Bull. Environ. Contam. Toxicol. (2002) 69:509–515

DOI: 10.1007/s00128-002-0091-9

Bulletin of Environmental Contamination and Toxicology

Concentration and Discrimination of Selected Trace Metals by Freshwater Mollusks

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Received: 15 November 2001/Accepted: 28 April 2002

One of the major problems in contemporary ecology is introduction of significant amounts of heavy metals into aquatic environment (Matshullat, 1997). Especially the high-suspended solid loads in the river have quite efficiently removed most soluble metals from the water and trapped them in the bottom sediment (Lau et al. 1998). From the environmental point of view, it is substantial to estimate the influence of trace metals on chemical and ecological equilibrium (Szefer, 1998; Szefer, 2000) and on mutual interaction between different elements of aquatic ecosystems, which can affect on the bioavailability of trace metals by aquatic organisms (Phillips, 1980). As the result of these interactions antagonistic or synergistic relationships between trace metals in living organism are observed (Phillips, Rainbow, 1993).

It is significant, that heavy metals are accumulated by certain species of living organisms, which sequestrate and concentrate these elements from aquatic environment (Pais, Jones, 1997; Prasad, 1997). In the consequence, some chosen species of plants and animals may be utilized as bioindicators of metals pollution in aquatic reservoirs, e.g. mollusks, which have long been regarded as promising bioindicators and biomonitoring subjects (Lau et al. 1998). They are largely influenced by trace metals (Locatelli, Torsi, Garai, 1999) and easily concentrate several elements from water phase (Phillips, 1980; Szefer et al., 1999). Additionally, they are abundant in many terrestrial and aquatic ecosystems, being easily available for collection (Lau et al. 1998).

The aim of this paper was determination of selected trace metals content in muscular tissue of freshwater mollusks (*Anodonta sp.*), come from the Zemborzyce Reservoir (Lublin, Poland) and examination their potential as biomonitors for heavy metal pollution in freshwater ecosystems. For this purpose, the concentration and discrimination factors (proposed by Szefer and Szefer, 1991) for Cd, Cr, Pb and Zn content in mollusks relative to superficial water and bottom sediments were estimated.

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MATERIALS AND METHODS

The Zemborzyce Reservoir is a man-made lake on the Bystrzyca River, near Lublin, Poland (Fig. 1). Superficial water, bottom sediments and muscular tissue of freshwater mollusks (*Anodonta sp.*) from this reservoir were analyzed for Cd, Cr, Pb and Zn content by atomic absorption spectrometry (AAS).

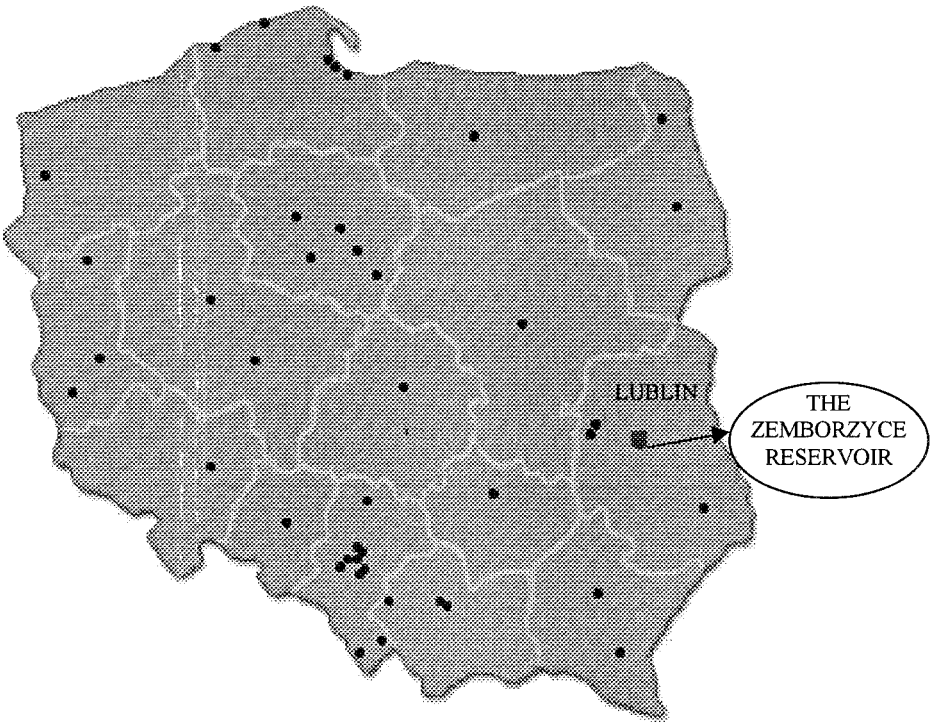

Figure 1. The map of Poland with the location of Lublin and the Zemborzyce Reservoir

Superficial water was collected from 10 sampling stations in autumn 1999 (Fig. 2), using plastic vessels. Immediately after sampling, water was filtered by 0,45-μm Millipore filter and then acidified. As a consequence, the measurements were made for dissolve metals. Because of ultra - trace level of examined elements their direct determination was impossible, in spite of using very sensitive analytical method - electrothermal atomic absorption spectrometry (ET AAS). For this reason, water samples were preconcentrated 20 - fold in the graphite tube of the spectrometer to obtain measurable analytical signal.

Bottom sediments were collected from 10 sampling stations in autumn 1999 (Fig. 2), using the plastic tubular spoon. Samples were air-dried, crushed, sieved through the 1-mm nylon sieve and frozen at - 18°C in plastic containers before further treatment. For the digestion process about 1-g sediment samples were

weighted with accuracy ± 0.0001 g. Digestion were carried out with aqua regia using the microwave stove. After digestion and filtration throw high-density filter paper, the solutions were quantitatively transferred into plastic 50-ml flasks and undertaken to AAS measurements.

Mollusks were manually collected from 10 sampling sites (Fig. 2) - 3 from each station, from the sediment were they usually dwelled, in autumn 1999. Samples of muscular tissue were thoroughly cleaned from sediments and frozen (- 18°C). For particular determinations, three parallel samples of the muscular tissue, about 1-g, were taken to the analysis. Samples were digested in the microwave stove, using 10 ml of nitric acid on each sample. Then the filtrates were quantitatively transferred into plastic 50-ml flasks and measured by AAS method.

The determination of Cd, Cr, Zn and Pb in superficial water, bottom sediments and muscular tissue was carried out using atomic absorption spectrometers: SpectrAA 880Z (electrothermal atomization, Zeeman background correction) and SpectrAA 880 (flame atomization, deuterium background correction), Varian, Australia. Samples of mollusks and sediments were digested using the microwave stove MARS 5, CEM, USA. In overall procedures the spectrapure quality reagents (Merck, Germany) were used.

RESULTS AND DISCUSSION

Superficial water, bottom sediments and muscular tissue of freshwater mollusks (*Anodonta sp.*) were screened for the level of Cd, Cr, Pb and Zn. Table 1 shows average trace metals content in investigated objects.

Table 1. Average trace metals content in muscular tissue of freshwater mollusks (*Anodonta sp.*), superficial water and bottom sediments from the Zemborzyce Reservoir (Lublin, Poland)

SAMPLE		TRACE METALS CONTENT (ppb)			
		Cd	Cr	Pb	Zn
Freshwater mollusks	MEAN	51.0	123	115	18700
	SD	26.5	34.0	28.0	7800
	RSD	0.52	0.28	0.24	0.42
Superficial Water	MEAN	0.050	1.25	0.45	17.0
	SD	0.025	0.60	0.25	8.65
	RSD	0.50	0.48	0.55	0.50
Bottom sediments	MEAN	118	2150	1160	13200
	SD	75.0	975	659	2660
	RSD	0.63	0.45	0.57	0.20

Figure 2. The map of the Zemborzyce Reservoir (Lublin, Poland) with 10 sample stations

The results from the analysis indicate that bottom sediments from the Zemborzyce Reservoir (Tab. 1) contain (average): 118 ppb (Cd), 2150 ppb (Cr), 1160 ppb (Pb) and 13200 ppb (Zn). According to Misztal and Small (1984) bottom sediments and under-water soils of the Zemborzyce Reservoir, especially from the eastern side, contain large amounts of peat, which is a good adsorbent of metals ions. It is assumed that trace metals in solvable form are adsorbed in considerable amounts by the peat basis of this reservoir. In consequence, in spite of relatively large amount of heavy metals transported to the reservoir, superficial water (Tab. 1) contains ultra-trace quantities of examined elements: 0.050 ppb (Cd), 1.25 ppb (Cr), 0.45 ppb (Pb) and 17.0 ppb (Zn).

The availability of investigated metals in bottom sediments provides the opportunity for aquatic animals to biomagnification these metals and later remobilisation them through the food chain. Both chemical composition of bottom sediments and chemical form of trace metals have essential influence on assimilating these elements by water organisms which live and feed in sediments, e.g. by mollusks (Szefer et al., 1996, 1999). Accumulation of examined trace metals by mollusks was observed. The average contents of determined elements (Tab. 1) were 51.0 ppb (Cd), 123 ppb (Cr), 115 ppb (Pb) and 18700 ppb (Zn).

The efficiencies of trace metals biomagnification by freshwater mollusks (*Anodonta sp.*) were studied based on concentration and discrimination factors, estimated for Cd, Cr, Pb and Zn content in mollusks relative to superficial water and bottom sediments.

The concentration factors (CF) were calculated according to the formula, introduced by Szefer and Szefer (1991):

$$CF = C_1 / C_2;$$

where:
C_1 – average content of examined element in mollusks,
C_2 – average content of examined element in water / sediment.

The discrimination factors (DF) were calculated as follows, after Szefer and Szefer (1991):

$$DF = (C_1/C_2)_x / (C_1/C_2)_s;$$

where:
$(C_1/C_2)_x$ – ratio of average content of two elements in mollusks,
$(C_1/C_2)_s$ - ratio of average content of two elements in water / sediment.

Table 2 presents average concentration (CF) and discrimination factors (DF) for Cd, Cr, Pb and Zn content in muscular tissue of mollusks (*Anodonta sp.*) relative to superficial water and bottom sediments.

Table 2. Average concentration (CF) and discrimination (DF) factors for trace metals content in muscular tissue of freshwater mollusks (*Anodonta sp.*) relative to superficial water and bottom sediments, from the Zemborzyce Reservoir (Lublin, Poland)

	CONCENTRATION FACTOR (CF) FOR			
Relative to	Cd	Cr	Pb	Zn
Superficial Water	981	97.6	250	1094
Bottom sediments	0.43	0.06	0.10	1.42

	DISCRIMINATION FACTOR (DF) FOR					
Relative to	Cd/Cr	Cd/Pb	Cd/Zn	Cr/Pb	Cr/Zn	Pb/Zn
Superficial Water	10.1	6.53	1.00	0.65	0.09	0.14
Bottom sediments	7.64	4.37	0.33	0.58	0.04	0.07

The adaptability of trace metals bioaccumulation by mollusks cannot be directly reflected on the metals content in water or sediment sample. The influence on the bioaccumulation may also have the feeding habit, growth rate and age of the organism. Moreover, the biomagnification of trace metals may greatly depends on hardness of water, pH and acid-volatile sulphide of the water and sediment (Lau et al. 1998), what will be the subject of our future investigations.
Our preliminary study on the bioaccumulation suggests that freshwater mollusks (*Anodonta sp.*) have a greater affinity to Zn and Cd than Pb and Cr. This fact can be explained by small solubility of Pb and Cr compounds in sediments. Because living organisms accept elements in solvable form so Pb and Cr are incomplete assimilated metals. Finally, based on obtained factors it was established that mollusks accumulation ability may be draw in the following order: Zn > Cd > Pb > Cr. This range is the effect of different trace metals bioavailability, which mainly depends on metals solubility, the pH value of the water phase and the composition of bottom sediments. This thesis may be confirmed by speciation research, what will be the subject of our future study.

The concentration and discrimination factors for Cd, Pb and Zn for freshwater mollusks (*Anodonta sp.*), achieved in present investigation, were compared with factors reported by Szefer and Szefer (1991) for seawater mollusks (*Mytilus edulis*), from the Gdańsk Bay (Poland). These authors concluded relevant factors for mollusks relative to seawater and associated sediments (Zn > Cd > Pb). According to them seawater mollusks have greater sufficiency to bioaccumulation of Zn and Cd than Pb and may be good bioindicators of these metals in seawater. This comparison confirmed that both seawater mollusks and freshwater mollusks may be very useful as bioindicators for trace metals, especially for Zn and Cd, pollution in aquatic environments.

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