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Letter to Editor

Distribution and Environmental Mobility of Selected Trace Metals in the Zemborzyce Reservoir

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Abstract

The content of selected trace metals (Cd, Cr, Hg, Pb, Zn) and their distribution in superficial water, bottom sediments and in muscular tissue of fishes (roach, perch, bream) and mollusks (taken from the Zemborzyce Reservoir) were examined using atomic absorption spectrometry (AAS). A comparison of the trace elements content in investigated constituents of the Zemborzyce Reservoir was carried out. Superficial water contains micro-trace quantities of examined metals. Bottom sediments are characterized by a smaller content of Cd, Pb and Zn, in comparison to the previous data. Accumulation of Cd is very similar for all examined fishes. The highest level of Cr was found in roaches. Perches indicate best accumulation ability of Hg, Pb and Zn. Mollusks show excellent accumulation ability to all studied elements.

Keywords: trace metals, bottom sediments, superficial water, soft tissue

Introduction

In recent years anthropogenic activity has introduced significant amounts of trace metals into aquatic environments [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 falls of atmospherical dust [2]. Important sources of pollution are also elements washed away from soils containing mineral manures and plant protection agents. Much pollution discharged by rivers and introduced into reservoirs is caused by mobility and deposition processes. In aquatic environments most trace elements appear in insoluble forms, due to oxygenation processes and sorption through organic and mineral fraction of sediments. In stagnant reservoirs trace metals appear in soluble forms (Cd, Zn) or as incorporated in small fixed parts (Cu, Hg) or even support in designed proportions in solvable and associated forms (Pb) [3]. Trace metals species in bottom sediments depend on environmental conditions. Mobile forms dominate in river-sediments (connected with carbonates and with Fe and Mn hydroxides), due to oxygenation processes [4]. Most trace metals in aquatic reservoirs are concentrated [5] in bottom sediment [6].

The introduction of large amounts of elements into aquatic environments is destructive to the chemical equilibrium and, as a consequence, for the biological equilibrium. The tolerance of ecosystems to chemical changes is varied and depends on the buffer abilities of environmental factors - soils, water and plants and animals [7].

All living organisms react to environmental changes, but in the estimation of the chemical qualities of the environment most useful are bioindicators, which react strongly or selectively for metals. Sensitive bioindicators of trace elements in aquatic environments are mollusks

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and fishes, which accumulate chemical compounds from the water phase [8] - mollusks are especially useful due to their specific habit of existence - on the surface of sediment [9, 10].

The aim of this paper was determining trace metals content in superficial water, bottom sediments and the muscular tissue of fishes and mollusks and signifying the distribution and environmental mobility of examined elements. By comparison of environmental components of the Zemborzyce Reservoir and the studied trace metals contents some suggestions on bioavailability were presented.

Materials and Methods

Area Descriptions

The Zemborzyce Reservoir is a man-made lake on the Bystrzyca River (Lublin, Poland), from which the following fishes are caught and consumed: roach *(Rutilus rutilus),* bream *(Abramis bramd)* and perch *(Perca fluviatilis).* Also, mollusks *(Anodonta sp.)* are caught and exploited in the nourishment of livestock animals.

The characteristic feature of the Bystrzyca River is yearly transportation of suspension, especially growing during the spring-flows. A significant influence on the composition of superficial water and bottom sediments of the Zemborzyce Reservoir is exerted by loamy suspension (the main component of rocks and soils of the drainage area). Farms, situated at the upper course of the Bystrzyca River, have also essential meaning for the characteristic of the Zemborzyce Reservoir. The participation of agriculture in water polluting in the drainage area is large. Also, collectors of communal wastes and pollution flowing to the upper part of the Bystrzyca River have strong influence on the characteristic of sediments carried to the reservoir [11]. Moreover, bottom sediments and under-water soils of the Zemborzyce Reservoir, especially from the eastern side, contain large amounts of peat [12].

Experimental Procedures

Superficial water was collected from 10 locations (Fig. 1) of the Zemborzyce Reservoir in autumn (1999). Samples were collected in plastic vessels. Before analysis, water was filtered using the 0.45 µm Millipore filter. Trace metals content was determined immediately after sample collecting. Direct determination of examined elements was impossible, in spite of using very sensitive analytical method (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 locations (Fig. 1) of the Zemborzyce Reservoir in autumn (1999). Samples were collected using a plastic tubular spoon. Samples were air-dried, crushed, sieved through a 1 mm nylon sieve and stored in plastic containers. Next, about 1 g sediment samples (weighted with accuracy ± 0.0001 g) were digested using the microwave stove. The filtrates

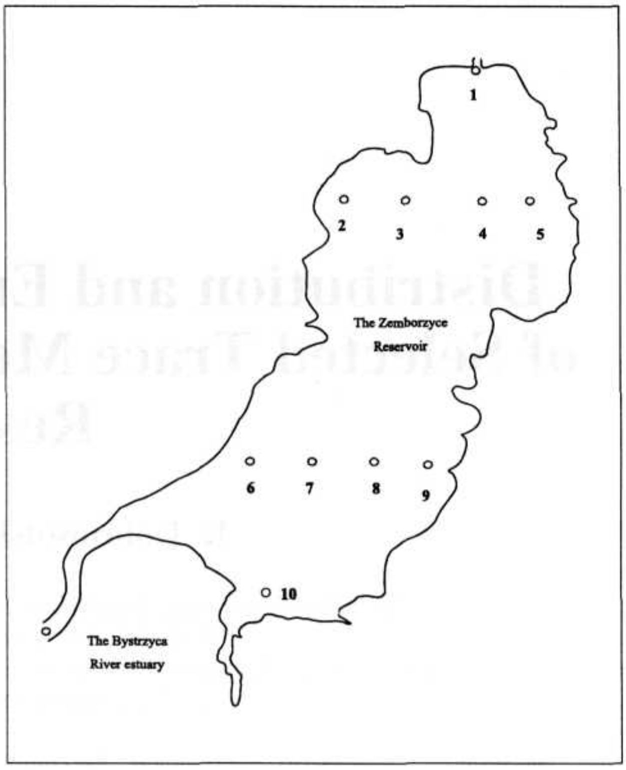

Fig. 1. The map of the Zemborzyce Reservoir (Lublin, Poland) with points of sample collection of superficial water and bottom sediments.

were quantitatively transferred into plastic 50 ml flasks and undertaken to AAS measurements.

Fish were caught from the Zemborzyce Reservoir in autumn (1999). Samples of muscular tissue were frozen (-18°C) before analysis. 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.

Mollusks were collected from the shores of the Zemborzyce Reservoir 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 for analysis. The digestion was carried out identically as in the fish analysis.

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. For mercury determination the Hg - analyzer AMA 254 (Czech) was applied. Samples of fishes, mollusks and sediments were digested using the microwave stove MARS 5, CEM, USA. In overall procedures spectrapure quality reagents (Merck, Germany) were used.

Results and Discussion

Trace metals contents in superficial water, bottom sediments and muscular tissue of fishes and mollusks taken from the Zemborzyce Reservoir are presented in Tables 1-7.

Table 1. Trace metals content in bottom sediments from the Zemborzyce Reservoir (Lublin, Poland).

Sample	Content (ppm)				
	Cd	Cr	Hg	Pb	Zn
1	0.049	2.29	0.02	0.5	13.5
2	0.049	2.24	0.019	0.5	12.5
3	0.149	3.24	0.017	0.5	15.5
4	0.248	3.68	0.018	2.48	16.9
5	0.099	1.55	0.016	1.99	15.9
6	0.049	0.7	0.011	1.49	9
7	0.148	2.73	0.014	0.99	13.9
8	0.236	2.38	0.018	1.06	12.9
9	0.06	1.98	0.015	1.12	13.4
10	0.099	0.69	0.012	0.99	8.9
MIN	0.049	0.69	0.011	0.5	8.9
MAX	0.248	3.68	0.02	2.48	15.9
MEAN	0.118	2.15	0.016	1.16	13.2
SD	0.075	0.975	0.003	0.659	2.66
MEDIAN	0.099	2.26	0.016	1.02	13.4
The Bystrzyca River estuary	0.525	27.2	0.028	19.7	91.8

Bottom sediments (Tab. 1) from the estuary of the Bystrzyca River into the Zemborzyce Reservoir are characterized by significant contents of investigated metals: 0.52 ppm (Cd), 27.2 ppm (Cr), 0.028 ppm (Hg), 19.7 ppm (Pb) and 91.8 ppm (Zn). However, 16 years ago Misztal et al. [11] stated that trace metals content in bottom sediments before the estuary of the Bystrzyca River into the Zemborzyce Reservoir were slightly higher: 1.70 ppm (Cr), 30.0 ppm (Pb) and 100.0 ppm (Zn). Comparing our results to data obtained by Misztal we stated that trace metals content in bottom sediments of the Zemborzyce Reservoir shows a decreasing tendency (excluded Cr content). This fact can be caused by less intensive industrial activities in the upper run of the Bystrzyca River and also by the presence of local municipal treatment plants.

Bottom sediments from the Zemborzyce Reservoir (Tab. 1) contain (average): 0.118 ppm (Cd), 2.15 ppm (Cr), 0.016 ppm (Hg), 1.16 ppm (Pb) and 13.2 ppm (Zn). According to Bojar [13] trace metals contents in bottom sediments from the Zemborzyce Reservoir were 19.7 ppm (Zn), 0.178 ppm (Cd) and 2.54 ppm (Pb). We obtained almost identical results in our research. On the other hand, Solecki et al. [14] found surprisingly high levels of Zn, Pb and other elements in bottom sediments from the Zemborzyce Reservoir. According to these authors, average content of examined elements in bottom sediments was: Pb - 25.8 ppm (min - 10 ppm, max - 50 ppm) and Zn - 50.2 ppm (min - 12 ppm, max - 92 ppm). It seems that bottom sediments containing large amounts of Zn and Pb were collected not far from shores of the reservoir, so it is probably the reason of higher trace metals levels.

According to Misztal et al. [12] 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 [15]. We can assume that trace metals in soluble form are adsorbed in considerable quantities by the peat basis of this reservoir. In consequence, in spite of relatively large amounts of heavy metals transported to the reservoir, superficial water (Tab. 2) contains ultra-trace quantities of examined elements: 0.052 ppb (Cd), 0.76 ppb (Pb) and 17.1 ppb (Zn). Perhaps this means that the sorption capacity of the peat is still inexhaustible.

Table 2. Trace metals content in superficial water from the Zemborzyce Reservoir (Lublin, Poland).

Sample	Content (ppb)				
	Cd	Cr	Hg	Pb	Zn
1	0.086	< LOD	< LOD	0.61	4.53
2	0.077	< LOD	< LOD	0.81	20.2
3	0.017	< LOD	< LOD	0.4	10.3
4	0.022	< LOD	< LOD	0.46	30.5
5	0.027	< LOD	< LOD	1.21	20.4
6	0.082	< LOD	< LOD	1.06	24.8
7	0.073	< LOD	< LOD	1.01	26.1
8	0.031	< LOD	< LOD	0.52	9.6
9	0.056	< LOD	< LOD	0.82	16.8
10	0.048	< LOD	< LOD	0.69	8.31
MIN	0.017	–	–	0.4	4.53
MAX	0.086	–	–	1.21	30.5
MEAN	0.052	–	–	0.76	17.1
SD	0.026	–	–	0.27	8.66
MEDIAN	0.052	–	–	0.75	18.5

LOD – limit of detection

Both chemical composition of bottom sediment [6] and chemical form of trace metals have essential influence on assimilating these elements by water organisms which live and feed in sediment, e.g. by mollusks [9, 10]. Accumulation of Zn, Pb and Cr by mollusks was observed. The average contents of determined trace metals (Tab. 3) were 51.1 ppb (Cd), 123 ppb (Cr), 115 ppb (Pb) and 18,700 ppb (Zn). Based on these results we stated that mollusks' ability to accumalate appears in the following order: Zn > Cd > Pb > Cr > Hg. This range is probably the effect of different trace metals bioavailability, which 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, which will be the subject of our future study.

Table 3. Trace metals content in muscular tissue of mollusks *(Anodonta sp.)* from the Zemborzyce Reservoir (Lublin, Poland).

Sample	Content (ppb)				
	Cd	Cr	Hg	Pb	Zn
1	92.7	156	< LOD	120	29100
2	96.7	155	< LOD	177	21570
3	25.6	179	< LOD	96.9	12870
4	28.1	115	< LOD	64.5	12300
5	18.7	72	< LOD	118	9590
6	52	95	< LOD	128	20800
7	43.2	114	< LOD	107	12400
8	37.8	82	< LOD	94.9	33700
9	59	131	< LOD	119	19600
10	57.2	126	< LOD	121	15800
MIN	18.7	72	–	64.5	9590
MAX	96.7	179	–	177	33700
MEAN	51.1	123	–	115	18700
SD	26.6	34.2	–	28.7	7836
MEDIAN	47.6	121	–	119	17700

LOD – limit of detection

The average Cd content in the muscular tissue of fish from the Zemborzyce Reservoir (Tab. 4-6) was 4.20 ppb (roach), 6.05 ppb (perch) and 5.1 ppb (bream). By comparison, Bulinski et al. [16] stated that the average Cd content in the muscular tissue of market chilled breams was 35 ppb. Moreover, Gajewska et al. [17] stated that the average Cd content in freshwater fishes was 30 ppb (perch) and 81 ppb (bream). It is apparent that fishes from the Zemborzyce Reservoir contain one range of order of the Cd content less than in the cited cases.

The average Cr content in the muscular tissue of fish (Tab. 4-6) was 31.8 ppb (roach), 28.1 ppb (perch) and 15.3 ppb (bream). On the other hand, Bulinski et al. [16] stated that the average Cr content in market chilled breams was 494 ppb. The large Cr level in fish, determined by Bulinski, could have been caused by an inexact analysis method (dry ashing and F AAS). The Cr content in fish has not been well documented in the literature, so it is difficult to compare our results to other data.

The average Hg content in the muscular tissue of fish (Tab. 4-6) was 28.9 ppb (roach), 42.2 ppb (perch) and 30.3 ppb (bream). According to Gajewska and Nabrzyski [17] the average Hg content in the muscular tissue of freshwater fish from Polish lakes was 47 ppb (bream) and 26 ppb (perch). Both our data and those cited above are very closed.

Table 4. Trace metals content in muscular tissue of Roach *(Rutilus rutilus)* from the Zemborzyce Reservoir (Lublin, Poland).

Sample	Content (ppb)				
	Cd	Cr	Hg	Pb	Zn
1	2.43	35.9	28.1	14.1	5930
2	1.32	33.2	29	23.6	9750
3	6.85	41.6	33.9	23.3	7780
4	7.94	46.5	25	49.8	1400
5	3.92	9.54	31.2	23.8	5600
6	2.78	24.3	26.1	28.6	5700
7	2.14	16.7	23.4	12.3	1250
8	2.81	28.3	25.8	26.5	5300
9	6.26	46.8	34.9	42.1	6180
10	5.59	35.2	32.2	27.9	6760
MIN	1.32	9.54	23.4	12.3	1250
MAX	7.94	46.8	34.9	49.8	9750
MEAN	4.2	31.8	28.9	27.2	5565
SD	2.28	12.3	3.95	11.4	2590
MEDIAN	3.37	34.2	28.6	25.2	5815

Table 5. Trace metals content in muscular tissue of Perch *(Perca fluviatilis)* from the Zemborzyce Reservoir (Lublin, Poland).

Sample	Content (ppb)				
	Cd	Cr	Hg	Pb	Zn
1	1.43	47.4	42	21.1	6650
2	2.52	31.2	39.1	27.8	6920
3	5.84	20.2	26.1	34.8	7160
4	4.38	27.7	33	19.3	7180
5	3.28	28.1	31.8	29.1	6850
6	5.69	23.1	46.4	27.8	7140
7	8.13	45.4	67.9	42.4	8300
8	9.58	18.8	45.4	41.2	7430
9	10.8	11.6	38.1	50.7	6670
10	8.82	27.9	52.7	36.3	7500
MIN	1.43	11.6	26.1	19.3	6650
MAX	10.8	47.4	67.9	50.7	8300
MEAN	6.05	28.1	42.2	33.0	7180
SD	3.18	11.2	11.9	14.6	487
MEDIAN	5.77	27.8	40.6	31.9	7150

Table 6. Trace metals content in muscular tissue of Bream *(Abramis brama)* from the Zemborzyce Reservoir (Lublin, Poland).

Sample	Content (ppb)				
	Cd	Cr	Hg	Pb	Zn
1	5.4	9.52	29.1	16.1	5220
2	7.05	17.2	30.3	12.8	4150
3	6.23	20.5	31	20.2	4790
4	4.09	13.7	30	12.3	4580
5	1.76	9.53	27.2	15.2	5240
6	4.75	15.9	32.6	19.4	4220
7	6.26	21.8	35.4	19.8	4260
8	6.45	18.6	28.4	18.8	4850
9	3.84	12.6	27.1	18.1	4320
10	4.92	14.2	31.9	16.3	4720
MIN	1.76	9.52	27.1	12.3	4150
MAX	7.05	21.8	35.4	20.2	5240
MEAN	5.1	15.3	30.3	16.9	4635
SD	1.57	4.24	2.56	2.84	399
MEDIAN	5.16	15.1	30.2	17.2	4650

Table 7. Average trace metals content in superficial water, bottom sediments and in muscular tissue of fishes and mollusks from the Zemborzyce Reservoir (Lublin, Poland).

Sample	Content (ppb)				
	Cd	Cr	Hg	Pb	Zn
Roach *(Rutilus rutilus)*	4.20	31.8	28.9	27.2	5565
Perch *(Perca fluviatilis)*	6.05	28.1	42.2	33.0	7180
Bream *(Abramis brama)*	5.1	15.3	30.3	16.9	4635
Mollusks *(Anodonta sp.)*	51.1	123	< LOD[1]	115	18700
Superficial water	0.052	< LOD[2]	< LOD[3]	0.76	17.1
Bottom sediments	118	2150	16	1160	13200

[1] LOD (limit of detection) - for Hg - 2.5 ppb;
[2] LOD (limit of detection) - for Cr - 0.2 ppb;
[3] LOD (limit of detection) - for Hg - 0.5 ppb;

The average Pb content in the muscular tissue of fish (Tab. 4-6) was 27.2 ppb (roach), 33.0 ppb (perch) and 16.9 ppb (bream). On the other hand, Bulinski et al. [16] stated that the average Pb content in market chilled breams was 125 ppb. According to Gajewska et al. [18] the average Pb content in the muscular tissue of fishes from Kamienski Lake was 124 ppb (roach) and 108 ppb (bream). Moreover, Gajewska and Nabrzyski [17] stated that the average Pb content in the tissues of freshwater fish was 118 ppb (perch) and 153 ppb (bream). Comparing this data we noted that the Zemborzyce Reservoir belongs to unpolluted lakes.

The average Zn content in the muscular tissue of fish (Tab. 4-6) was 5.56 ppm (roach), 7.18 ppm (perch) and 4.64 ppm (bream). Zn does not belong to elements with especially toxic activity for living organisms, so it is not a frequent object of investigations. However, correlating Zn content with Cd content we can foresee the sources of the pollution with these two elements [19].

Comparing trace metals contents in the muscular tissue of roach, perch and bream (Tab. 7) we stated that the Cd accumulation is very similar for all examined fishes and roaches accumulate the majority of Cr. Perch (predacious fish) show great accumulation abilities of Hg, Pb and Zn. Trace elements pass into their organisms from lower links of the food chain.

Comparing trace elements contents in fish from the Zemborzyce Reservoir to fish from other reservoirs [17, 18] we stated that the pollution of fish in this reservoir is incomparably smaller and the trace element levels do not exceed limits admissible by law.

Comparing examined fish to mollusks (Tab. 7) we established that the Zn, Cd, Pb and Cr accumulation is considerably higher in mollusks, which is the result of their living and feeding in bottom sediments.

The content of studied metals for fish and mollusks was in wide range (see Tables 3-6). The differences in metal content between species may be the result of different feeding habits, different fish age, or both.

Moreover, it was stated (Tab. 7) that in spite of a large Cr content in bottom sediments, Cr does not pass to superficial water. This fact can be explained by the low solubility of Cr compounds in sediments. Living organisms accept elements in solvable form so Cr is the least assimilated metal, in relation to its content in sediment. Pb shows a similar tendency. The large assimilation of Hg is probably caused by the existence of organic Hg forms [20].

Comparing trace metals content in examined compounds of the Zemborzyce Reservoir to other reservoirs [14, 17, 18], we stated that this reservoir is incomparably less polluted than others.

Conclusions

1. Trace metals content in bottom sediments from the Zemborzyce Reservoir shows a decreasing tendency. This fact can be caused by less intensive industrial activities in the upper run of the Bystrzyca River and also by the presence of local municipal treatment plants.

2. Trace metals in solvable forms are adsorbed by the peat basis of the Zemborzyce Reservoir. In consequence, in spite of relatively large amounts of heavy metals trans ported to the reservoir, superficial water contains ultra-trace quantities of examined elements.

3. We stated that Cd accumulation is very similar for all examined fish, with roach accumulating the majority of Cr. Perch (predacious fish) show great accumulation abilities of Hg, Pb and Zn. Trace elements pass to their organisms from lower links of the food chain.

4. Comparing trace elements contents in fish from the

Zemborzyce Reservoir to fish from other reservoirs we established that pollution of fish in this reservoir is incomparably smaller, and trace element levels do not exceed limits admissible by law.

5. We found that Zn, Cd, Pb and Cr accumulation is considerably higher in mollusks, what is the result of their living and feeding in bottom sediments.

6. In spite of large Cr content in bottom sediments, Cr does not pass to superficial water (small solubility of Cr compounds in sediments). Living organisms accept el ements in solvable forms so Cr is the least assimilated metal in relation to its content in sediment. Pb shows a similar tendency. The large assimilation of Hg is prob ably caused by the existence of organic Hg forms.

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