Aquatic Ecology (2006) 40:221–236
DOI 10.1007/s10452-004-7341-3

Bioaccumulation of trace elements in roach, silver bream, rudd, and perch living in an inundated opencast sulphur mine

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Received 9 February 2004; accepted in revised form 6 December 2004

Key words: Ecology, Freshwater fish, Microelements, Sediment, Speciation

Abstract

The contents of Cd, Pb, Cu, Mn, Fe, and Sr were determined in bottom sediment and fish in Piaseczno lake (inundated opencast sulphur mine, southern Poland) from April 2001 to January 2002. To determine the mobility and availability of these elements in the 0–5 cm layer of the sediment, a 6-step sequential extraction procedure was applied. Generally, in the sediment the amounts of Cd were low, of Pb and Cu were elevated, but of Mn, Fe, and Sr were very high. Risk of contamination of water by Sr and Mn estimated using individual contamination factor was much higher than by Cd, Pb, Cu and Fe. A relationship was found between the contents of the metals in some fish tissues and their trophic habits. According to bioconcentration factor Sr and Mn, which posed the highest risks to water contamination were concentrated to a greatest degree in benthivorous fish.

Introduction

Accumulation of trace elements in fish living in contaminated waters depends on many factors, such as content of the elements in water and food organisms, physicochemical features of abiotic habitat (e.g. pH, alkalinity, salinity), and duration of exposure. The total quantity and distribution of elements in fish is also related to the species, individual age and size, feeding habit, different affinities to particular tissues, different uptake, deposition, and excretion rates, and individual susceptibility (Håkanson 1984; Jezierska and Witeska 2001). A clear relationship between the total element content in sediment and fish has rarely been found only under conditions of high element loadings (Burrows and Whitton 1983; Bendel Young and Harvey 1991; Gurierri 1998; Cain et al. 2000; Martinez et al. 2002; Smolders et al. 2003).

Studies on partitioning of trace elements in the aquatic environment provide a good approach to showing their real activity. A sequential leaching procedure has been successfully applied to describe environmentally mobile (and therefore available to biota) and stable fractions (Calmano and Förstner 1983; Batley 1990; Hlavay and Polyák 1998; Weisz et al. 2000; Todorovic et al. 2001; El Bilali et al. 2002). Some environmental conditions (for instance pH, redox, salinity, organic complexes) influence the remobilisation of elements from sediment (Förstner 1986; Galvez-Cloutier and Dubé 1996; Anderson and Pempkowiak 1999; La Force et al. 1999; Nowack et al. 2001; Cappuyns and Swennen 2004).

Elements bound to different phase of bottom sediment are incorporated at different rates by organisms which live and feed there. Therefore, the element content in invertebrates is more closely correlated with the respective form of element speciation in the sediment (Tessier et al. 1984; Bendel Young and Harvey 1991; Bervoets et al. 1997, 1998; de Bisthoven et al. 1998; Klavinš et al. 1998) than to the total element content. In the predicting metal concentration in fish from its binding forms in the sediment the individual contamination factor (ICF, Ikem et al. 2003) may be used. This factor reflects the risk of contamination of a water body by a pollutant deposited in the sediment. To check this hypothesis fish species differing in proportion of benthic food should be studied.

The aim of this study was to investigate the content of trace elements in selected tissues of fish species living in an unusual inland water environment characterized by relatively high mineralisation and salinity, especially to estimate (1) the level of concentration of these elements in fish tissue, and (2) the relationship between element binding forms in the sediment and its content in fish.

Material and methods

Study area

Piaseczno lake near Tarnobrzeg in southeastern Poland (55°35′ N, 35′ 21° E) is a water body which originated in an opencast sulphur mine that was closed in 1971. The mining uncovered Holocene and Pleistocene mud, sand, gravel and Sarmatian clayey deposits, sulphur-bearing limestone, gypsum, and the Baranów sands (Pawlowski et al. 1985). When mining ceased a lake was formed by natural filling of the mine with highly mineralised Tertiary and Quaternary waters. The water level rose to the altitude of 121.8 m at which is artificially kept until now to control the depression cone over the area of Tarnobrzeg mining field. At present the Piaseczno lake has an area of ca. 63 ha and maximum depth of 21.5 m (Żurek 2002) and is a meromictic water body owing to its basin morphology. Water is well oxygenated from the surface to the depth of 5–7.5 m (8.8–13.4 mg/l), whereas poorly in the near-bottom layer (< 1.9 mg/l). Such differences in dissolved oxygen concentration undoubtedly affected vertical fish distribution. Permanent occurrence of fishes is possible down to the depth at which the amount of oxygen becomes limiting (about 3–5 mg/l, depending on specific demands). The pH ranges from 7 to 8.5. The water is very hard (510–1605 mg $CaCO_3$/l) and rich in Cl^- and SO_4^{2-} anions (200–5000 mg/l and 300–1000 mg/l, respectively).

Sample collection

Samples of the upper layer (0–5 cm) of the bottom sediment (36, in total) were collected at nine points (1a, 1b, 1c, depth 1 m; 2a, 2b, 2c, depth 5 m; 3a, 3b, 3c, depth 10 m; Figure 1) in spring (3 April 2001), summer (18 July 2001), autumn (6 November 2001) and winter (15 January 2002). The stations were located along three transects differing in density of submerged macrophytes, slope gradient, and thickness of the sediment layer. Samples were taken using a polyethylene corer (diameter 4 cm) and placed into plastic containers that were previously rinsed with double-distilled water. One sediment sample contained three subsamples taken from particular locality. For each sample, total element contents were determined. In samples collected on 3 April and 18 July 2001 the phase-specific binding forms of the elements were also studied.

Fishes were collected in 2001 (11 September) and 2002 (9 July and 25 September). On each sampling date a set of gill nets (10–70 mm mesh size) was used. It was composed of seven nets of fixed 10-mm linear difference in mesh size which allowed to reduce the effect of selectivity of this fishing gear. Fishes were placed individually in polyethylene bags and chilled on ice during transport to the laboratory. In total, 78 specimens of four species, i.e. 44 roaches *Rutilus rutilus* (L.), 15 perches *Perca fluviatilis* L., 13 silver breams *Blicca bjoerkna* (L.), and 6 rudds *Scardinius erythrophthalmus* (L.) were selected for element content analyses (Table 1). All of these species feed on zooplankton in their early life stages, after which their diet includes increasing proportion of macroinvertebrates. However, as adults they show some differences in diet composition. Silver bream becomes mainly benthivorous, perch piscivorous, roach is an omnivore,

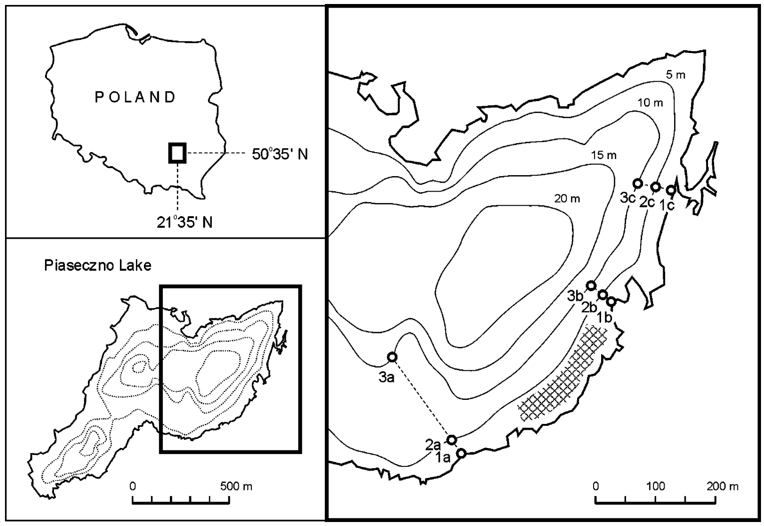

Figure 1. Location of sampling points (open circles) and fish collecting area (cross-hatching) in Piaseczno lake.

Table 1. Fish collected for analyses of the content of trace elements (LT – total length, LC – standard length).

Species	*n*	LT (cm)		LC (cm)		Weight (g)		Age (years)	
		Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.
Roach	44	14.6	31.6	11.6	25.0	30.3	454	3+	10+
Silver bream	13	14.3	22.3	10.8	25.5	25.5	116	2+	6+
Rudd	6	15.7	33.8	12.5	26.9	28.5	571	3+	9+
Perch	15	8.2	27.2	6.7	22.9	5.1	258	1+	4+

while the diet of rudd includes a significant proportion of aquatic plants.

Analytical methods

Samples of sediment used for determination of total contents of Pb, Cu, Mn, Fe, and Sr were dried at 105 °C for ≥ 24 h, and then ground (3 g of the sediment and 0.3 g of paraffin, MERCK Hoechst wax C micropowder) in a planetary mill (Pulverisette 7, Fritsch) at 500 rpm for 5 min. Tablets (2.7 g, 31 mm in diameter) were then prepared in a pallet die (Graseby–Specac), under a pressure of 25 t for about 5 s. The measurements were carried out using an energy-dispersive X-ray spectrometer (ED 2000, Oxford Instruments). The element contents were based on standard sediments IAEA–SL1 and IAEA–SL3 obtained from the International Atomic Energy Agency.

Sediment samples used to determine the total Cd content were dried at 105 °C for ≥ 24 h, and then homogenized using the planetary mill (Pulverisette 5) with teflon grinding balls. Triplicates of approximately 0.5 g of dry sediment were digested with 15 ml conc. HNO_3 in tubes on the heated block of a Tecator Digestion System 12, in conjunction with an Autostep 2000 controller set to 120 °C for 2 h. After digestion, the content of each tube was 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. Then the flask was filled with double-distilled water.

Analyses for a operationally defined phase-specific binding form of the elements in the sediment were carried out according to the method originally described by Tessier et al. (1979) and modified by Förstner and Calmano (1982). Six fractions were obtained as indicated in Table 2: (F1)

Table 2. Sequential extraction scheme for fractionations of Cd, Pb, Cu, Mn, Fe, and Sr in the sediment of Piaseczno lake (after Förstner and Calmano 1982). Dry mass of the sediment sample: 0.5 g.

Step	Fraction	Extracting solution	pH	Volume of solution (ml)	Conditions
1[a]	Exchangeable (F1)	1 mol $l^{-1}CH_3COONH_4$	7	10	Shake 2 h, at room temperature
2[a]	Carbonates (F2)	1 mol $l^{-1}CH_3COONa$ + CH_3COOH	5	10	Shake 5 h, at room temperature
3[a]	Easily reducible phases (Mn oxide, amorphous Fe hydroxides) (F3)	0.1 mol l^{-1} $NH_2OH{\cdot}HCl$	2	50	Shake 12 h, at room temperature
4[a]	Moderately reducible phases (mainly poorly crystalline Fe-oxyhydroxides) (F4)	0.2 mol l^{-1} $(NH_4)_2C_2O_4$ + 0.2 mol l^{-1} $H_2C_2O_4$	3	50	Shake 24 h, at room temperature
5[b]	Organic/sulphides (F5)	(a) 30% (v/v) H_2O_2	2	15	2 h 85 °C
		(b) 1 mol l^{-1} CH_3COONH_4	7	50	Shake 12 h, at room temperature
6[c]	Residual (F6)	65% HNO_3		20	2 h, 120 °C

[a]Extractions 1–4: the samples remain in the centrifuge vessels; after extraction the solutions were centrifuged with 3500 rpm; then filtered (mesh 0.45 μm).
[b]Extraction 5: The residue obtained after step 4 was transferred into a 100-ml beaker; H_2O_2 was added, and digested on a sand bath. Addition of H_2O_2 was repeated three times until the solution finished to bubble. Then the solution was evaporated until nearly dry; ammonium acetate was added and after shaking the solution was centrifuged.
[c]Digested at 120 °C and centrifuged.

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/sulphides, and (F6) residual. The analyses of fractions: exchangeable, carbonate, easily reducible, and moderately reducible were conducted under oxygen-free conditions. All volumetric flasks were washed and soaked in 30% HNO_3 for 48 h and then thoroughly rinsed with double-distilled water before analyses.

Collected fishes were measured and dissected immediately after delivery to the laboratory. In each specimen age was determined by counting the annual rings on scales. The samples of dorsal muscle, gills, liver, and kidney were taken and dried in an oven at 60 °C for 48 h. Then they were homogenised and digested with a mixture of pure (MERCK) nitric and perchloric acid (4:1) on the heated block of a Tecator Digestion System 12, in conjunction with an Autostep 2000 controller according to the method of Frank (1984). Some smaller samples (mainly of kidney) were digested in quartz vessels on a heated plate. Initial digestion was at room temperature for 24 h, followed by careful heating at temperature of 40 °C for 2 h to prevent frothing, after which the temperature was raised to the 225 °C for 4 h. Samples were then allowed to cool and final solutions were made up to 10 ml with double-distilled water. They were stored cool to analyses.

The trace element concentrations were measured with Perkin–Elmer 403 atomic absorption spectrophotometer equipped with a Graphite Furnace (HGA–74) and determined according to the manual recommendations. Instrument calibration was performed using calibration solutions of trace elements prepared from the 1000 mg/l metal stock solution (purchased from the Central Office of Measures, Warsaw) immediately before analysis. The calibration curve were checked with replicate analyses of calibration solutions at the start and subsequently at every tenth sample analysed. Analysis of blank for sediment and fish samples was conducted to check the purity of reagents and all results were corrected for blanks. The percentage coefficient of variation of total Cd in triplicate sediment sample analyses ranged within 1.2–8.7%. The accuracy of the sequential extraction scheme was checked up by comparing the sum of concentrations from the six fractions to the total element concentration. The determined rates for all elements ranged from 82 to 111%.

Statistical analysis

The significance of differences in the partitioning of trace elements between studied fractions in the sediment were estimated using Wilcoxon test (Sokal and Rohlf 1987). The individual contamination factors (ICF) were calculated by modified formula given by Ikem et al. (2003). The results of the extraction study were used. For an individual element the sum of the four 'mobile' fractions (i.e. the exchangeable, carbonate bound, easily reducible, and sulphidic/organic forms) was divided by the 'immobile' one (i.e. moderately reducible, and residual fractions). Bioconcentration factor (BCF) was calculated as the ratio of the mean element content in fish tissue to its mean content in the sediment (BCF) in summer. The factor indicates the ability of fish to accumulate the trace elements regardless of the way the element is taken up. For each element, tissue, and fish species the average values and standard deviations were calculated (as μg/g dry weight). As the series of results were not equal and of low numbers the significance levels of element concentration differences between studied fish organs were assessed using Wilcoxon test, whereas those between species using Mann–Whitney test (Sokal and Rohlf 1987). In small specimens the sampling of appropriate amounts of small organs (mainly kidney) was difficult or impossible in some cases. Because the total number of silver bream and rudd was small the relationships between fish length, age and metal concentrations in tissues were calculated only for roach and perch.

Results and discussion

Concentration of elements in fish

Contents of trace elements in particular tissues

The results indicate different affinities of trace elements to various organs of the studied fish species (Table 3). Cadmium accumulated in a great degree in kidney and its content there was always higher that in liver. Similarly, Pb accumulated mostly in the kidney of roach and perch, while roughly in the same degree in liver and kidney of silver bream. In perch also the contents of Cd and Pb in the liver, kidney, and gills were similar. Copper accumulated to a high degree in the liver of roach, whereas the levels of its accumulation in the liver, kidney, and gills of silver bream and perch were similar. Manganese and strontium accumulated mostly in the gills of all the studied species. Iron concentrated mainly in the liver (roach), kidney (perch) or in the liver, kidney and gills (silver bream). The lowest contents of all elements were always found in the muscle tissue. Above results show that only in the case of Mn and Sr it is possible to indicate one main storage organ (i.e. gills) for all studied species.

Above results are in concordance with many authors who pointed on the kidney as a storage organ for Cd and Pb, and the liver for Cu. Kroupa and Hatrvich (1990) found the highest Cd and Pb content in the kidney and Cu in the liver of roach from the Lužnice river (Czech Republic). Müller and Prosi (1978) reported the highest Cd content in the kidney and Cu content in the liver of roach from the Neckar and Elsenz rivers. Andres et al. (2000) reported a decrease of Cd contents in the order kidney > liver > intestine > gills > muscle in roach and perch from the Lot river (France). Higher contents of Cd in the kidney than in the liver and muscle of roach was also found by Brown et al. (1986), and of Cd and Pb in perch by Berninger and Pennanen (1995).

High concentration of the studied elements (especially Mn, Sr, Fe, and Cu) in the gills in fishes from Piaseczno lake may be related with their elevated content in water, and may indicate this route of contamination. Gills are the main target of direct contamination, play a significant role in metal uptake, storage, transfer to the internal organs via blood transport, and also excretion. An experimental study of Segner (1987) and Drbal and Svobodová (1980) indicated a considerable increase of Cu in the gills of roach and carp, *Cyprinus carpio* L. especially in the beginning of waterborne exposure. Manganese and strontium generally showed a great affinities to the fish gills (Moiseenko et al. 1995; Jezierska and Witeska 2001; Szarek-Gwiazda and Amirowicz 2003).

Considering all the studied species and tissues the average content of investigated elements was in following ranges: (in μg/g dry wt.) Cd: 0.1–0.6, Pb: 1.2–7.1, Cu: 4–34, Mn: 11–110, Fe: 47–685, and Sr: 4–157 (Figure 2). They were compared to those found in fish from water bodies polluted to a different degree (Håkanson 1984; Barak and Mason 1990; Dobicki 1990; Kroupa and Hartvich 1990;

Table 3. The significance of differences between concentrations of selected trace elements in studied organs of fish species collected in Lake Piaseczno in 2001–2002.

Organs	Species								
	Roach			Silver bream			Perch		
Cd									
Liver	➢			➢			➢		
Kidney	0.001	➢		0.01	➢		0.05	➢	
Muscle	0.001	0.001	➢	0.01	0.01	➢	0.01	0.02	➢
Gills	0.05	0.001	ns	0.05	0.01	0.01	ns	ns	0.01
Pb									
Liver	➢			➢			➢		
Kidney	0.05	➢		ns	➢		0.05	➢	
Muscle	0.01	0.001	➢	0.01	0.01	➢	0.01	0.05	➢
Gills	ns	0.01	0.05	0.02	ns	0.01	ns	ns	0.01
Cu									
Liver	➢			➢			➢		
Kidney	0.001	➢		ns	➢		ns	➢	
Muscle	0.001	0.001	➢	0.01	0.01	➢	0.01	0.05	➢
Gills	0.001	ns	0.001	ns	ns	0.01	ns	ns	0.01
Mn									
Liver	➢			➢			➢		
Kidney	ns	➢		ns	➢		ns	➢	
Muscle	0.01	0.001	➢	0.01	0.01	➢	0.01	0.05	➢
Gills	0.001	0.001	0.001	0.01	0.01	0.01	0.01	0.05	0.01
Fe									
Liver	➢			➢			➢		
Kidney	0.05	➢		ns	➢		0.02	➢	
Muscle	0.001	0.001	➢	0.01	0.01	➢	0.01	0.01	➢
Gills	0.001	ns	0.001	ns	ns	0.01	0.01	0.01	0.01
Sr									
Liver	➢			➢			➢		
Kidney	ns	➢		ns	➢		0.05	➢	
Muscle	0.05	0.05	➢	0.01	0.01	➢	0.01	0.05	➢
Gills	0.001	0.001	0.001	0.01	0.01	0.01	0.01	0.05	0.01

The presented values are the significance levels obtained using Wilcoxon test (ns – not significant).

Malarevskaya and Karasina 1991; Glushankova and Pashkova 1992; Marek 1997; Szarek-Gwiazda and Amirowicz 2003). In general, the content of Cd in fish tissues in Piaseczno lake appeared to be within the ranges reported from unpolluted ecosystems. The contents of Pb in the liver and kidney of the studied fish were elevated as compared to these found in the unpolluted waters, but they were lower than in highly polluted water bodies. The content of Cu in fish tissues (except gills) was similar to those found in polluted water bodies. Content of copper in the gills of all the studied species was very high. The concentrations of Mn and Fe in the liver, kidney, and gills, and of Sr (mainly in the gills) were much higher than those determined in other waters. Perhaps, these concentrations were related to extremely high contents of those elements in the environment of Piaseczno lake. In recent papers by Cain et al. (2000), Martinez et al. (2002), and Smolders et al. (2003) are reported elevated concentrations of trace elements in fish under conditions of high element loadings in sediment.

Interspecific differences

All studied species had similar Cd contents in the liver and gills (Table 4). Roach (and silver bream) had the highest content of Cd in the kidney, while rudd the lowest one. Roach and rudd had similar Cd content in the muscle, which was higher than in perch and silver bream. Glushankova and

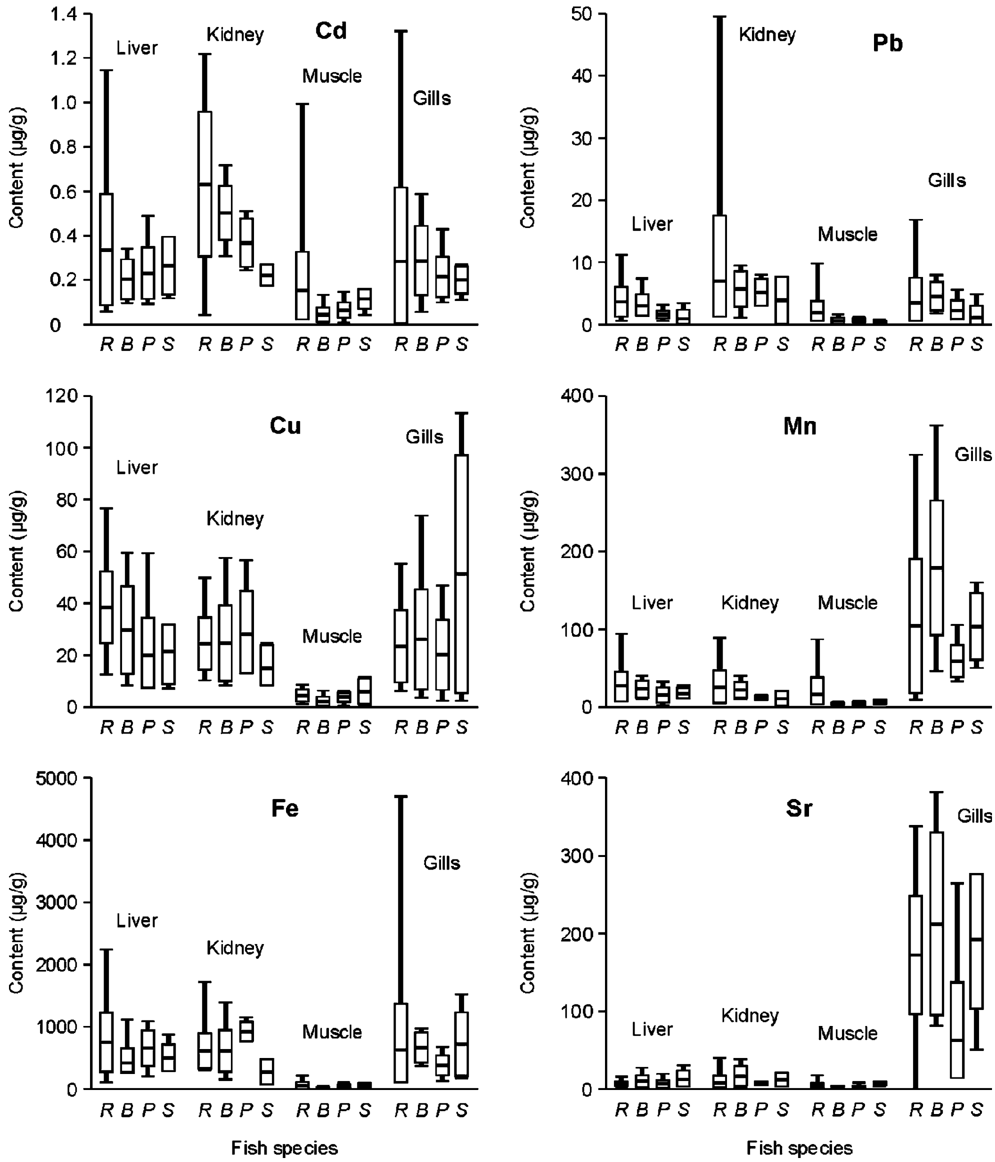

Figure 2. Mean values (µg/g dry wt.; horizontal bars), standard deviations (boxes), and ranges (vertical bars) of trace elements in the tissues of fishes collected in Piaseczno lake in 2001: R – roach, *Rutilus rutilus* (L), *B* – silver bream, *Blicca bjoerkna* (L.), *P* – perch, *Perea fluviatilis* L., *S* – rudd, *Scardinius erythrophthalmus* (L.).

Pashkova (1992) found elevated content of Cd in the liver of roach in comparison with perch. Elevated content of Cd in liver and gills of whitefish, *Coregonus lavaretus* (L.) feeding on invertebrates as compared to piscivorous perch was also found by Amundsen et al. (1997). Andres et al. (2000) found that roach had higher level of Cd in liver, kidney, gills, and muscle than perch. The similar contents of Cd in the muscle of roach and perch found Dobrowolski and Skowrońska (2001).

The contents of Pb in the liver of roach and silver bream were higher than those in perch and rudd. Except the higher content in silver bream than in rudd Pb contents in the kidney in studied species were similar. Roach had the highest Pb content in the muscle, silver bream and perch lower and similar, while rudd the lowest. Silver bream had the highest content of Pb in the gills, roach and perch lower, whereas rudd the lowest. Also Glushankova and Pashkova (1992) found an

Table 4. The significance of differences between concentrations of selected trace elements in fish species collected in Lake Piaseczno in 2001–2002.

Species	Organs											
	Liver			Kidney			Muscle			Gills		
Cd												
Roach	➘			➘			➘			➘		
Silver bream	ns	➘		ns	➘		0.01	➘		ns	➘	
Perch	ns	ns	➘	0.05	0.05	➘	0.02	ns	➘	ns	ns	➘
Rudd	ns	ns	ns		0.05		ns	0.05	ns	ns	ns	ns
Pb												
Roach	➘			➘			➘			➘		
Silver bream	ns	➘		ns	➘		0.01	➘		0.05	➘	
Perch	0.01	0.05	➘	ns	ns	➘	0.01	ns	➘	ns	0.05	➘
Rudd	0.01	0.05	ns		0.05		0.001	0.05	0.05	0.02	0.05	0.05
Cu												
Roach	➘			➘			➘			➘		
Silver bream	ns	➘		ns	➘		0.01	➘		ns	➘	
Perch	0.001	0.05	➘	ns	ns	➘	ns	ns	➘	ns	ns	➘
Rudd	ns	ns	0.05		ns		ns	ns	ns	ns	ns	ns
Mn												
Roach	➘			➘			➘			➘		
Silver bream	ns	➘		ns	➘		0.01	➘		0.01	➘	
Perch	ns	0.05	➘	ns	0.05	➘	0.05	ns	➘	ns	0.05	➘
Rudd	ns	ns	ns		ns		ns	ns	ns	ns	ns	0.05
Fe												
Roach	➘			➘			➘			➘		
Silver bream	0.01	➘		ns	➘		0.01	➘		ns	➘	
Perch	ns	0.05	➘	0.001	0.05	➘	ns	0.05	➘	ns	0.05	➘
Rudd	ns	ns	ns		ns		ns	ns	ns	ns	ns	ns
Sr												
Roach	➘			➘			➘			➘		
Silver bream	ns	➘		ns	➘		ns	➘		ns	➘	
Perch	ns	ns	➘	ns	ns	➘	0.05	ns	➘	0.001	0.05	➘
Rudd	ns	ns	ns		ns		ns	ns	0.05	ns	ns	0.05

The presented values are the significance levels obtained using Mann–Whitney test (ns – not significant).

elevated content of Pb in the liver and muscle of roach in comparison with perch.

The content of Cu in fish tissues (with a few exceptions) was similar. Perch had significant lower content of Cu in the liver than remaining species. Copper content in muscle was higher in roach than in silver bream. Similarly to above results the content of Cu in liver greater in roach than in perch was found by Glushankova and Pashkova (1992).

Roach, perch, and rudd had similar contents of Mn (except its greater content in muscle of roach than in perch) and Fe (except its greater content in kidney of perch than in roach). Silver bream had higher Mn content in gills in comparison to other species, and in the liver and kidney than perch, whereas in the muscle the lower one than roach. Silver bream had lower content of Fe in the liver, kidney, and muscle than roach and perch, while in the gills the higher than in perch. Also Glushankova and Pashkova (1992) found not any considerable differences in the Fe content in muscle and liver of roach and perch from Pskovsko-Chudskoye lake. However, the analogous contents in perch from Virts'yarv lake were higher, as well as in both lakes the contents of Fe in perch gills were higher than in roach.

The content of Sr in the tissues of studied species of fish was similar. The only exception was perch. Significantly lower content of Sr in the gills of perch than in remaining species, and in the muscle of perch than in roach and rudd was found.

Above results showed some interspecific differences in trace elements accumulation in fish from Piaseczno lake. These differences were greater in the case of Cd and Pb and smaller in the case of Cu, Mn, Fe, and Sr concentration. The omnivorous roach had usually similar or higher contents of selected elements (except Fe) than remaining fish. Benthivorous silver bream had usually similar content of the elements (except Fe) like roach (with exception of lower contents of Cd, Pb, Cu, Mn and Fe in muscles). Among the studied species silver bream had the highest contents of Pb and Mn in gills. Piscivorous perch had similar or lower contents of the elements than in other species (with exception of Fe, which contents in some tissues were usually higher than those in roach and silver bream). Rudd which in summer feeds mainly on plants had the lowest contents of Cd in the kidney, and Pb in the muscle and gills. The obtained results indicate that omnivorous roach, which is common and often abundant in many kinds of Central European inland waters, and benthivorous silver bream, which occurs mainly in lowland rivers and lakes are of the fish species most tolerant for some trace elements and can accumulate them in considerable amounts, greater than other species inhabiting the same water body. As concerns roach, the similar results obtained Chevreuil et al. (1995); Petkevičiūtė and Merčiulionienė (1999), and Andres et al. (2000).

Interspecific variation in the accumulation of trace elements depends on many factors like different rate of assimilation of heavy metals from water and food as well as on the allocation of metals into different organs and tissues. Various fish species have different sensitivity to heavy metals and the ability for homeostatic control, detoxification and rejection (Allen-Gill and Martynov 1995). Olsson and Kille (1997), and De Boeck et al. (2003) explained most of the interspecific differences by different induction in metallothionein (MT) gene. De Boeck et al. (2003) found that giebel, *Carassius auratus gibelio* (Bloch) which was very resistant to copper polluted environments showed a significant positive relationship between tissue copper concentrations and MT levels in gill, liver and muscle tissues.

Jezierska and Witeska (2001) on the basis of several publications concluded that interspecific differences are mostly influenced by feeding habits of fish, i.e. different feeding activity, food composition, and feeding sites. Amundsen et al. (1997) and Andres et al. (2000) also concluded that Cd concentrations in general are inversely correlated with trophic level. Langevoord et al. (1995) and Andres et al. (2000) indicated an important role of food quality on the level of metal bioaccumulation. According to the last source the assimilation of cadmium was greater when it was associated with the plants (roach) than detritus (bream). Langevoord et al. (1995) obtained different Cd bioaccumulation in carp whether this metal was provided *via* contaminated zebra mussel *(Dreissena polymorpha)* than *Chironomus riparius* larvae. Thus, the lack of general regularities in accumulation of trace element in fish through trophic chain found in this study and confirmed by other authors may be explained by the flexibility of fish feeding habits what is the common feature of most species. Diet composition may substantially change in seasons or even in diel cycle as an effect of changing density and/or activity of prey organisms. In general, in most cases in the diet of a fish species predominate not the most appropriate but the most available food items.

Concentrations of trace elements with respect to fish length, weight, and age

In general, all correlations between fish length, weight, age and trace element concentration in studied tissues of roach and perch were very weak (Table 5). Only in two cases the determination coefficients were greater than 0.5, in perch strontium concentration in muscles was negatively correlated with total length (Sr (μg/g) = 10.14–0.3604 LT (cm), $n = 15$, $p < 0.01$) and weight (Sr (μg/g) = 5.510–0.02272 W (g), $n = 15$, $p < 0.01$). There are not too many data in the literature describing relationship between length, weight, or age and trace element concentrations in fish tissues, and the results are often divergent. The relationship between length and trace element contents in roach and perch tissues was studied by Carru et al. (1996) and Barak and Mason (1990). Similarly to our results Carru et al. (1996) found the lack of relationship between length of roach and perch and Cd, Pb, Cu, Fe, Mn, and Pb concentrations in the muscles. Also Barak and Mason (1990) found the lack of relationship between Cd concentration in liver and muscle and length in roach from River Chelmer and Brett. These authors found also the

Table 5. Determination coefficient (R^2) of the correlations between fish length, weight, age and trace element concentration in studied tissues.

Elements	Roach				Perch			
	Liver	Kidney	Muscle	Gills	Liver	Kidney	Muscle	Gills
Total length								
Cd	0.13	0.04	0.01	0.05	0.39	0.10	0.02	0.08
Pb	0.40	0.14	< 0.01	0.04	< 0.01	< 0.01	0.05	0.12
Cu	0.09	0.06	0.05	0.02	< 0.01		0.05	0.12
Mn	0.12	0.01	0.01	< 0.01	< 0.01		0.09	0.37
Fe	0.01	< 0.01	0.02	0.01	0.32	0.24	0.08	< 0.01
Sr	0.19	< 0.01	0.47	0.26	0.18	0.19	0.70	0.20
Weight								
Cd	0.07	0.04	0.03	0.01	0.47	0.18	0.00	0.08
Pb	0.19	0.12	0.01	0.04	< 0.01	0.02	0.10	0.37
Cu	0.09	0.08	0.07	0.04	< 0.01		0.10	0.17
Mn	0.12	0.01	< 0.01	0.01	0.07		0.07	0.21
Fe	0.01	< 0.01	0.03	< 0.01	0.21	0.12	0.16	0.05
Sr	0.22	0.01	0.34	0.02	0.29	0.33	0.61	0.06
Age								
Cd	0.12	0.08	0.01	0.06	0.40	0.01	0.02	0.06
Pb	0.29	0.05	< 0.01	0.05	0.03	0.18	0.04	0.00
Cu	0.04	0.04	0.02	0.01	0.03		0.04	0.18
Mn	0.08	< 0.01	< 0.01	< 0.01	0.05		0.04	0.41
Fe	0.01	< 0.01	0.02	< 0.01	0.29	0.20	0.20	0.07
Sr	0.14	< 0.01	0.14	0.10	0.23	0.33	0.42	0.20

Table 6. Total concentrations (mean ± SD) of trace elements in the bottom sediment: (Cd, Pb, Cu and Sr in μg/g dry wt., Fe and Mn in mg/g dry wt.) of Piaseczno lake in 2001–2002.

Season	Cd	Pb	Cu	Mn	Fe	Sr
Spring	0.27 ± 0.12	23.4 ± 5.7	46.0 ± 12.4	5.788 ± 7.566	24.288 ± 8.564	543.6 ± 594.4
Summer	2.1 ± 0.76	22.1 ± 6.9	44.7 ± 11.0	3.928 ± 3.129	21.677 ± 3.682	567.1 ± 943.0
Autumn	1.9 ± 0.65	22.8 ± 10.6	40.6 ± 11.4	3.468 ± 2.546	27.287 ± 19.905	323.4 ± 261.1
Winter	0.53 ± 0.21	25.4 ± 8.9	43.8 ± 11.5	8.171 ± 8.215	22.314 ± 5.716	529.2 ± 709.7

Each value is the mean of 9 concentrations calculated for Stations 1a, 1b, c, 2a, 2b, 2c, 3a, 3b, 3c.

lack of relationship between length of roach and Pb concentration in liver in the River Chelmer, and positive correlation in River Brett. Similarly to our result other authors found the lack of relationship between the weight of roach and content of Cd and Pb (Pružina et al. 1993), and Cd, Pb, and Cu (Řehulka 2001) in the muscle. The negative correlation between roach weight and Pb content in the muscle was found by Kostecki (2000). According to Kroupa and Hartvich (1990), Allen-Gil and Martynov (1995) and Řehulka (2001) trace element contents in the muscle of roach is independent from age. A decrease in the Cd, Pb, and Zn contents in the liver and kidney with increasing age of roach from polluted River Luznice was found by Kroupa and Hartvich (1990). The lack of strong positive correlation between weight, age and metal (Cd, Pb, Cu) content in muscle of roach and perch, as well in liver of perch was found by Håkanson (1984).

Relation between element binding forms in the sediment and its content in fish

Total element contents in the sediment

Mean contents of investigated trace elements in sediment show some seasonal differences (Table 6). Contents of cadmium were higher in summer and autumn, while the lowest was recorded in spring. An inverse pattern occurred in the case of Mn, which contents were lower in summer and autumn than in spring and winter. Contents of all the remaining elements showed negligible changes between seasons, with exception of Sr in autumn. A detailed description of horizontal and seasonal differentiation of the elements in the sediment is given by E. Szarek-Gwiazda, J. Galas, A. Wróbel, M. Ollik, and A. Frankiewicz, unpubl. No statistical significant differences between particular seasons were found.

In general, the content of Cd in the sediment of the Piaseczno lake was rather low, Pb and Cu elevated, whereas Mn, Fe, and Sr very high (Table 6) in comparison to unpolluted water bodies. Obtained contents of trace element in the sediment were compared to those given by Turiekian and Wedepohl (1961) for shales (in μg/g dry wt.: Cd 0.3, Pb 20, Cu 45, Mn 850, and Sr 400). They were also compared to those found in bottom sediments of 112 Polish lakes (Bojakowska et al. 2000) in which the contents of trace elements ranged (in μg/g dry wt.): Cd from < 0.5 to 12.0, Pb from < 5 to 157, Cu from < 10 to > 50, Sr from < 50 to > 500. The contents of trace element in the bottom sediment of the Piaseczno lake were determined mainly by natural geochemical peculiarities of the region and they remained in the range of values found in the rocks of the catchment area or in Tertiary and Quaternary waters (E. Szarek-Gwiazda, J. Galas, A. Wróbel, M. Ollik, and A. Frankiewicz, unpubl.). Some part of element load may be caused by emission from a chemical industry plant and a power station located ca. 5 and 30 km far from Piaseczno lake, respectively.

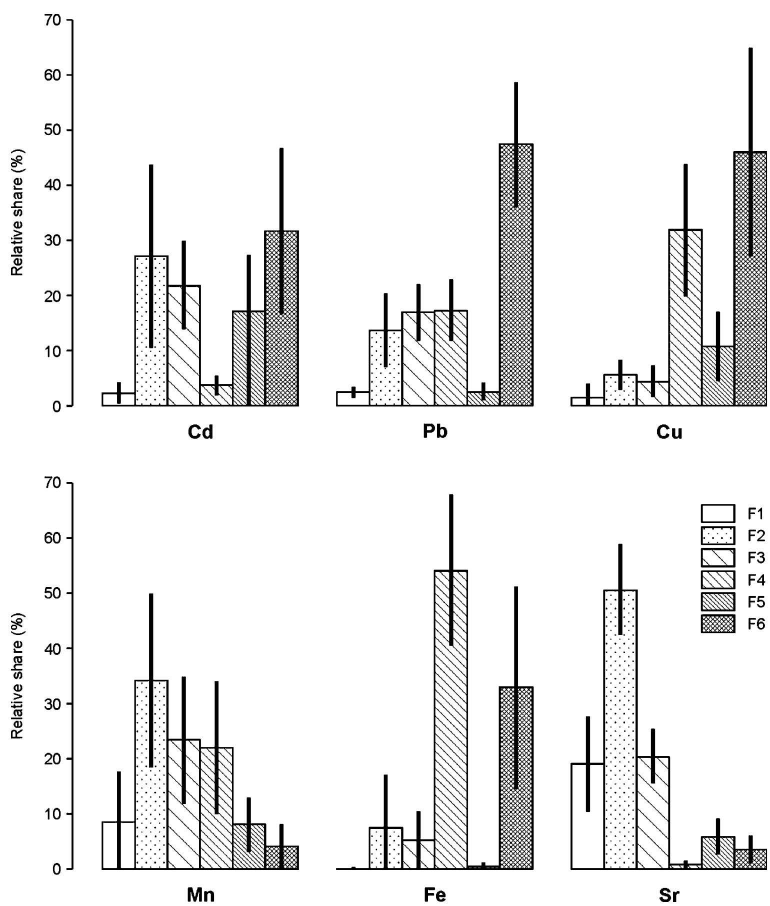

Figure 3. Mean percentages and standard deviations of binding forms of selected trace elements in the bottom sediment of Piaseczno lake in 2001 ($n = 18$; nine sampling Stations and two season). Fractions: F1 – exchangeable, F2 – carbonate, F3 – easily reducible, F4 – moderately reducible, F5 – organic/sulphides, F6 – residual.

Table 7. Statistical significance of the differences between contents of the studied elements in particulate fractions in the sediment of Piaseczno lake.

Elements	Fractions	Sampling dates									
		3 April 2001					18 July 2001				
Cd	F1	➩					➩				
	F2	0.01	➩				0.01	➩			
	F3	0.01	ns	➩			0.01	ns	➩		
	F4	ns	0.01	0.01	➩		ns	0.01	0.01	➩	
	F5	0.01	0.01	0.01	ns	➩	0.01	ns	ns	0.01	➩
	F6	0.01	ns	ns	0.01	0.05	0.01	0.01	0.01	0.01	ns
Pb	F1	➩					➩				
	F2	0.01	➩				0.01	➩			
	F3	0.01	ns	➩			0.01	0.01	➩		
	F4	0.01	ns	ns	➩		0.01	0.01	ns	➩	
	F5	ns	0.01	0.01	0.01	➩	ns	0.01	0.01	0.01	➩
	F6	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Cu	F1	➩					➩				
	F2	ns	➩				0.01	➩			
	F3	ns	ns	➩			0.01	0.01	➩		
	F4	0.01	0.01	ns	➩		0.01	0.01	0.01	➩	
	F5	0.01	0.01	0.01	0.01	➩	0.01	ns	0.01	0.01	➩
	F6	0.01	0.01	0.05	ns	ns	0.01	0.01	0.01	0.01	0.01
Mn	F1	➩					➩				
	F2	0.01	➩				0.01	➩			
	F3	ns	0.01	➩			0.01	0.01	➩		
	F4	ns	0.01	ns	➩		0.01	ns	ns	➩	
	F5	ns	0.01	ns	0.05	➩	ns	0.05	0.01	0.01	➩
	F6	0.01	0.01	0.01	0.01	0.01	ns	0.01	0.01	0.01	ns
Fe	F1	➩					➩				
	F2	0.01	➩				0.01	➩			
	F3	0.01	ns	➩			0.01	0.01	➩		
	F4	0.01	0.01	0.01	➩		0.01	0.01	0.01	➩	
	F5	0.01	0.01	0.01	0.01	➩	ns	ns	0.01	0.01	➩
	F6	0.01	ns	ns	0.01	0.01	0.01	0.01	0.01	ns	0.01
Sr	F1	➩					➩				
	F2	0.01	➩				0.01	➩			
	F3	0.01	0.01	➩			ns	0.01	➩		
	F4	0.01	0.01	0.01	➩		0.01	0.01	0.01	➩	
	F5	ns	0.01	0.01	0.01	➩	0.01	0.01	0.01	0.01	➩
	F6	0.01	0.01	0.01	0.01	ns	0.01	0.01	0.01	0.01	0.01

F1 – exchangeable, F2 – carbonate, F3 – easily reducible, F4 – moderately reducible, F5 – organic/sulphides, F6 – residual.

Binding forms of the elements in the sediment

Results of the sequential extraction carried out in surface layer (0–5 cm) of the sediment showed that trace elements displayed different degrees of association with the six targeted fractions (Figure 3). Differences between concentrations of an element in particulate fractions were significant in most cases (Table 7). Most of Cd load was associated with F2, F3, F5 and F6. Majority of Pb was associated with the F6, then F2, F3, F4, whereas Cu with F4 and F6. Manganese was mainly associated with F2, F3, and F4, Fe with the F4 and F6, whereas Sr with F2, and then F1 and F3. Among studied elements, only Sr was found in considerable amount in the most mobile and available, i.e. exchangeable phase. The content of trace elements in benthic organisms frequently correlates with this phase in sediment (Calmano and Förstner 1983; Babukutty and Chacko 1995). Strontium can pass easily from the F1, which includes this element adsorbed to exchange sites on the surface of sediment particles, into the water when environmental conditions change (Förstner 1986).

A great part of Cd, Pb, Mn, and Sr was found in carbonate and easily reducible phase, i.e. in the

Table 8. The values of the bioconcentration factors (BCF) of selected trace elements in the tissues of silver bream *Blicca bjoerkna* (L.), roach *Rutilus rutilus* (L.), perch *Perca fluviatilis* L., and rudd *Scardinius erythrophthalmus* (L.) in Piaseczno lake in 2001.

Species	Liver	Kidney	Muscle	Gills	Liver	Kidney	Muscle	Gills
	Cd				Pb			
Roach	0.34	0.63	0.15	0.28	0.14	0.30	0.08	0.15
Silver bream	0.20	0.50	0.04	0.29	0.13	0.24	0.03	0.19
Perch	0.23	0.37	0.06	0.21	0.07	0.22	0.03	0.10
Rudd	0.26	0.22	0.11	0.20	0.04	0.17	0.01	0.05
	Cu				Mn			
Roach	0.88	0.56	0.10	0.53	0.005	0.005	0.003	0.019
Silver bream	0.68	0.56	0.05	0.60	0.004	0.004	0.001	0.034
Perch	0.46	0.64	0.09	0.46	0.003	0.002	0.001	0.011
Rudd	0.49	0.35	0.13	1.18	0.003	0.002	0.001	0.020
	Fe				Sr			
Roach	0.032	0.026	0.002	0.027	0.015	0.020	0.010	0.38
Silver bream	0.017	0.025	0.001	0.028	0.021	0.037	0.007	0.47
Perch	0.028	0.038	0.002	0.016	0.013	0.016	0.006	0.14
Rudd	0.020	0.012	0.002	0.030	0.027	0.025	0.013	0.42

phases which are moderately mobile and available to organisms (Bendel Young and Harvey 1991; Lacerda et al. 1992; Bervoets et al. 1997, 1998). The carbonate fraction is influenced by pH and the elements may be released from this phase to the water under conditions of lowering pH. Amorphous ferromanganese oxyhydrates with their associated elements may be dissolved under reductive condition in the sediment (processes involved in the diagenetic remobilisation), leading to an increase in these element contents in the interstitial water (Batley 1990; van der Berg et al. 1998).

Most of Cu and Fe were found in the moderately reducible phase, which implies that these elements were strongly linked to the sediments, and in general had little potential for remobilisation. Fe/Mn oxides exist as nodules, concretions, cement between particles, or as a coating on particles and are very good trace element scavengers. The influence of Mn and Fe oxides on element sorption and distribution has been studied by many authors (Tessier et al. 1985, 1996; El Bilali et al. 2002; Ikem et al. 2003).

Higher portions of Cd was bound to organic matter. This fraction including metals present in both natural organic matter (due to complexation and peptization) and living organisms (as a result of bioaccumulation of metals). Some part of trace elements may be released from this phase to the water environment as a consequence of organic matter decay. Organic matter may modify the availability of certain elements to organisms, e.g. may reduce Fe availability to chironomid larvae (Bendel Young and Harvey 1991).

Most of Pb, Cu, and Fe were found in the immobile residual fraction. The residual phase represents metals largely embedded in the crystal lattice of the sediment fraction and should not be available for remobilisation under usually occurring conditions.

The risk of contamination of a water body by the elements was estimated using individual contamination factors (ICF; Ikem et al. 2003). The calculated values of ICF for the elements were following: Cd 2.9 ± 3.1, Pb 0.6 ± 0.2, Cu 0.3 ± 0.3, Mn 7.3 ± 15.9, Fe 0.2 ± 0.2, and Sr 30.9 ± 15.4. The result indicated that Sr posed the highest risks to water contamination followed by Mn, Cd, Pb, Cu, and Fe. The elements with higher values of ICF have potential higher possibility to be remobilized from the sediment. Higher portion of those element was bound with a mobilizable fractions (i.e. exchangeable species, carbonate bound metals, easily reducible, and sulphidic/organic).

The results show a considerable variability in the amounts of elements bound to particular phase in the sediment of Piaseczno lake between the studied stations as well studied dates (Figure 3). For instance, in the reducible phase there were found: Cd (5.6–52.9%), Pb (30.0–63.7%), Cu (6.5–75.9%) and Fe (2.7–80.2%), and in the carbonate phase: Cd (0.4–37.1%), Pb (6.4–28.6%), Mn (2.5–61.5%), Sr (33.7–67.4%), and Fe (0.01–26.3%). The observed large fluctuations in the partitioning of trace elements between different binding phase in various site of the bottom sediment indicated the differences in availability of particular elements to organisms (invertebrates, fish) living in various sites of the littoral.

Element bioconcentration in fish

According to the maximum values of BCF (Table 8) for the fish tissues (G, gills; K, kidney; L, liver) the general patterns of the elements bioconcentration in the studied species were following:

Cd	roach (K) > silver bream (K) > perch (K) > rudd (L)
Pb	roach (K) > silver bream (K) > perch (K) > rudd (K)
Cu	rudd (G) > roach (L) > silver bream (L) > perch (K)
Mn	silver bream (G) > rudd (G), roach (G) > perch (G)
Fe	perch (K) > roach (L) > rudd (G) > silver bream (G)
Sr	silver bream (G) > rudd (G) > roach (G) > perch (G)

In general, the species which take great portion of their food burrowing in bottom substrate (i.e. roach and silver bream) achieved higher ranks in above patterns than those which forage mainly in macrophyte beds or are predatory (rudd and perch). In silver bream the Sr and Mn, which posed the highest risks to water contamination (according to the highest ICF) were bioconcentrated to a greatest degree. Elements with considerably lower ICF values were bioconcentrated in other species, Cd and Pb in roach, Cu in rudd, and Fe in perch. Then, these results showed that the elements with high ICF were in higher degree bioconcentrated in benthivorous fish (mainly in gills). It seems possible that binding strength of an element in the sediment may influence its accumulation rate in such species. Maybe the only two cases of not so weak correlation between element content and individual features of fish (length, weight, age) presented in the Chapter 3.1.3. support this supposition. Small perch (i.e. more invertebrate-eating, and feeding rather on benthic than planktonic organisms) accumulates more Sr than large which becomes predatory. However, it must be stated that the sediment of Piaseczno lake is heavily contaminated by Sr and Mn. Therefore, this hypothesis remains to be checked in next studies in other water bodies.

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