Original Research

The Study of Trace Metal Levels in Select Environmental Components of the Zemborzyce Reservoir

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Abstract

The concentration of Cd, Cr, Pb and Zn in water, sediments and fish samples from the man-made Zemborzyce Reservoir (Lublin, Poland) were examined in this study. The analytical procedures of metal determination were validated by application of certified reference materials. Moreover, concentration factors for Cd, Pb and Zn in the muscular tissue of fish were estimated and discussed with respect to their content in superficial water. Obtained data suggest that freshwater fish accumulate investigated metals in the consequent order: Zn > Cd > Pb > Cr. It was confirmed that freshwater fish could be used as selective bioindicators of trace metals in freshwater reservoirs.

Keywords: trace metals, bioindicators, fish, accumulation

Introduction

One of the major problems in contemporary ecology is the path of heavy metals introduced into aquatic environments due to anthropogenic activity [1]. Anthropogenic water pollution is connected with sewage (industrial and communal), with lixiviation of chemical matter from dumping grounds of different waste materials and with the fall of atmospheric dust [2]. Important sources of pollution are also elements washed away from soils, containing mineral manures and plant protection agents. Much pollution discharge by rivers and introduced into reservoirs is caused by mobility and deposition processes [3].

In recent decades industrial development and urbanization has led to significant pollution of aquatic environments. The introduction of hazardous trace metals into natural reservoirs has resulted in dramatic changes in the physicochemical and biological equilibrium. The excessive concentration of these pollutants in the environment is very dangerous for the water plants and animals. Determination of total trace elements content in sediments is not sufficient for aquatic ecosystem condition assessments. Trace elements may occur in different mineral forms and chemical compounds, and different bindings with minerals and organic components of the sediments. Metals in sediment phases other than exchangeable ions are in chemical equilibrium with the adsorbed metals and serve as a reservoir for metals in water. Moreover, metals in sediment other than adsorbed (exchangeable) ions are often available to living organisms and need to be considered because of the long-term biotransformation in sediments. The investigation of these forms gives more information on trace metals mobility, bioavailability and toxicity [4].

Chemical speciation analysis is widely engaged in partitioning of the total concentration of metal forms. The essentially recognized procedure of metal partitioning in

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solids is a sequential scheme proposed by Tessier (1979). However, this procedure in its original form and in modified versions is disruptive. Using the insufficient selective extraction solvents, co-precipitation and re-precipitation processes and sorption of metals on a solid are the main limitations of these schemes. Moreover, the reproducibility of the above schemes is rather poor. For this reason The European Community's and Bureau of References and the Standard, Measurements and Testing Programme recommended the use of the single extraction or application three-step BCR procedure [5]. For single extraction an EDTA or acetic acid is recommended and a few SRM are available, e.g. BCR 483 or BCR 484. It is worth mentioning that chelating agents such an EDTA form stable water-soluble complexes and may result in the limitation of the precipitation and readsorption of previously realized metals [6-7].

All living organisms react on environmental changes, but in the estimation of the chemical qualities of the environment most useful are bioindicators, which react strongly or selectively on indicated elements. Sensitive biomonitors of trace element pollution in aquatic environment are fish, which accumulate chemical compounds from the aqueous phase and almost certainly may be applied as selective bioindicators especially for Zn and Cd. It is suggested that the distribution of trace metals in the organs and alimentary tracts of fish, and especially the low level of the elements in fish and plants, are linked to the abiotic components of the water environment and they are not easily accessible for organisms [8-10].

The aim of this paper is to determine selected trace metals content (Cd, Cr, Pb and Zn) in the muscular tissue of freshwater fish (roach, perch, and bream), in superficial water and in the bottom sediments from the man-made Zemborzyce Reservoir (Lublin, Poland) and, after that, to evaluate concentration factors (CF) for Cd, Pb and Zn content in the muscular tissue of fish relative to superficial water. Finally, the factors were computed to establish the accumulation order and to examine fish for use as biomonitors of trace metal pollutants in freshwater environments. The differences in concentration factors were particularly discussed in respect to the bioavailability of trace metals from sediments.

Experimental Procedures

The Zemborzyce Reservoir (Fig. 1) is a man-made lake on the Bystrzyca River near Lublin, Poland. This reservoir was created by raising the water level of the Bystrzyca River for flood control and for supplying the lower river with water during drought. It also plays a recreational role for the citizens of Lublin and serves for non-intensive fish breeding. The water of the Bystrzyca River flowing

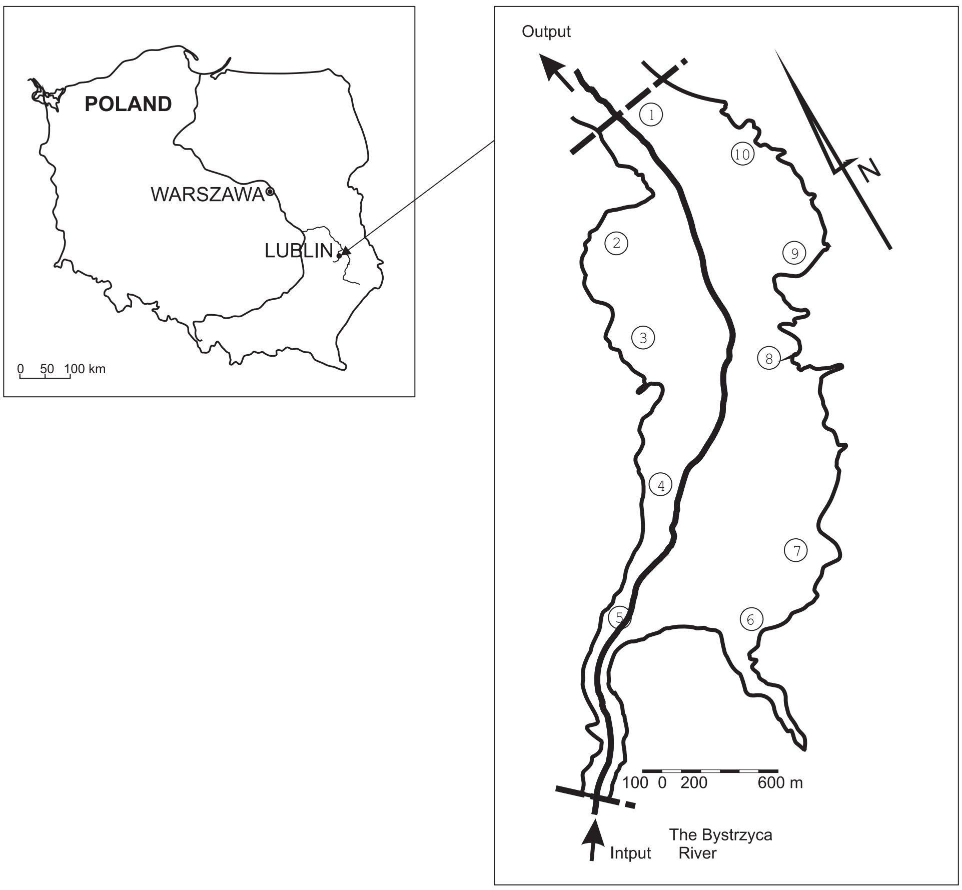

Fig. 1. The location of sampling points in the Zemborzyce Reservoir.

into the reservoir is considerably polluted and turbid. This pollution comes from several food factories, which discharge their waste into the river, while the turbidity of the water is caused by susceptibility of the loess deposits of the river basin to erosion. This creates good conditions for rapid eutrophization of the reservoir and its swallowing [11]. Superficial water, bottom sediments and muscular tissue of freshwater fish – roach (*Rutilus rutilus*), perch (*Perca fluviatilis*) and bream (*Abramis brama*) – from this reservoir were analyzed for Cd, Cr, Pb and Zn content by atomic absorption spectrometry (AAS).

Superficial water was collected by specially designed tube samplers [12] in autumn 2003 from 10 sample locations (Fig. 1). Before the analysis, samples were filtered through cellulose nitrate filters with a pore diameter < 0.45 μm (Sartorius, Goettingen, Germany). Trace metals content were determined immediately after sample collection. In spite of using a sensitive analytical method – electrothermal atomic absorption spectrometry (ET AAS) – direct determination of examined elements was impossible because of their ultra-trace level. For this reason, water samples were preconcentrated 20-fold in the graphite tube of the spectrometer to obtain a measurable analytical signal.

Bottom sediments were collected by means of a tubular sampler of the Kajak type that allowed taking about 15 cm deep samples [13] in autumn 2003 from 10 sample locations (Fig. 1). Samples were air-dried, crushed, sieved and stored in plastic containers. For the analysis of the total metals content in sediments 1 g sediment samples were digested by using the microwave stove in 12 mL combination of concentrated nitric acid and hydrochloric acid in the molar ratio 1:3. After that samples were filtered carefully through Whatman 541. Next, the filtrates were quantitatively transferred into plastic 50 mL flasks and undertaken to AAS measurements. In the case of the metal extraction from sediments into EDTA solution 3 g of the sediment was extracted by 20 mL 0.05 M EDTA at room temperature for 6 h. The suspensions were stirred during EDTA extraction by means of a water bath shaker.

Fish were caught in autumn 2003 from 10 sample locations (Fig. 1). Taking into account that trace metal accumulation by fish depends mainly on age, size and the position of fish in food chains, mature specimens with maximum differences of length less than 5% were chosen for the investigation. After collection samples were cleaned with deionized water and were frozen (-18°C) until dissected. For particular determinations, three parallel samples of the muscular tissue, about 1 g, were taken for analysis. Samples were digested in a microwave oven 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.

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

Surface water (SPS – SW 1), lake sediment (SL 1) and Oyster tissue (SRM 1566) with certified Cd, Cr, Pb and Zn contents were used for validating procedures. These materials were used as received and in the case of the lake sediment no additional grinding was performed.

Results and Discussion

The content of trace metals for studied components of ecosystem is presented in Tables 1, 2. It can be expected that the equilibrium of analyte between particular environmental components depends on the critical parameters responsible for the kinetic processes that lead to this state. For the studied system the critical parameters should be ordered as follows: the composition and physicochemical properties of river-water supplying this reservoir, a type of the floated soil forming bottom this man-made lake, current of flowing streams, seasonal parameters, and physicochemical and biological abilities of particular environmental components for concentration of trace metals. Trace metals content, available to fish and other living organisms in the aquatic environment, depends on physicochemical conditions and also on distribution patterns inside the ecosystem. Waterborne metals are deposited in the bottom sediments, taken up from the water and concentrated by aquatic organisms [14].

The chemical composition of bottom sediments in the Zemborzyce Reservoir was examined and described by Misztal and Small [11]. The authors presented detailed data on the bottom sediments composition in respect to the topography of the reservoir. Taking into account the previous data and our results it was stated that bottom sediments (Table 1) from the estuary of the Bystrzyca River (point 1) contain comparable average content of Cr and Zn in the lake on the contrary to Cd and Pb. It means that immobile deposition of Cr and Zn in lake sediments takes place whereas Cd and Pb are washed from the flow nature reservoir. This thesis confirms the content of Cd and Pb in sediments taken in point 5 localized nearly the river leaving from the lake. The highest trace metals deposition in the sediment is observed for point 8, where water-river forms a corner stream. Generally, the differences of trace metals content deposition in the sediment for particular points seems to be the result of sedimentation and sorption processes. Moreover, these processes play a key role in the shaping of concentration factors and may control trace metals concentrations in associated superficial water [15].

The yield of trace metals extraction into 0.05 M EDTA solution is shown in Table 1. Worth noting is the fact that the extraction yield was similar practically for particular trace metal, independent of the collection point. However, the highest yield of extraction is observed for zinc, the lowest for chromium. This behavior explains the difference of trace metals mobility and bioavailability for studied sediments. It is visible that extraction ability is situated in the following order: Zn > Cd > Pb > Cr. Probably the same order in bioavailability can be expected. Taking into account the above remarks, the chemical characteristic of bottom sediments gives undoubtedly more information on trace metals mobility, bioavailability and toxicity.

Superficial water (Table 2) from the Zemborzyce Reservoir contains ultra-trace quantities of examined elements, regardless of the relatively large amount of heavy metals

Table 1. The average total trace metals content and EDTA extractable fraction in the bottom sediments from the Zemborzyce Reservoir (Lublin, Poland).

Element	Parameter		
	T [mg/kg, d.w.]	EF [mg/kg]	EF [%]
Cd			
mean ± SD min – max median	0.118 ± 0.076 0.039 – 0.248 0.099	0.039 ± 0.025 0.013 – 0.081 –	33.5 ± 0.86 32.7 – 35.0 –
Cr			
mean ± SD min – max median	2.15 ± 0.98 0.69 – 3.68 2.26	0.053 ± 0.025 0.014 – 0.094 –	2.43 ± 0.20 2.03 – 2.58 –
Pb			
mean ± SD min – max median	1.16 ± 0.67 0.45 – 2.48 1.02	0.287 ± 0.164 0.112 – 0.605 –	24.9 ± 0.83 23.3 – 26.2 –
Zn			
mean ± SD min – max median	13.2 ± 2.66 8.9 – 16.9 13.4	5.14 ± 1.07 3.33 – 6.55 –	38.8 ± 0.78 37.4 – 39.6 –

T – total content, EF – EDTA extractable fraction content

Table 2. The average trace metals content in the superficial water and muscular tissue of Bream (*Abramis brama*), Roach (*Rutilus rutilus*) and Perch (*Perca fluviatilis*) from the Zemborzyce Reservoir (Lublin, Poland).

Sample	Content [μg/kg, w.w.]			
	Cd	Cr	Pb	Zn
Superficial water				
mean ± SD min – max median	0.052 ± 0.027 0.017 – 0.086 0.052	< LOD*	0.76 ± 0.27 0.41 – 1.21 0.75	17.2 ± 8.68 4.53 – 30.5 18.5
Bream (*Abramis brama*)				
mean ± SD min – max median	5.08 ± 1.57 1.76 – 7.05 5.16	15.4 ± 4.24 9.52 – 21.8 15.1	16.9 ± 2.84 12.3 – 20.2 17.2	4635 ± 399 4150 – 5240 4650
Roach (*Rutilus rutilus*)				
mean ± SD min – max median	4.20 ± 2.28 1.32 – 7.94 3.37	31.8 ± 12.3 9.54 – 46.8 34.2	27.2 ± 11.4 12.3 – 49.8 25.2	5565 ± 2591 1250 – 9750 5815
Perch (*Perca fluviatilis*)				
mean ± SD min – max median	6.05 ± 3.19 1.43 – 10.8 5.77	28.1 ± 11.2 11.6 – 47.4 27.8	33.1 ± 9.91 19.3 – 50.7 31.9	7180± 487 6650 – 8300 7150

* LOD (limit of detection) – for Cr – 0.2 μg/kg

transported into the reservoir. As Misztal and Small [11] have reported, bottom sediments and under-water soils of the Zemborzyce Reservoir, especially from the eastern side, contain large amounts of peat, which is a good metal ions adsorbent. As a consequence trace metals in soluble form are adsorbed in considerable amounts by the peat basis of the reservoir.

Despite relatively low trace metals levels in the superficial water, fish from the examined reservoir contain relatively high amounts of Cd, Cr, Pb and Zn (Table 2). This feature results in the metals uptake and accumulation from the lower links of the food chain. The differences in bioavailability between species are caused probably by different positions of studied fish in particular food chains and also by varied feeding habits, growth rate and fish age. For these reasons the average values of trace metal contents are taken into consideration in further studies. Beyond a shadow of a doubt, predacious fish (perch), which are situated on the top of the aquatic food chain, uptake and accumulate a large amount of trace metals and could be the best trace metals bioindicators [16-17]. Trace metals concentration for Cd, Cr, Pb and Zn were lower than those found in fish from polluted reservoirs reported earlier [14.18]. On other hand environmental factors such as acidification, salinity, hypoxia, hardness, temperature and other metals affect metals toxicity to fish via metals speciation and the distribution and metabolism in the fish organism [19-20].

The measured and the reference values of standard reference materials are given in Table 3. The measured value and the reference value are compared and it was found that for Cd, Cr, Pb and Zn the measured values differ significantly from reference values ($p < 0.05$). The higher value of uncertainty for the lake sediment was probably caused by the lack of homogeneity. The reproducibility of the applied procedures was evaluated by relative standard deviation (% RSD) from 10 repeated measurements. For all analyzed elements the percentage RSD of sub-samples was in the range of 6-8%, with exception of the lake sediment (11-18%).

Furthermore, concentration factors (CF) for Cd, Pb and Zn content in the muscular tissue of examined fish relative to superficial water were estimated according to the formula proposed by Szefer and Szefer [21]:

$$CF = C_1 / C_2$$

where:
C_1 – average content of examined element in fish,
C_2 – average content of examined element in water.

Table 3. Validation of the proposed method against the certified reference materials.

Values	Element			
	Cd	Cr	Pb	Zn
SPS – SW 1 (Surface water) [µg/L]				
Certified	0.51 ± 0.01	2.04 ± 0.01	5.1 ± 0.1	19.0 ± 1.0
Found	0.50 ± 0.01	2.05 ± 0.01	5.2 ± 0.1	18.5 ± 1.1
SL 1 (Lake sediment) [mg/kg]				
Certified	0.260 ± 0.050	104 ± 9.0	37.7 ± 7.4	223 ± 10
Found	0.240 ± 0.020	99.0 ± 7.0	38.3 ± 3.2	217 ± 9.8
SRM 1566 (Oyster tissue) [mg/kg]				
Certified	3.5 ± 0.4	0.69 ± 0.27	0.48 ± 0.04	852 ± 14
Found	3.35 ± 0.3	0.81 ± 0.10	0.46 ± 0.04	844 ± 28

Table 4. The average concentration factors (CF) for trace metals content in the muscular tissue of freshwater fish relative to superficial water from the Zemborzyce Reservoir (Lublin, Poland).

Sample	Concentration factors (CF)		
	CF (Cd)	CF (Pb)	CF (Zn)
Roach (*Rutilus rutilus*)	134	42	488
Perch (*Perca fluviatilis*)	158	48	576
Bream (*Abramis brama*)	129	25	389

The average concentration factors for Cd, Pb and Zn content in the muscular tissue of fish relative to superficial water are shown in Table 4. Obtained factors suggest that freshwater fish have a greater affinity to Zn and Cd than Pb. This conclusion is confirmed by earlier reported order in bioavailability for capability of trace metals extraction by EDTA solution. In the end, based on the all experimental data, it was stated that accumulation ability of freshwater fish for examined trace metals occurs in the following order: Zn > Cd > Pb > Cr. This range is probably the incidental effect of different trace metals bioavailability, which depends mainly on metals solubility, the pH value of the water phase and the composition of bottom sediments of the reservoir as well as the ability for preconcentration of particular trace metals by fish.

Finally, it was concluded that the multipart study on the trace metals content for particular ecosystem components is a promising method to establish the equilibrium state for the examined system. It was pointed out that based on this attitude critical parameters responsible for trace metals' ability to accumulate by leaving water organisms should be found.

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