1) is generally regarded as potentially the most mobile fraction, while carbonate (F2), easily reducible (F3) and organic/sulfidic (F5) phases are regarded as moderately mobile and available to organisms. Carbonates exist as cements and coatings that coprecipitate with heavy metals. Lowering pH dissolves carbonates and releases the associated heavy metals (Batley 1990). In the Dobczyce Reservoir the pH in the sediment ranged from 7.0 to 7.5, and was similar in both parts of the reservoir. The easily-reducible fraction included those metal portions occluded in an Mn-oxide matrix that may be released under reducing conditions, caused primarily by the decomposition of organic matter (Förstner et al. 1986, Song and Müller 1995, van den Berg et al. 1998, van Rysen et al. 1998). Metals bound to organic matter may be remobilized as a result of diagenetic processes in the oxic upper layers of the sediment (Guo et al. 1997, van den Berg et al. 1998, Eggleton and Thomas 2004). If the redox potential (Eh) rises, metals associated with sulfides may be released into the overlying water. Metals in the moderately-reducible fraction are more strongly bound to sediment particles and are rather immobile. Dissolution of Fe compounds is relatively small during normal metabolic processes (Tessier et al. 1996). The residual phase represents metals that should not be available for remobilization under usual conditions.

The studied metals were bound to different operationally-defined phases in the sediment of the Dobczyce Reservoir; therefore, they have different potentials for remobilization (Fig. 2). In general, in both parts of the reservoir, Cd was mainly bound to moderately mobile F2 and F3 phases, while Pb was associated primarily with F2, F3, F4, and F6. The majority of Zn was associated with immobile F6, while a smaller amount was associated with F2, F3, and F4. Mn was primarily associated with moderately mobile F2 and F3 in the upper part of the reservoir and with F2 and F4 in the lower part. Fe was bound primarily to F4 and F6, and, in part, to F3.

In order to estimate the risk of contamination by pollutants deposited in the sediment in the studied sections of the reservoir, the individual contamination factor (ICF) was calculated (Table 2). According to the ICF results, Cd had the highest possibility of being released from the sediment. Among the remaining elements, Pb and Mn had a higher possibility of release than Zn and Fe. There were no significant differences in the ICF for Cd, Pb, Zn, and Fe between the two sections of the reservoir; however, the ICF for Mn was significantly higher ($p<0.05$) in the upper region. Thus, the potential risk of water and biota contamination by Cd, Pb, Zn, and Fe deposited in the sediment was similar in both parts of the reservoir, while the contamination risk of Mn was higher in the upper part of the reservoir.

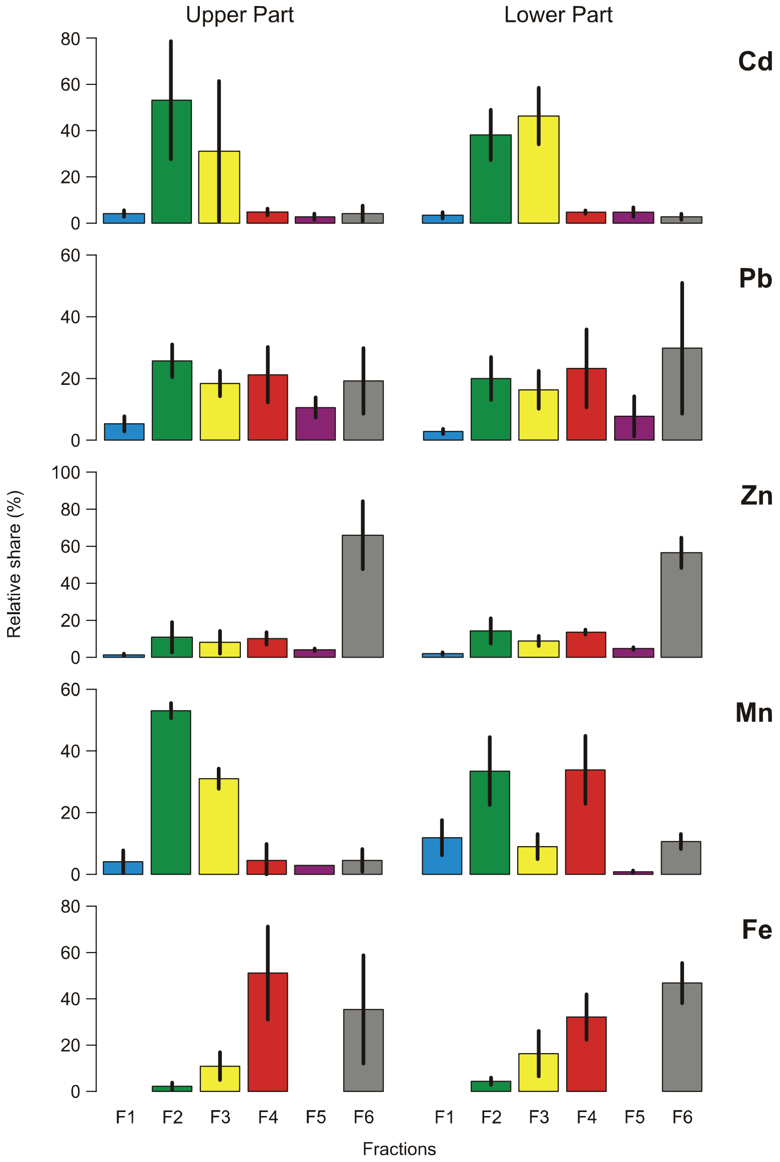

Fig. 2. Mean percentages and standard deviations of binding forms of selected trace elements in the bottom sediment of Dobczyce Reservoir in 2003 (n=4 for upper and n=4 for lower sections of the reservoir). Fractions: F1 – exchangeable, F2 – carbonate, F3 – easily reducible, F4 – moderately reducible, F5 – organic/sulfides, F6 – residual.

Element concentration in fish tissues

Various elements showed different affinities to the studied fish organs and tissues (Fig. 3). Trace element concentrations differed significantly between fish tissues in most cases (Table 3). Cd concentrated primarily in the kidney,

Table 3

Significance of differences in the concentrations of selected trace elements in the organs of fish species collected in the Dobczyce Reservoir. Values presented are the significance levels obtained using the Wilcoxon test (ns – not significant)

Organs	Species								
	Roach			Bream			Pikeperch		
Cd									
Liver	⇘			⇘			⇘		
Kidney	0.02	⇘		0.01	⇘		0.01	⇘	
Muscle	0.01	0.01	⇘	0.01	0.01	⇘	0.01	0.01	⇘
Gills	0.01	0.01	ns	0.01	0.01	0.01	0.01	0.01	0.01
Pb									
Liver	⇘			⇘			⇘		
Kidney		⇘			⇘			⇘	
Muscle	0.01		⇘	0.01		⇘	0.01		⇘
Gills	0.05		ns	0.05		0.05	0.02		0.01
Zn									
Liver	⇘			⇘			⇘		
Kidney	0.01	⇘		ns	⇘		0.01	⇘	
Muscle	0.01	0.01	⇘	0.01	0.05	⇘	0.01	0.01	⇘
Gills	0.01	0.01	0.01	0.05	ns	0.01	0.01	0.02	0.01
Mn									
Liver	⇘			⇘			⇘		
Kidney	ns	⇘		0.01	⇘		0.01	⇘	
Muscle	0.01	0.01	⇘	0.01	0.01	⇘	0.01	0.01	⇘
Gills	0.01	0.01	0.01	0.01	0.01	0.01	ns	0.01	0.01
Fe									
Liver	⇘			⇘			⇘		
Kidney	ns	⇘		ns	⇘		0.01	⇘	
Muscle	0.01	0.01	⇘	0.01	0.01	⇘	0.01	0.01	⇘
Gills	ns	ns	0.01	ns	ns	0.01	0.02	0.01	0.01

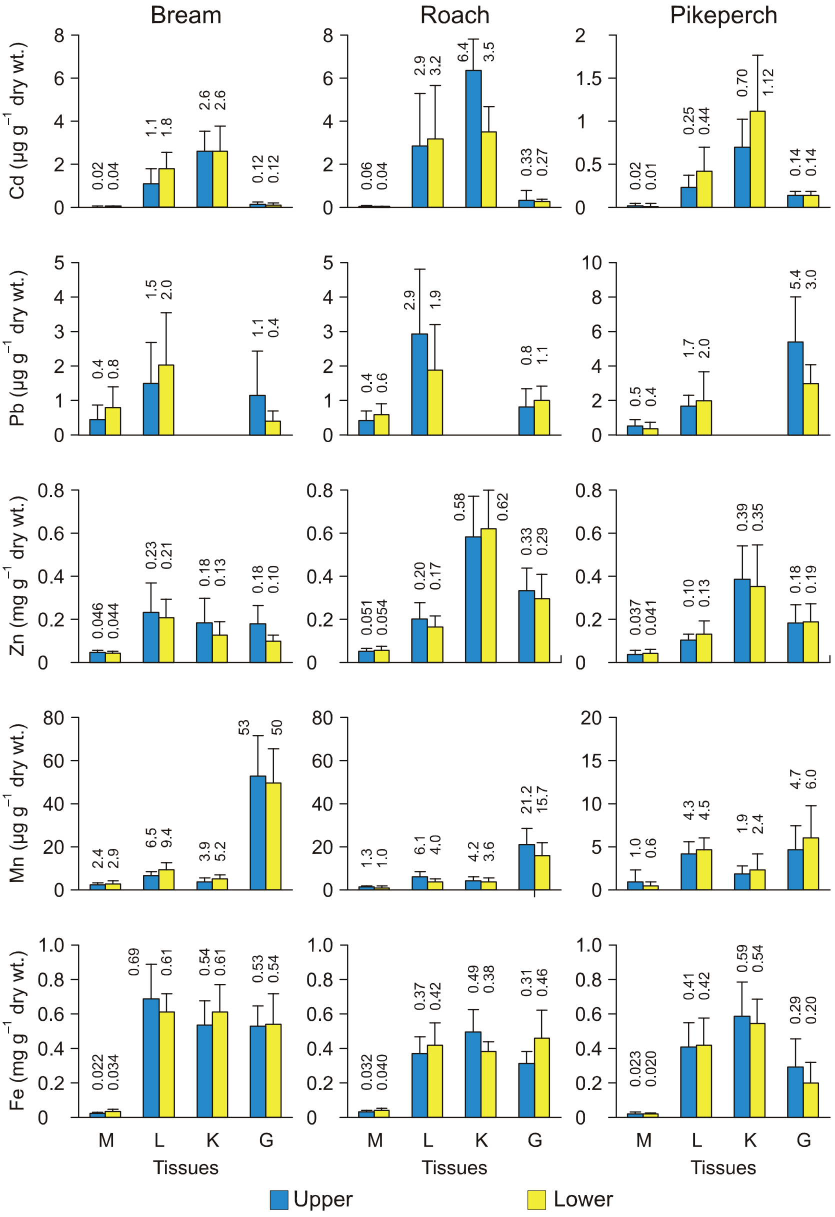

Fig. 3. Concentrations of studied elements (mean and standard deviations) in fish tissues (G – gills, K – kidney, L – liver, M – muscle) in the upper and lower sections of the Dobczyce Reservoir. Note modified scale in Cd, Pb, and Mn concentrations in pikeperch.

followed by the liver, gills, and to a lesser degree in the muscle of all the fish species. In bream and roach, the highest concentration of Pb was found in the liver, while the lowest was noted in muscle. In pikeperch, Pb was concentrated mainly in the gills, followed by the liver and muscle. The Pb content in the kidney of the fish was not studied. Zn concentrated mostly in the kidney and liver (bream), while the lowest concentration was found in the muscle. In roach and pikeperch, Zn was concentrated in the kidney, followed by the gills, liver, and muscle. The highest Mn concentration was found in all species in the gills with lower concentrations in the liver, kidney, and muscle. Only in the case of pikeperch were there no significant differences between Mn content in the gills and liver. In roach and bream the concentration of Fe in the liver, kidney and gills was similar and higher than in the muscle. In pikeperch, the highest concentration of Fe was in the kidney, while lower concentrations were found in the liver and gills and the lowest in muscle.

The current results concur with earlier studies by Brown et al. (1986), Morsy and Protasowicki (1990), Carpene et al. (1994), Moiseenko et al. (1995), Andres et al. (2000), Bervoets et al. (2001), and Szarek-Gwiazda and Amirowicz (2003). According to these authors, many elements are accumulated preferentially in specific organs and tissues, such as Cd and Pb in the kidney; Zn in the gills, liver, spleen, gonads, kidney, and digestive tract; and Mn in gills. For waterborne metal contamination, elevated concentrations of trace elements are usually detected in the gills of various fish species (Protasowicki and Chodyniecki 1988, Morsy and Protasowicki 1990, Perkowska and Protasowicki 2000). In some cases, the results of the current study indicated interspecific differences in metal accumulation in fish tissues (i.e., Pb concentrated in the liver of bream and roach, but in the gills of pikeperch).

Trace element concentrations in fish muscle were low in the Dobczyce Reservoir. According to Polish law, the levels of Cd in fish muscles cannot exceed 0.05 and Pb 0.2 µg g^{-1} wet weight. Assuming 80% moisture, these values can be converted into dry weight as Cd 0.25 and Pb 1.0 µg g^{-1} dw. The concentrations found in the current study were considerably lower and below permissible limits for human consumption.

Interspecific differences

Cadmium content was higher in roach tissues in comparison to bream and pikeperch (Table 4). The pattern of Cd accumulation in bream and pikeperch was not clear. Concentrations of Cd in bream were higher in the liver and kidney, but lower in the gills. In most cases, the studied species had similar Pb content in the muscle and liver. The exception was Pb content in the gills. The highest Pb content was found in pikeperch, while the lowest was in bream. The

Table 4

Significance of differences in trace element concentrations among fish species in the Dobczyce Reservoir in 2003. The values presented are the significance levels obtained using the Mann–Whitney test (ns – not significant)

Species	Organs							
	Muscle		Liver		Kidney		Gills	
Both Stations								
Cd								
Bream	➷		➷		➷		➷	
Roach	0.05	➷	ns	➷	0.001	➷	0.001	➷
Pikeperch	ns	0.01	0.001	0.001	0.001	0.001	0.05	0.05
Pb								
Bream	➷		➷		➷		➷	
Roach	ns	➷	ns	➷		➷	0.05	➷
Pikeperch	ns	ns	ns	ns			0.001	0.001
Zn								
Bream	➷		➷		➷		➷	
Roach	ns	➷	ns	➷	0.001	➷	0.001	➷
Pikeperch	ns	0.05	0.001	0.001	0.001	0.001	0.02	0.01
Mn								
Bream	➷		➷		➷		➷	
Roach	0.001	➷	0.001	➷	ns	➷	0.001	➷
Pikeperch	0.001	0.001	0.001	ns	0.001	0.02	0.001	0.001
Fe								
Bream	➷		➷		➷		➷	
Roach	0.05	➷	0.001	➷	0.05	➷	0.05	➷
Pikeperch	ns	0.001	0.001	ns	ns	0.05	0.001	0.05

Zn content in roach was always higher than in pikeperch, but was similar (liver, muscle) or higher (kidney, gills) than in bream. Similar to Cd, the pattern of Zn accumulation in bream and pikeperch was not clear. The Zn content in the muscle of bream and pikeperch was similar, but in the liver it was higher in bream, while in the kidney and gills it was higher in pikeperch. Mn showed a high affinity for bream tissues and the lowest affinity for those of pikeperch. A higher Fe content was found in bream than in roach (except muscle) and pikeperch (except muscle and kidney). Differences in the Fe content in tissues between roach and pikeperch were not clear. Higher Fe content was found in the muscle and gills in roach, although it was noted in the kidney in pikeperch.

In summary, the highest contents of Cd and Zn were found in the benthivorous roach, the highest Mn and Fe in planktivorous/benthivorous bream, while Pb contents in all species were similar (except in the gills). Predatory pikeperch exhibited elevated metal contents in the gills (i.e., Cd and Zn in comparison to bream, and Pb relative to roach and bream) and elevated Fe content in the kidney in comparison to roach.

Higher concentrations of some trace elements in the tissues of benthivorous or omnivorous fish than in the predators was also observed by Protasowicki (1991; Cu and Zn in the muscle of roach *vs*. pikeperch), Glushankova and Pashkova (1992; Pb in the muscle and Cd, Pb, and Cu in the liver of roach vs. perch), Amundsen et al. (1997; Cd in the muscle of whitefish, *Coregonus lavaretus* (L.), feeding on invertebrates vs. piscivorous perch), Blanchard et al. (1999; Cd, Pb, and Cu in roach vs. perch and pikeperch), Andres et al. (2000; Cd in the muscle, kidney and gills of roach vs. perch), and Łuczyńska et al. (2006; Cu and Fe in the muscle of roach and bream vs. pike and perch).

Similar trace element concentrations in the tissues of different fish species have been reported by many authors: Cd in the muscle of roach and perch (Dobrowolski and Skowrońska 2001); Fe in roach and perch from Pskovsko-Chudskoye Lake (Glushankova and Pashkova 1992); Cd and Pb in roach, bream, and pikeperch (Protasowicki 1991); Cd in roach, bream, and perch (Dobrowolski and Skowroński 2001); Cd, Pb, Cu, and Zn in crucian carp, German carp, carp, white bream, bream, tench, perch, roach, common walleye, pike, and rudd (Marek 1997); Cu in pike, perch, pikeperch, bream, roach, and tench (Sobczyński et al. 1995); Zn in roach and perch (Blanchard et. al. 1999); Cd, Pb, Cu, and Zn in roach and pike, and Cu and Zn in bream and pike (Scharenberg et al. 1994); Cd and Pb in roach, bream, and perch (Protasowicki et al. 1983); Fe in the liver of roach and perch from Pskovsko-Chudskoye Lake (Glushankova and Pashkova 1992); Cd, Pb, Cu, and Zn in the liver and gills in bream, perch, roach, and pike (Marek 1997); Cd in roach, silver bream, and rudd (Szarek-Gwiazda and Amirowicz 2006).

Inversely, higher concentrations of metals in the tissues of predatory species in comparison with non-predatory species have also been determined, as follows: Zn in the muscle of pike, perch, and pikeperch as compared to that in bream, roach, and tench (Sobczyński et al. 1995); Pb and Zn in perch as compared to roach and bream (Dobrowolski and Skowrońska 2001); Fe in the gills of perch as compared to that in roach in Virts'yarv Lake (Glushankova and Pashkova 1992). Łuczyńska et al. (2006) reported the following sequence of Zn concentration in the muscle of fish: pike> roach>perch>bream.

Interspecific variation in trace element accumulation in fish tissues can be explained by different rates of assimilation of heavy metals from water and food as well as by the allocation of metals into different organs and tissues of various fish species (Allen-Gill and Martynov 1995), the feeding habits of fish (i.e., different feeding activity, food composition, and feeding sites; Jezierska and Witeska 2001), food quality, for instance plants or detritus (Langevoord et al. 1995, Andres et al. 2000), or differential induction of the MT gene in various fish species (Olsson and Kille 1997, De Boeck et al. 2003). Elevated trace element contents in the gills and kidney in pikeperch relative to bream may be explained by different levels of activity, energy expenditures, or the oxygen demands of these species.

Differences between locations

The mean concentrations and standard deviations of the studied elements in fish in the upper and lower sections of the reservoir are presented in Figure 3. In most cases, the SD : mean ratio was close to 1, which indicates high variability in trace element concentrations in fish species living in this water body. Similarly high variation was found previously by Kuznetsova et al. (2002) in the Bratsk Reservoir and by Farkas (2003) in bream from Lake Balaton. Kuznetsova et al. (2002) explained the results by means of the relatively large number of studied individuals (20–40 ind.).

The differences between trace element concentrations in the fish from the studied sections of the Dobczyce Reservoir were significant in a few cases. Higher concentrations of Cd (kidney, $p<0.01$), and Mn (muscle, $p<0.02$; liver, $p<0.05$) in roach, Zn (gills, $p<0.01$) in bream, and Pb (gills, $p<0.05$) in pikeperch were detected in the upper part of the reservoir in comparison to those in the lower part. Higher concentrations of Cd (muscle, $p<0.01$; liver, $p<0.05$), Fe (muscle, $p<0.05$), and Mn (liver, $p<0.01$) were detected in bream in the lower part of the reservoir in comparison with those in the upper part.

The study results indicated that Cd and Mn were more available for benthivorous roach in the upper part of the reservoir. As mentioned above, element concentrations in the sediment were similar in both parts of the reservoir. However, Mn was a more mobile element in the sediment of the upper part of the reservoir as compared to the lower one. This might result in higher Mn concentration in roach tissues there. Higher concentrations of Zn and Pb in the gills of fish in the upper part of the reservoir compared to the lower part may be related to the elevated content of these elements in the water and indicate the metal uptake route by fish. The gills are particularly susceptible to metal-induced structural and functional disturbances (Jezierska and Witeska 2004). After short-term exposure, the gills, or the digestive tract and liver, usually show a high load of toxicants, whereas concentrations in kidney, bones, and muscle increase more slowly but the accumulated chemicals are more persistent than in other organs (Köck et al. 1996).

The absence of differences in the concentration of Cd, Mn, and Fe in the gills of fish between the upper and lower parts of the reservoir may indicate that element uptake from water via the gills was similar in both parts of the reservoir. The differences observed in the accumulation of trace elements in the muscle, liver, and kidney of fish between studied locations may be caused by differences in diet and food quality. In general, bream can shift between plankton and bottom feeding depending on the abundance of food organisms (Hoogenboezem et al. 1992). Zooplankton was the only food component of bream in the lower part of the Dobczyce Reservoir during a study in the late 1990s (Pociecha and Amirowicz 2003). In unpolluted or slightly polluted water environments, the dominant route of metal uptake in fish is through the digestive tract.

Metal bioconcentration in fish

Cd and Zn was bioconcentrated in fish tissues in the highest quantities (Fig. 4). The bioconcentration factor (BFC) for Cd was higher (for roach approximately tenfold) in comparison to that for Pb, Mn, and Fe. Lead was bioconcentrated to the highest degree in pikeperch, Mn in bream, while Fe was bioconcentrated to a similar degree in all the species studied. High Cd bioconcentration in the benthivorous roach was probably related to fish

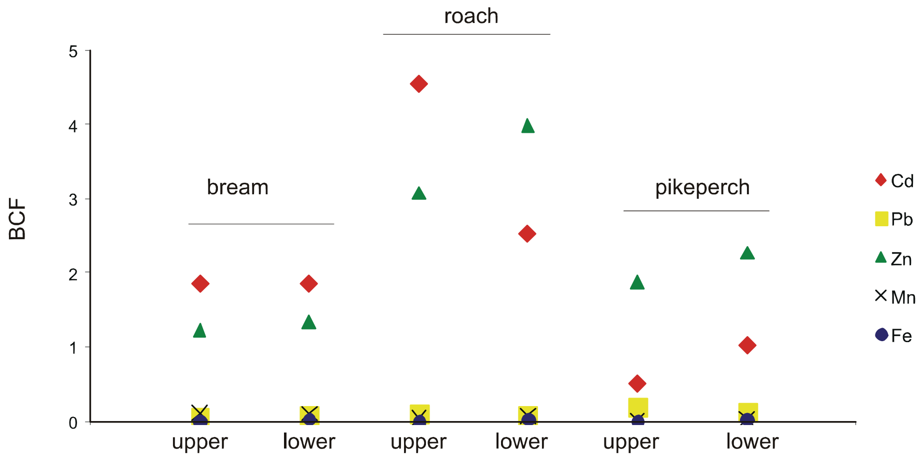

Fig. 4. Values of the bioconcentration factors (BCF) of selected trace elements in the tissues of the studied fish from the Dobczyce Reservoir in 2003.

behavior, as this species forages for food by burrowing into the sediment, where Cd was the most mobile and available element (according to ICF results, but not metal content in the exchangeable fraction, F1). It is well known that metals associated with the exchangeable phase in the sediment are the most mobile and bioavailable. However, changes in physicochemical environmental parameters (e.g., pH, redox potential) at the water-sediment interface may cause the mobilization of pollutants associated with moderately mobile phases, such as carbonate, easily reducible, and organic/sulfide. Therefore, metal bioconcentration in fish tissues (BCF) was probably related to ICF. Despite high ICF values for Mn in the upper part of the reservoir, its bioconcentration (BCF) in fish was relatively low. Mn is an essential element and its amount in fish can be homeostatically controlled. Therefore, the relation between metal mobility in the sediment and its bioconcentration in fish was probably more pronounced in the case of the unessential element (Cd) than the essential one (Mn). Zinc was bioconcentrated in fish tissues in the Dobczyce Reservoir to a considerable degree. However, high Zn bioconcentration in roach could not be related to its mobility in the sediment. Zinc is an essential element and is always present in relatively high concentrations in animal tissues. A similar result, namely higher Cd content in roach in comparison with other species such as rudd, which forages mainly on macrophytes, and perch, which is predatory, was reported by Szarek-Gwiazda and Amirowicz (2006) for Piaseczno Lake. These authors linked high Cd bioconcentration in roach to its high mobility in the sediment.

CONCLUSION

This study examined trace element concentrations in three fish species with different feeding behaviors (i.e., roach – benthivore, bream – planktivore/benthivore, pikeperch – piscivore) and in the bottom sediments in the upper and lower sections of the Dobczyce Reservoir in southern Poland. A six-step extraction procedure was applied to determine the binding forms of trace elements in the sediment. The sediment was polluted to a low degree by Cd and was relatively unpolluted by Pb, Zn, Mn, and Fe. Total element concentrations were similar in the upper and lower sections of the reservoir. Cd was the most mobile element in the sediment. The Individual Contamination Factor (ICF), which indicates the potential risk of water and biota contamination by elements present in the sediment, was approximately tenfold higher for Cd than for Pb, Zn, Mn, and Fe.

Trace element concentrations differed significantly between fish tissues as well as between fish species. Cd was mostly concentrated in the kidney, Pb and Mn in the liver and gills (Pb in the kidney was not studied), Zn in the kidney and liver, and Fe in the liver, kidney, and gills. The lowest concentrations of trace elements were always found in muscle. Generally, the highest concentrations of Cd and Zn were found in benthivorous roach and Mn and Fe in planktivorous/benthivorous bream, while Pb contents in all species were similar (except in the gills). The results obtained confirmed that benthivorous (roach) or planktivorous/benthivorous (bream) species usually accumulated higher concentrations of trace elements than piscivorous fish.

Differences between the trace element concentrations in fish from the upper and lower sections of the Dobczyce Reservoir were detected in a few cases. This indicated that the availability of trace elements to fish can differ even within a small polluted water body. This may result in variability in the trace element concentrations of fish inhabiting a water body.

According to the BCF results, Cd and Zn were bioconcentrated in fish tissues to the highest degree. The BFC for Cd was higher (for roach approximately tenfold) in comparison to Pb, Mn, and Fe. High Cd bioconcentration in benthivorous roach was probably connected to its behavior. This fish feeds by burrowing in the bottom sediment, where Cd was the most mobile and available element (according to the ICF). Therefore, it is permanently exposed to contamination by this element mainly through the digestive tract (as it takes food items from the bottom sediment) and the gills (by processing benthic particles prior to ingestion).

REFERENCES

Allen-Gil S.M., Martynov V.G., 1995, *Heavy metal burdens in nine species of freshwater and anadromous fish from the Pechora River, northern Russia*, Sci. Total Environ., 160/161: 653-9

Amirowicz A., 1998, *Consequences of the basin morphology for fish community in a deep-storage submontane reservoir,* Acta Hydrobiol., 39(Suppl. 1): 35-56

Amundsen P-A., Staldvik F.J., Lukin A.A., Kashulin N.A., Popova O.A., Reshetnikov, Y.S., 1997, *Heavy metal contamination in freshwater fish from the border region between Norway and Russia*, Sci. Total Environ., 201: 211-24

Andres S., Ribeyre F., Tourencq J.N., Boudou A., 2000, *Interspecific comparison of cadmium and zinc contamination in the organs of four fish species along a polymetallic pollution gradient (Lot River, France),* Sci. Total Environ., 248: 11-25

Barak N.A.E., Mason C.F., 1990, *Mercury, cadmium and lead concentrations in five species of freshwater fish from eastern England*, Sci. Total Environ., 92: 257-63

Batley G.E., 1990, *Trace element speciation: analytical methods and problems*, CRC Press, Inc. Boca Raton, Florida, USA

Bervoets L., Blust R., Verheyen R., 2001, *Accumulations of metals in the tissues of three spined stickleback (Gasterosteus aceleatus) from natural fresh waters*, Ecotoxicol. Environ. Saf., 48: 117-27

Blanchard M., Teil M.J., Carru A-M., Garban B., Ollivon D., Chesterikoff A., Chevreuil M., 1999, *Biota contamination by PCBs and trace metals in the freshwater estuary of the River Seine (France),* Hydrobiologia., 400: 149-54

Brown M.W., Thomas D.G., Shurben D., Solbe J.F.L.G., Kay J, Cryer A., 1986, *A comparison of the differential accumulation of cadmium in the tissue of three species of freshwater fish: Salmo gairdneri, Rutilus rutilus and Noemacheilus barbatulus*, Comp. Biochem. Physiol., 84C: 213-17

Cain D.J., Carter J.L., Fend S.V., Luoma S.N., Alpers C.N., Taylor H.E., 2000, *Metal exposure in a benthic macroinvertebrate, Hydropsyche californica, related to mine drainage in the Sacramento River,* Can. J. Fish Aquat. Sci., 57(2): 380-90

Calmano W., Hong J., Förstner U., 1993, *Binding and mobilization of heavy metals in contaminated sediments affected by pH and redox conditions*, Wat. Sci. Technol., 28: 223-35

Carpene E., Gumiero B., Fedrizzini G., Serra R., 1994, *Trace elements (Zn, Cu, Cd) in fish from rearing ponds of Emilia-Romagna region (Italy),* Sci. Total Environ., 141: 139-46

Carru A-M., Teil M.J., Blanchard M., Chevreuil M., Chesterikoff A., 1996, *Evaluation of the roach (Rutilus rutilus) and the perch (Perca fluviatilis) for the biomonitoring of metal pollution,* J. Environ. Sci. Health., A31: 1149-58

De Boeck G., Ngo T.T.H., Van Campenhout K., Blust R., 2003, *Differential metallothionein induction patterns in three freshwater fish during sublethal copper exposure*, Aquatic Toxicology., 65(4): 413-24

Dobicki W., Polechoński R., 2003, *Relationship between age and heavy metal bioaccumulation by tissues of four fish species inhabiting Wojnowskie Lakes.* Acta Scient. Pol. –Piscaria, 2 (1): 27-44

Dobrowolski R., Skowrońska M., 2001, *Distribution and environmental mobility of selected trace metals in the Zemborzyce Reservoir,* Polish Journal of Environmental Studies, 10: 383-88

Eggleton J., Thomas K.V., 2004, *A review of factors affecting the release and bioavailability of contaminants during sediment disturbance events*, Environ Int., 30(7): 973-80

Farkas A., Salánki J., Specziár A., 2003, *Age- and size- specific patterns of heavy metals in the organs of freshwater fish Abramis brama L. populating a low contaminated site*, Water Research., 37: 959-64

Frank A., 1984, *Automatic wet ashing*, Association of Official Analytical Chemists., 7: pp. 5

Förstner U., Calmano W., 1982, *Bindungsformen von Schwermetallen in Baggerschlämmen*, Vom. Wasser., 59: 83-93, (in German)

Förstner U., Ahlf W., Calmano W., Kersten M., Salomons W., 1986, *Mobility of heavy metals in Dredged Harbor Sediments* [in:] *Sediments and water interactions,* Sly P.G. (ed.), Proc. 3rd Internat. Symp., Genewa, 1984, Springer., 371-80

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

Glushankova M.A., Pashkova I.M., 1992, *Heavy metals in tissues of fish of the Pskovsko-Chudskoye and Virts'yarv Lakes*, Tsitologiya, 34: 46-50

Głosińska G., Sobczyński T., Boszke L., Bierła K., Siepak J., 2005, *Fractionation of some heavy metals in bottom sediments from the middle Odra River (Germany/Poland),* Pol. J. Environ. Stud. 14(3): 305-17

Guo T., Delaune R.D., Patrick W.H., 1997, *The effect of sediment redox chemistry on solubility/chemically active forms of selected metals in bottom sediment receiving produced water discharge*, Spill Science and Technology Bulletin., 4(3): 165-75

Hongve D., 2003, *Chemical stratigraphy of recent sediments from a depth gradient in a meromictic lake, Nordbytjernet, SE Norway, in relation to variable external loading and sedimentary fluxes*, Journal of Paleolimnology, 30(1): 75-93

Hoogenboezem W., Lammens E.H.R.R., van Vugt Y., Osse J.W.M., 1992, *A model for switching between particulate-feeding and filter-feeding in the common bream, Abramis brama*, Environ. Biol. Fish., 33: 13-21

Ikem A., Egiebor N.O., Nyavor K., 2003, *Trace elements in water, fish and sediment from Tuskegee Lake, Southeastern USA*, Water, Air, and Soil Pollution., 149: 51-75

Jezierska B., Witeska M., 2001, *Metal toxicity to fish*, Wyd. Akademii Podlaskiej (Monografie, 42), Siedlce, pp. 318

Jezierska B., Witeska M., 2004, *The effect of metals on fish gill functions – gas and ion exchange (Review)*, Fresenius Environmental Bulletin, 13: 1370-78

Kostecki M., 2000, *Heavy metals in flesh and liver of some fish species in Dzierżono Duże dam-reservoir (Upper Silesia)*, Archives of Environmental Protection, 26(4): 109-25.

Köck G., Triendl M., Hofer R., 1996, *Seasonal patterns of metal accumulation in Artic char (Salvelinusalpinus) from oligotrophic alpine lakes related to temperature*, Can. J. Fish. Aquat. Sci., 53: 780-86

Kuznetsova A.I., Zarubina O.V., Leonova G.A., 2002, *Comparison of Zn, Cu, Pb, Ni, Cr, Sn, Mo concentrations in tissues of fish (roach and perch) from Lake Baikal and Bratsk Reservoir, Russia*, Environmental Geochemistry and Health., 24(3): 205-13

Langevoord M., Kraak M., Kraal M., Davids C., 1995, *Importance of prey choice for Cd uptake by carp (Cyprinus carpio) finger-lings*, J. N. Am. Benthol. Soc., 14: 423-29

Łuczyńska J., Brucka-Jastrzębska E., 2005, *The relationship between the content of lead and cadmium in muscle tissue and the size of fish from lakes in the Olsztyn Lake District of northeast Poland*, Arch. Pol. Fish., 13(2): 147-55

Łuczyńska J., Markiewicz K., Jaworski J., 2006, *Interspecific differences in the contents of macro- and microelements in the muscle of six species from lakes of the Olsztyn lake district (north-east of Poland)*. Polish Journal of Food and Nutrition Science, 15/56(1): 29-35

Marek J., 1990, *Heavy metals in the aquatic environment of the Barycz river-basin. Estimation of hazards to fish management*. Chemia i Inżynieria Ekologiczna, 4, S1, pp. 53 (in Polish)

Martinez E.A., Moore B.C., Schaumloffel J., Dasgupta N., 2002, *The potential association between mental deformities and trace elements in Chironomidae (Diptera) taken from a heavy metal contaminated river*, Arch. Environ. Contam. Toxicol., 42(3): 286-91

Morsy G., Protasowicki M., 1990, *Cadmium bioaccumulation and its effects on some hematological and histological aspects in carp, Cyprinus carpio L. at selected temperatures*. Acta Ichthyol. et Piscat., 20(1): 105-16

Müller G., 1981, *Die Schwermetallbelastung der Sedimente des Neckars und seiner Nebenflüsse. Eine Bestandaufnahme*, Chemiker-Zeitung., 6: 157-64

Moiseenko T.I., Kudryavtseva L.P., Rodyushkin I.V., Lukin A.A., Kashulin N.A., 1995, *Airborne contamination by heavy metals and aluminum in the freshwater ecosystems of Kola subarctic region (Russia),* Sci. Total. Environ., 160/161: 715-27

Olsson P.E., Kille E., 1997, *Functional comparison of the metal-regulated transcriptional control regions of metallothionein genes from cadmium-sensitive and tolerant fish species*, BBA-Gene Struct. Exp., 1350: 325-34

Perkowska A., Protasowicki M., 2000, *Cadmium and lead in fishes and in selected elements of the Świdwie Lake ecosystem*. Acta Ichthyol. et Piscat., 30(2): 71-84.

Pociecha A., Amirowicz A., 2003, *An attempt to determine the share of zooplankton in food consumed by fish in the limnetic zone of a eutrophic dam reservoir,* Oceanol. Hydrobiol. Studies., 32(2): 15-31

Protasowicki M., Chodyniecki A., Ociepa A., 1983, *Metale ciężkie w rybach przemysłowych poławianych w latach 1976-1980*. Zesz. Nauk. AR Szczec., 103: 181-98 (in Polish)

Protasowicki M., Chodynicki A., 1988, *Accumulation of Cd, Pb, Cu and Zn in carp* (*Cyprinus carpio* L.) *relative to metal contents in water and time of exposure*. Zesz. Nauk. AR Szczec., 1988, 133: 69-84.

Protasowicki M., 1991, *Long-term studies on heavy metals in aquatic organisms from River Odra mouth area*. Acta Ichthyol. et Piscat., suppl., 21: 301-9.

Rashed M.N., 2001, *Monitoring of environmental heavy metals in fish from Nasser Lake*, Environ. Internat., 27: 27-33

Smolders A.J.P., Lock R.A.C., Van der Velde G., Hoyos R.I.M., Roelofs J.G.M., 2003, *Effects of mining activities on heavy metal concentrations in water, sediment, and macroinvertebrates in different reaches of the Pilcomayo River*, South America Arch. *Environ*, Contam. Toxicol., 44(3): 314-23

Sobczyński T., Elbanowska H., Zerze J., Siepak J., Andrzejewski W., Mastyński J., 1995, *Bioaccumulation of heavy metals in fish of the lakes of the Wielkopolska National Park,* Morena 3: 111-16 (in Polish).

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

Sokal R.R., Rohlf F.J., 1987, *Biostatistics*, New York, W.H. Freeman and Company

Song Y., Müller G., 1995, *Biogeochemical cycling of nutrients and trace metals in anoxic freshwater sediments of the Neckar River, Germany*, Mar. Frashwater Res., 46: 237-43

Storelli M.M., Marcotrigiano G.O., 2001, *Heavy metal monitoring in fish, bivalve mollusc, water, and sediments from Varano Lagoon, Italy,* Bull. Environ, Contam. Toxicol., 66: 365-70

Svobodová Z., Čelechovská O., Kolářá J., Randák T., Žlábek V., 2004, *Assessment of metal contamination in the upper reaches of the Tichá Orlice River*, Czech J. Anim. Sci., 49: 458-64

Szarek-Gwiazda E., Mazurkiewicz-Boron 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., Amirowicz A., 2003, *Bioaccumulation of trace elements in roach, Rutilus rutilus (L.) in a eutrophicated submontane reservoir*, Chemia i Inżynieria Ekologiczna., 10: 445-53

Szarek-Gwiazda E., Amirowicz A., 2006, *Bioaccumulation of trace elements in roach, silver bream, rudd, and perch living in an inundated opencast sulphur mine*, Aquatic Ecology, (in press)

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

Tessier A., Fortin D., Belzile N., Divitre R., Leppard G.G., 1996, *Metal sorption to diagenetic iron and manganese oxyhydroxides and associated organic matter: narrowing the gap between field and laboratory measurements*, Geochim. Cosmochim. Acta., 60: 387-404

Turiekian K.K., Wedepohl K.H., 1961, *Distribution of the elements in some major units of the earth's crusts*, Bull. Geol. Soc. Am., 72: 175-92

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

Witeska M., Jezierska B., 2003, *The effects of environmental factors on metal toxicity to fish (Review),* Fresenius Environmental Bulletin, 12: 824-9

Wiechuła D., Loska K., Korus I., 2005, *Lead partitioning in the bottom sediment of Rybnik reservoir (southern Poland),* Water Air Soil Poll 164(1-4): 315-27

Zoumis T., Schmidt A., Grigorova L., Calmano W., 2001, *Contaminants in sediments: remobilization and demobilisation*, Sci. Total Environ., 266: 195-202