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Heavy Metals in Fish from Lakes in Latvia: Concentrations and Trends of Changes

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Abstract The purpose of this study was to evaluate the level of heavy metal contamination of perch (*Perca fluviatilis*) from inland waters in Latvia. The level of metal (Cd, Cu, Co, Pb, Ni, Mn, Zn, Fe) accumulation in fish tissues (muscle, liver, and gills) relative to contamination level, gender, age, and tissue type were studied in fish samples from 14 bog (dystrophic) lakes and 23 lakes of different trophic status. Samples from some sites in the vicinity of the largest cities had significantly increased metal levels. In contrast, fish tissues from bog lakes had very low metal levels, possibly because of the high concentrations of natural organic matter in these waters.

Keywords Heavy metals · Bog lakes · Fish

Heavy metals from natural and anthropogenic sources are released into aquatic ecosystems, where they pose a serious threat because of toxicity, long persistence, bioaccumulation, and biomagnification in the food chain (Kucykbay and Orun 2003; Pourang et al. 2005). The most common sources of heavy metals are atmospheric precipitation, wastewater, industrial discharge, and non-point sources. Sources of heavy metals are highly variable and regionally specific; the environmental contamination level of metals even for small territories is highly variable (Biksham et al. 1991; Allen-Gil and Martynov 1995).

In aquatic food webs, metals can accumulate and reach high concentrations in mollusks, macrophytes, predatory fish, and benthic feeding fishes (Chen et al. 2000). Accumulation of heavy metals in fish tissues can affect not only natural populations, but also their consumers. Considering the importance of fish in the human diet, consumption of contaminated fish could pose a significant threat to human health (Schmitt et al. 2006).

In freshwater systems, fish samples often are analyzed to estimate the trace metal pollution (Berninger and Pennanen 1995; Rashed 2001). However, many factors that influence the metal concentration in fish tissues are poorly understood. The biological availability of heavy metals is significantly influenced by the formation of complexes between the metals and natural organic, or humic, substances. Thus, it would be informative to study the availability of heavy metals to fish tissues in locales where the concentration of dissolved organic substances is high. The northern countries of Europe, including Latvia, contain a large number of wetlands and dark colored bodies of water (dystrophic waters) (Tao et al. 2000). Understanding the characteristics of metal accumulation in such dystrophic areas is of importance for the development of environmental monitoring systems.

The aims of this study were to determine the levels of heavy metals (Cd, Cu, Co, Pb, Ni, Mn, Zn, Fe) in the muscle, liver, and gills of perch (*Perca fluviatilis*) from inland waters of Latvia and to assess the metal accumulation characteristics that occur in comparatively uncontaminated waters and in brown water (dystrophic) bodies of water.

Materials and Methods

Perch (*P. fluviatilis*) were caught with a fishing rod in August 2002–2005 in 14 bog lakes and 23 lakes of different trophic states (6 mesotrophic; 12 eutrophic; 5 hypertrophic) in Latvia (Fig. 1). In addition, monitoring of metal concentration in perch tissues from Lake Burtnieks (sampling site 13, Fig. 1)

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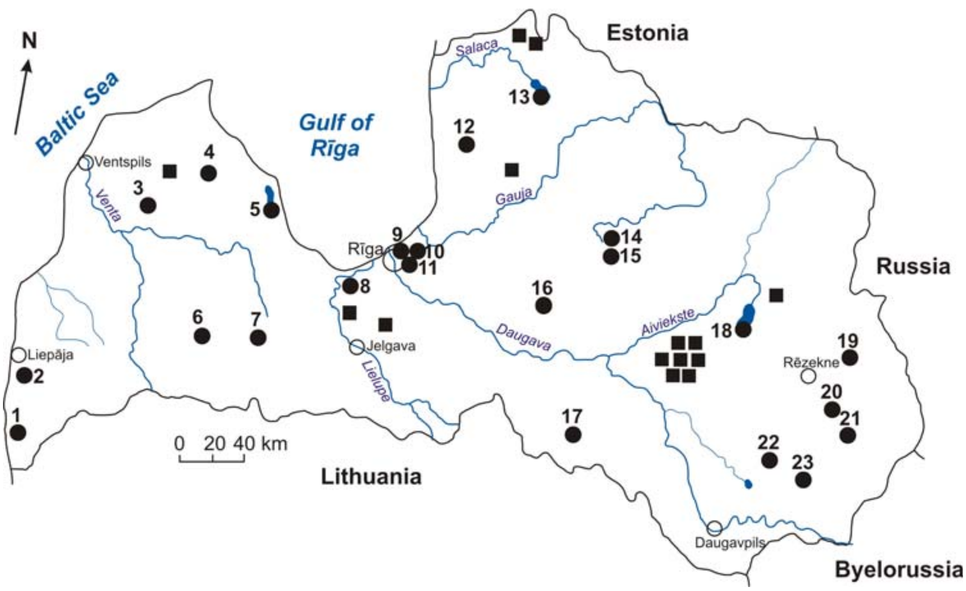

Fig. 1 Study area and fish sampling sites. Lakes (●) (1—Papes; 2—Liepajas; 3—Usmas; 4—Sasmakas; 5—Engures; 6—Cieceres; 7—Zebrus; 8—Babites; 9—Baltezers; 10—Kisezers; 11—Juglas; 12—Limbazu; 13—Burtnieks; 14—Alauksts; 15—Inesis; 16—Lobes; 17—Saukas; 18—Lubans; 19—Ludzas; 20—Raznas; 21—Ezezers; 22—Siveris; 23) and bog lakes (■)

was conducted from 1987 through 2007 (once yearly in August). The fish were measured for length, weighed, and in cooler transported to the laboratory, where the liver, gills, and a 2–5 g muscle sample were removed (one sample from each fish tissue). In each site 3–5 fishes were sampled. The age of each perch specimen was determined analysing the operculum. After dissection the samples were stored at –20°C until analysis. Sample preparation for analysis was carried out by wet digestion following Mason and Barak (1990). The procedure applied was as follows: an exactly 5 g sample was placed in a 50 mL Erlenmeyer flask and 10 mL of concentrated HNO_3 was added. After 15 min predigestion at room temperature, 10 mL of a mixture of concentrated HNO_3–$HClO_4$ (4:1 v/v) was added and the reaction was maintained on a hot plate at 70 ± 5°C for 24 h with gentle shaking until digestion was completed. The resulting solid residue was redissolved in deionized distilled water and transferred to a 25 mL measuring flasks and diluted with deionized water to 25 mL (three replicates were run for each metal analysis).

In all studied bodies of water, aquatic chemistry was analyzed using standard methods (2005) and total organic carbon using TOC-VSN (Shimadzu, Japan). Based on the suggestions of Goldstein and DeWeese (1999) for the development of monitoring programs, perch with the following characteristics were used in this study: mean length 18 cm; length range 12–22 cm; mean weight 52 g; weight range 23–108 g; age 2–7 years. However, in the bog lakes fish of the same size were much older (even up to 11 years), probably due to retarded growth in an environment characterized by acidic nutrient poor water and limited food availability. Metal analyses were performed using an atomic absorption spectrophotometer Perkin Elmer AAnalyst 200 (Perki Elmer, UK). The limits of detection were as follows: Cd (0.025 μg/L); Cu (0.03 μg/L); Pb (0.12 μg/L); Zn (0.03 μg/L); Co (0.020 μg/L); Ni (0.020 μg/L); Mn (0.015 μg/L); and Fe (0.10 μg/L). Results were expressed as micrograms of metal per wet weight gram of fish tissue. The accuracy of the determination was assessed by the analysis of reference material (Mussel NCS, ZC 78005; dogfish mussel DORM 2). Accepted recoveries of reference material ranged from 88% to 110%. The relative standard deviation in replicates and reference material was always below 10%. Statistical analyses were performed using Statgraphics Centurion XV (Statpoint Inc., USA). After testing for homogeneity of variance, the data set was tested by one-way analysis of variance (one-way ANOVA) and expressed as mean ± standard errors.

Results and Discussion

The study area covered the whole territory of Latvia. The dominance of natural and semi-natural habitats in the study area indicates a rather low level of anthropogenic impact. Commonly, lakes in Latvia have not been subjected to major anthropogenic pollution, with the exception of some sites in the vicinity of large cities, such as Riga, Daugavpils, Livani (Klavins et al. 1999).

The studied lakes varied quite a bit in their metal composition due to differing levels of anthropogenic impacts (Fig. 2). The lakes situated in the vicinity of cities (Liepaja, Riga, Ludza, Saldus, Broceni) or under the direct impact of industrial enterprises were considered to be contaminated; in contrast, the bog lakes because of their remote locations.

Fish were sampled from 37 lakes in August 1987 to 2007. The trophic status of the lakes varied from mesotrophic (6 lakes) to eutrophic (12 lakes) to hypertrophic (5 lakes) to dystrophic (bog lakes 14). Metal accumulation data obtained from more than 2,000 analyses follow a log-normal

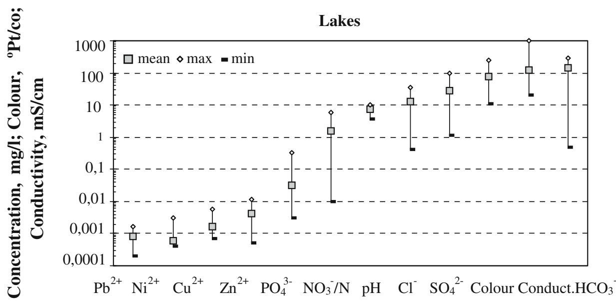

Fig. 2 Range of metal concentrations in waters of the studied lakes of Latvia

distribution, which is very common in biological data of metal concentrations. Muscle tissue, the liver, and the gills were analyzed because they play a role in the bioaccumulation process. The liver is the major organ involved in xenobiotic metabolism, while the gills are the primary site of metal uptake from the water, especially if metals are bound to particulate matter (Kargin 1998). Figure 3 shows the metal concentrations in these three tissues.

The mean concentrations of the studied metals are low compared to values reported in other studies, and the lowest values can be taken as background values for uncontaminated sites (Allen-Gil and Martynov 1995; Goldstein and DeWeese 1999; Chen et al. 2000; Rashed 2001; Kucykbay and Orun 2003). Muscle tissue had the lowest metal concentrations. The highest Cd, Pb, and Zn concentrations were found in liver, which supports the idea of metal accumulation in metabolically active tissues (Kargin 1998) that are rich in metallothionein.

Of the three tissue types analyzed, humans consume only muscle. Furthermore, the sampling and preparation of muscle tissue is easy. Thus, unless fish muscle cannot be considered to be a metal-accumulating tissue, it is the ideal tissue for use in monitoring programs.

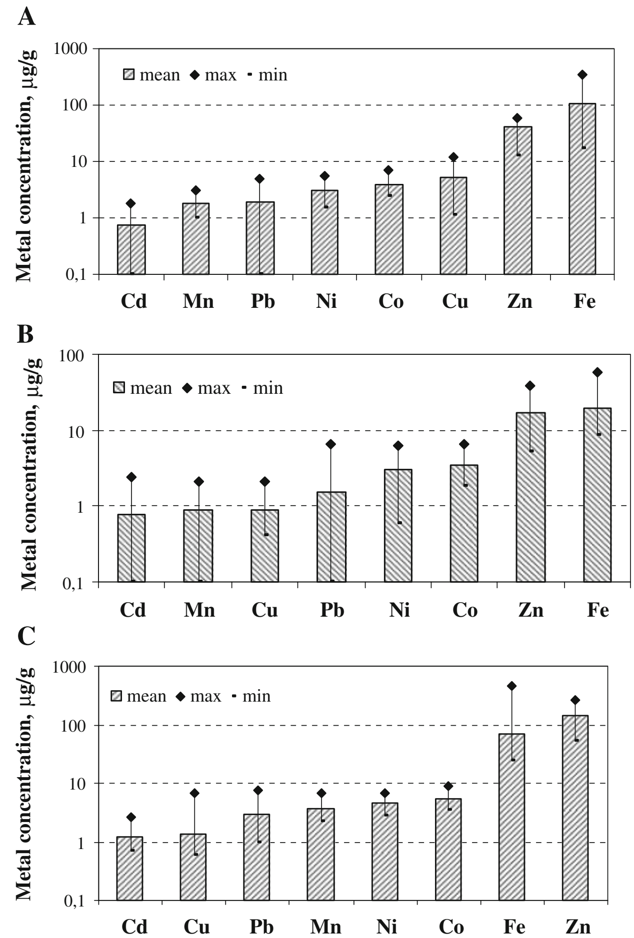

Fig. 3 Range of metal concentrations in different tissues of perch (*Perca fluviatilis*): (**a**) muscle; (**b**) liver; (**c**) gills

The correlation analysis of metal concentration, fish age, length, and weight (Table 1) indicates significant correlations between metals of presumably anthropogenic origin (Ni, Pb, Cd, Co), but also between metals such as Zn, Mn,

Table 1 The values and significance of the Pearson correlation coefficients between metal concentrations in the perch muscle and the weight, length, and age of the fish (n = 42)

	Pb	Ni	Cu	Cd	Co	Mn	Fe	Zn	Age	Length
Ni	**0.69**									
Cu	0.07	*0.35*								
Cd	**0.65**	**0.53**	*0.36*							
Co	**0.78**	**0.83**	*0.39*	**0.64**						
Mn	**0.60**	**0.68**	0.26	*0.36*	**0.61**					
Fe	*0.48*	**0.63**	**0.70**	**0.61**	**0.74**	*0.46*				
Zn	0.16	*0.43*	*0.37*	*0.34*	**0.52**	0.21	**0.52**			
Age	0.07	0.16	−0.16	−0.05	0.16	0.06	−0.04	*0.34*		
Length	−0.14	−0.04	−0.19	−0.17	−0.09	−0.06	−0.13	0.25	**0.63**	
Weight	−0.25	−0.11	−0.37	−0.20	−0.17	−0.09	−0.28	0.19	**0.60**	**0.87**

Bold: correlation is significant at the 0.01 level (2-tailed)

Italic: correlation is significant at the 0.05 level (2-tailed)

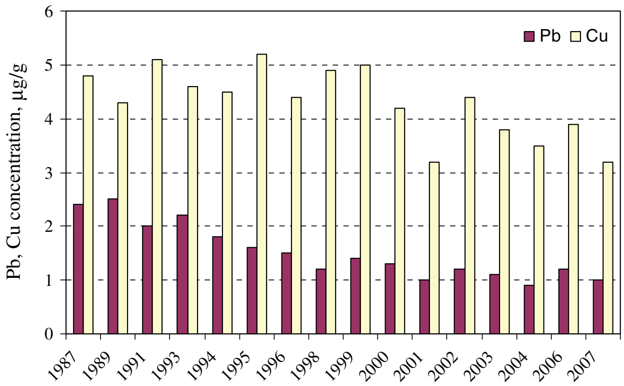

Fig. 4 Changes in lead and copper concentration in liver tissue of perch (*Perca fluviatilis*) from Lake Burtnieks (µg/g; mean values from 3 to 5 samples) from 1987 to 2007

and Fe, stressing common sources of their presence in fish tissues. Just as in our study a negative correlation between fish age and metal concentrations in fish tissues has been reported in the literature (Allen-Gil and Martynov 1995). Dietary habits may also have an impact on metal concentrations in different species.

Analysis of long-term (1987–2007) changes in Cu and Pb concentration in perch liver (Fig. 4) in fish taken from Lake Burtnieks demonstrates a reduction in Pb concentrations until 1998, when Pb concentration stabilized around ~1 µg/g. The changes in Pb concentration in the liver could be explained by a significant reduction of pollutant loading within the last decades and by the inclusion of Lake Burtnieks within the North Vidzeme Biosphere Reserve, which is under strict environmental regulations (Valters et al. 1999). This finding agrees well with results of other studies (Juhna and Klavins 2001). The concentrations of Cu for the same time interval are not so well expressed. Pb and Cu might have different sources. In the case of Cu, natural sources could be dominant; in this region of Latvia and in background sites, naturally elevated Cu concentrations have been found (Juhna and Klavins 2001). Our results suggest that *P. fluciatilis*, and the three tissue types selected, were good pollution indicators because they showed that the reduction of pollutants resulted in the temporal reduction of metal concentrations.

The range of metal concentrations in muscle, liver, and gill tissue of perch shows the pattern of change of metal concentration while also illustrating the accumulation tendencies of different metals in major tissue groups.

The highest metal concentrations were found in the liver and gills and the lowest in muscle tissue. In gills, the pattern of metal concentration was: Cd < Cu < Pb < Mn < Ni < Co < Fe < Zn; in liver it was Cd < Mn < Pb < Ni < Co < Cu < Zn < Fe; and in muscle it was Cd < Mn < Cu < Pb < Ni < Co < Zn < Fe. The metal concentrations differed significantly between males and females (Fig. 5), and females had higher concentrations in all studied tissues. This difference likely is influenced by differences in feeding habits and metabolism; females of a given length are older than males of the same length (Berninger and Pennanen 1995).

Metal concentrations in the fish tissues from the bog lakes (Table 2) were lower than those in samples from the mesotrophic and eutrophic lakes. In bog lakes, the metals

Table 2 Range of metal concentrations (µg/g) in muscle tissues of perch from dystrophic (bog) lakes and mesotrophic and eutrophic lakes in Latvia

Metal	Mesotrophic and eutrophic lakes	Dystrophic lakes
Cd	1.3 ± 0.4	0.4 ± 0.2
Mn	1.4 ± 0.3	0.4 ± 0.1
Cu	1.8 ± 0.2	0.5 ± 0.1
Pb	3.2 ± 0.4	1.4 ± 0.2
Ni	5.4 ± 0.8	1.2 ± 0.2
Co	5.6 ± 1.2	1.3 ± 0.2

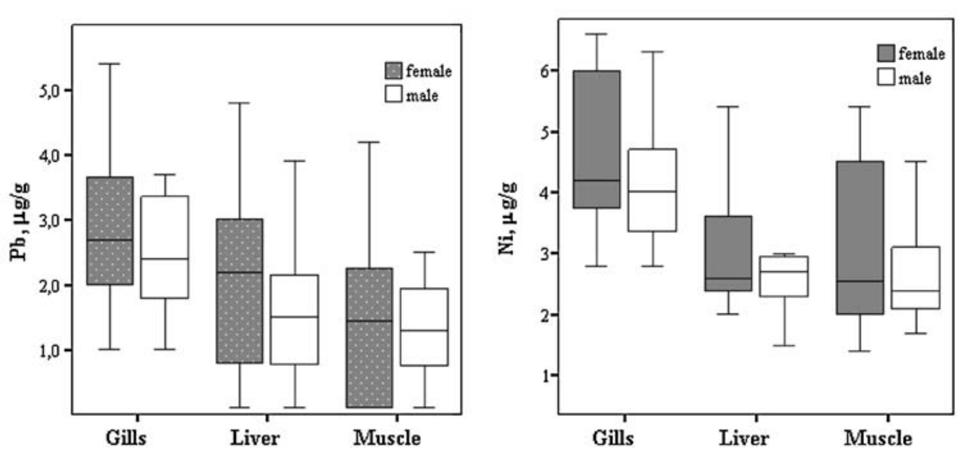

Fig. 5 Range of lead and nickel concentrations in perch liver tissue by gender

are from natural sources and atmospheric precipitation; a significant portion is bound to organic matter, which limits the availability of these metals to biological tissues.

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