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**Toxicology** 

# CADMIUM AND LEAD IN FISHES AND IN SELECTED ELEMENTS OF THE ŚWIDWIE LAKE ECOSYSTEM KADM I OŁÓW W RYBACH I WYBRANYCH ELEMENTACH

## EKOSYSTEMU JEZIORA ŚWIDWIE

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This paper provides information on the vertical distribution of cadmium and lead in the sediments, the amounts of the elements in the surface- and rain water, in selected fish organs, contents of their alimentary tracts, and in some plant species of the Świdwie Lake ecosystem. The levels and distribution of the analysed metals in the lake sediments gave evidence of their anthropogenic origin. The distribution of cadmium and lead in the organs and alimentary tracts of fishes, and especially the low level of the elements in fishes and plants suggests that the metals are linked to the abiotic components of the lake environment and they are not easily accessible for the organisms. The best bio-indicators of the pollution-level with cadmium and lead in the lake ecosystem are: the rudd, *Scardinius erythrophtalmus* L. and the roots of cattail, *Typha angustifolia*.

#### INTRODUCTION

The natural circulation of elements has been subjected to various alterations resulting from the environmental pollution caused by human economy. This poses not only a threat to the ecological ecosystem balance by endangering the development and life of the organisms, but has also an indirect and direct effect on human health. Cadmium and lead belong to the group of highly toxic elements, and even though their traces are present in the organisms of plants and animals, no evidence has been found for their indispensability.

The total content of metal in water can be divided into two fractions: metal bounded in suspended matter and the dissolved fraction (Głażewski 1992). The proportion of these two fractions of heavy metals in natural waters depends on many physical and chemical factors, such as salinity, complexing components of the dissolved organic matter, forms of metal occurrence, composition and effective surface of the suspended matter molecules (Revis et al. 1989). Even small amounts of heavy metals present in waters are very quickly

accumulated in the bottom sediments (Strzebońska 1997) and the level of their presence in lake sediments can be a pollution indicator (Kwapuliński et al. 1991; Warda and Bubicz 1992; Gonet and Cieślewicz 1997). To verify the anthropogenisation level of the sediments, the results are compared with so-called "background levels" or "geo-chemical values", estimated on the basis of the mean values of the elements concentration in the earth's crust or the concentration in "clean places" occurring in the area studied (Carral et al. 1995). Another method involves sediments core analysis, and the comparison of the amounts of metals in younger, upper layers with the older, deeper layers (Protasowicki et al. 1993; Klavins et al. 1995).

Cadmium is absorbed by fishes through the alimentary tract as well as through the gills, and is accumulated in the gills, kidney, and liver (Spry and Wiener 1991). This element is not bio-magnified in the food chain (Protasowicki and Morsy 1993); also the size and the age of fish do not affect its content (Spry and Wiener 1991). Lead, absorbed by fish mainly from water, is accumulated in the gills, kidney, liver, and the bones (Spry and Wiener 1991). Lead, like cadmium, is not bio-magnified (Protasowicki and Morsy 1993; Berg et al. 1995).

In the research of water environment quality, water plants are used for monitoring the heavy metal content and pollution from the other sources (Sawidis et al. 1995). Metals and other mineral substances are absorbed mainly through the roots, and their distribution in plants depends on many factors; among them: kind of metal, occurrence of some other elements, as well as features of species and individual plants (Woźny 1993). Cadmium is easily absorbed in the form of cations, hydrogenised ions, and organometallic chelates. Transportation of cadmium inside the plant is also easy, but when the absorption is higher, the element is accumulated mainly in the roots, even when absorbed by leaves. Lead absorption by plants is a passive process and it is directly proportional to the occurrence of the dissolved forms in the soil. The higher lead concentration in the soil solution, the higher its concentration in the plants; however, much higher amounts of lead occur in the roots than in the above-ground parts (Kabata-Pendias and Pendias 1993).

The aim of this study was to determine the content levels and distribution of toxic heavy metals, cadmium and lead in the selected elements of the Świdwie Lake ecosystem, and to recognize its sources. An attempt was also undertaken to identify the species which would be good bio-indicators of environmental pollution with the above metals.

#### MATERIAL AND METHODS

Materials used in this study were taken in the years 1995–96. The method and the sampling sites were described in the previous publication (Perkowska and Protasowicki 1999).

The samples of sediments, fishes, and plants were mineralised in the mixture of nitric acid and perichloride acid in the proportion of 4:1. The samples of water were mineralised with addition of nitric acid according to the procedure EPA 200.7 (EPA/600/4-79/020, 1983). The lead and cadmium contents in the fish tissues were determined with the flame atomic absorption spectrometry method (FAAS) with the use of Varian Techtron A 1200 apparatus. The lead and cadmium contents in the water, plants, and the sediments were determined with the inductively coupled plasma atomic emission spectrometry method (ICP-AES) in the Jobin Yvon JY-24 apparatus.

All samples were analysed in triplicate. Some parallel blank samples were also taken. Mean values of relative standard deviations (RSD) from the parallel repetitions were 4.69% for cadmium and 5.34% for lead. The detection limits of cadmium and lead were 0.01  $\mu$ g/g and 0.04  $\mu$ g/g respectively in the biological materials and sediments while 0.1  $\mu$ g/dm³ and 1.0  $\mu$ g/dm³ in the water. The accuracy of the analyses was controlled by adding standard solutions. Average values of the salvages of the analysed elements in water, sediments, fishes, and plants matter were 89–102% for Cd and 92–107% for Pb. Statistical calculations were made with the aid of MS Excel 7.0 software. Statistics were taken on significance level  $\alpha$  = 0.05.

#### RESULTS AND DISCUSSION

 $\label{eq:Table 1} Table \ 1$  Cadmium and lead occurrence [µg/dm³] in the inlet and outlet waters of Świdwie Lake and in the rain water

Type of water	n	Cd		Pb	
		Range	Mean ±SD	Range	Mean ±SD
inlet	32	< 0.1-1.1	$0.5 \pm 0.3$	< 1-11	3 ±3
outlet	8	< 0.1–0.8	0.2 ±0.3	< 1–7	3 ±2
rain water	8	< 0.1–0.5	0.2 ±0.2	3-233	73 ±89

SD - standard deviation

Cadmium and lead concentrations found in surface waters taken on the inlet and outlet of Lake Świdwie were low (Tab. 1), as in the waters described as not polluted with these metals. Similar levels of cadmium and lead were

recorded in the waters of the Rynna Kórnicka lakes (Jeszke et al. 1994). Warda and Bubicz (1992) reported similar contents of cadmium in the waters of the Zemborzyckie Lake drainage area. Higher contents of cadmium and lead than were found in Świdwie Lake were reported from big polluted rivers of Poland (Jędrczak and Czyrski 1990; Siepak 1992) and from a heated reservoir near the Rybnik Power Plant (Loska et al. 1994b).

On a larger scale cadmium occurred in the inlet waters (Tab. 1), in which the amount of this element was over twice as much as in rainwater. The biggest difference of the amount of the analysed elements between surface waters and rain waters was found in the case of lead. In the rain waters the average concentration of lead was 73 µg/dm<sup>3</sup> and it was

over 22 times higher than the average value found in the inlet waters. It proves that the rain water is an important source of lead in Świdwie Lake. Many researchers pointed out that high level of trace elements are present even in areas placed far from the direct influence of the pollution. This phenomenon is explained as a result of the atmospheric deposition. Smith and Hamilton (1992), who measured lead occurrence in the sediments of two lakes in southeast Australia, stated that in the lake influenced by anthropogenic pollution during an 80-year period the amount of lead in the sediments increased 90 times, whereas in the lake not exposed directly to human-source pollution, it increased only 35 times. Taking into account this data and the authors' own results, it can be concluded that the atmospheric influx is a serious source of lead in Świdwie Lake.

Determination of the natural levels of trace elements in sediments and their possible polluting effect is a complicated matter, because most of the Earth surface is, on a bigger or smaller scale, influenced by humans. In the publications by various authors concerning the estimated values of the "geo-chemical background", some divergences of opinion, regarding the same elements can be found (Förstner and Müller 1974; Kabata-Pendias and Pendias 1993; Kozak et al. 1994; Carral et al. 1995). Therefore the present attempts to assess possible pollution of the Świdwie Lake sediments with cadmium and lead are based on two elements: comparison of the Świdwie Lake rerults with those found elsewhere, and the actual analysis of the vertical distribution of the metals studied in the sediment cores.

Table 2

Lead and cadmium occurrence [μg/g d.w.] in Świdwie Lake sedmients according to the depth.

Depth b.b.	C	Cd .	Pb		
[cm]	Range	Mean ±SD	Range	Mean ±SD	
0-2.5	0.06-7.58	2.48 ±2.18	0.7-470.2	128.2 ±138.3	
2.5–5	0.10-3.01	1.46 ±0.92	1.7-80.1	47.4 ±29.1	
5–7.5	0.08-4.88	1.39 ±1.43	1.2-32.0	24.1 ±25.5	
7.5–10	0.11-4.01	1.29 ±1.22	1.7–39.4	21.5 ±15.3	
10–12.5	0.08-2.79	1.12 ±0.93	2.7–55.7	21.9 ±16.3	
12.5–15	0.05-2.52	$0.98 \pm 0.82$	1.9-39.0	16.8 ±12.5	
15–17.5	0.05-1.82	0.75 ±0.67	1.4-30.2	12.2 ±11.5	
17.5–20	0.05-2.07	$0.76 \pm 0.76$	0.8-28.5	11.3 ±12.1	

b.b., below bottom SD, standard deviation

Cadmium found in the Świdwie Lake sediments occurred as deep as 20 cm below bottom (b.b.) and its content ranged from 0.05 to 7.58 μg/g dry weight (d.w.) (Tab. 2). Some of the concentrations were higher than the contents found in the sediments of the selected lakes of Piła voivodship (Gonet and Cieślewicz 1997) and the drainage basin of Zemborzyckie

Lake (Warda and Bubicz 1992). However, the contents were lower than those occurring in the waters described as polluted with this metal (Kwapuliński et al. 1991; Protasowicki and Niedźwiecki 1991; Protasowicki et al. 1993; Loska et al. 1994a; Protasowicki et al. 1997b).

Some of the concentrations of lead in the top layer of sediments (site 2—470.2; site 6—174.4; site 9—214.9; site 10—153.9  $\mu$ g/g d.w.) are nearly the same, or even higher than the amounts found in waters qualified as polluted with this metal (Głażewski 1991; Loska et al. 1994a; Protasowicki et al. 1993, 1997a, 1997b; Perkowska and Protasowicki 1996). Förstner and Müller (1974) stated that the natural content of lead in aluvial sediments of rivers did not exceed 40  $\mu$ g/g d.w., while for the estuary sediments in the Galicia region (Spain), Carral et al. (1995) established the geo-chemical background as 53  $\mu$ gPb/g d.w. In bottom sediments taken from the analogical layer of the selected lakes of Piła voivodship, lead concentration did not exceed 70.9  $\mu$ g/g d.w. (Gonet and Cieślewicz 1997).

Comparison of vertical distribution of the metals proved that the deeper the sediments occurred, the smaller content of cadmium and lead they had. In the surface layer of the sediment 0-2.5 cm b.b., there was over three times more cadmium than in the section of the lowest content of this element, which was 15-17.5 cm b.b. On the other hand the surface layer contained on average 11 times more lead than the layer 17.5-20 cm b.b. Along with the depth, the average content of organic matter decreased as well, but the proportion calculated analogically was only about 1.5 (Perkowska and Protasowicki 1999). Not all the cores of sediments showed the same regularity, because of the differences in the structure of sediments analysed, and especially because of the different content of organic matter. That is why the content of organic matter can be to some extent a factor determining the vertical distribution of metals in the top layer of sediments. However, in case of such multiplied concentration of lead, it can be assumed anthropogenic factors were the principal contributor. The affect of these factors cannot be excluded in the case of cadmium either. Many researchers observed increased amounts of cadmium and lead in the top layer of sediments in comparison to deeper layers. Głażewski (1991), Davis and Galloway (1993), Protasowicki et al. (1993), Klavins et al. (1995), and Lent and Alexander (1997) described them in their publications. However, the content of metals in sediments increases sometimes along with the depth. For example, the cores of sediments, analysed by Loska et al. (1994a) in the heated water reservoir near the Rybnik Power Plant had a lower concentration of cadmium in the top layer of sediments than in deeper layers.

As the statistical analysis proved, the localisation of the sampling sites influenced significantly the occurrence of cadmium and organic matter in the cores of sediments of Świdwie Lake. The same dependence was not proved for lead. The sampling sites (s) arranged in decreasing order according to the content of cadmium, lead, and organic matter show the following patterns:

Cd: s2 > s7 > s10 > s6 > s1 > s9 > s4 > s3 > s8 > s5

Pb: s2 > s6 > s10 > s7 > s9 > s1 > s3 > s4 > s5 > s8

Organic matter: s2 > s1 > s10 > s9 > s6 > s4 > s7 > s3 > s5 > s8

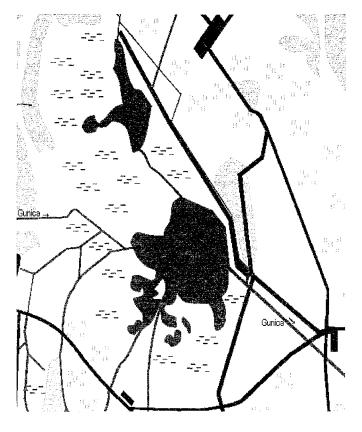


Fig. 1. Sediment sampling sites

The sites marked in bold print are those in which the content of the metals was higher than average for all cores. These points are situated in the southern part of the lake (Fig. 1). It means that the waters of the Gunica River and of the southern part of its drainage basin, flowing directly into Świdwie Lake seem have substantial influence on the cadmium supply, and to some extent also the lead supply to the lake. While no evidence was given that the inlet and outlet waters of the lake varied significantly in

their contents of the analysed metals—in all eight water sampling-takings the concentration of cadmium was higher in the inlet waters of the Gunica River compared to the outlet waters, while for lead, four of such cases were recorded. The highest concentrations of the metals were recorded at the site situated near the inlet of the river. The southern and western parts of the drainage feature: cultivated fields, meadows, a number of human settlements, the state border crossing in Lubieszyn, animal waste utilisation plant, and fish ponds. The sediments from site 8, situated near the outlet of the river contained very small amounts of the metals, which could be partially related to the accumulation of the suspended matter in the lake. The suspended matter is blamed for delivering the main load of pollutant. However, the small amount of the metals found in the sediments from this site can be explained by their mechanical composition. It was a mineral sediment, which was at least partially, if not totally, created from a nearby eroding embankment. It must be mentioned also that although fishing is forbidden, some poaching does occur and it results in the presence of pieces of metallic lead in the sediments. During a two-year period of

sampling of the lake, the researchers extracted several of such lead sinkers. So it cannot be ruled out that this fact could also influence the values of the lead content in the sediments.

Cadmium content in the muscles of fishes from Swidwie Lake ranged from 0.01 to 0.04, and lead—from 0.22 to 0.99 µg/g wet weight (w.w.). The highest concentration of these elements was in the fish gills—cadmium 0.08 and lead 2.13 µg/g w.w. Although these values are relatively low, they are not minimal, as can be illustrated by the results obtained elsewhere in the world. For example, the average content of cadmium found by Allen-Gil and Martynov (1995) in the muscles of fishes from the Pechora River (Siberia), from the areas situated far from the influence of anthropogenic pollution, were distinctly lower than from Świdwie Lake and they amounted to 0.005-0.012 µgCd/g and 0.008-0.021 µgPb/g w.w. Compared with the fishes from Świdwie Lake, some more cadmium and comparable contents of lead were found in the muscles of roach and perch from the Odra River estuary (Protasowicki 1991), and also in the organs and tissues of roach, rudd, white bream, and perch from the Miedzyodrze area (Wecowska 1997). Some of the research concerning the contents of cadmium and lead in the tissues of freshwater fishes present the results in which the levels of these elements are much higher than those found in the fishes from Świdwie Lake. The muscles of pike from the Szczecin Lagoon studied in the period of 1980-81, contained several times more cadmium and lead than was found in the present project (Garcia-Gasiun 1982). Szulkowska-Wojaczek et al. (1992) found in the muscles of perch, roach, pike, and rudd, taken from the fish ponds of southwestern Poland 0.08-0.68 ugCd/g w.w. and 0.45-3.52 µgPb/g w.w. Presented data suggest that the contents of cadmium and lead found in the muscles of fishes from Świdwie Lake are as low as in fishes from waters not polluted with these metals.

The distribution of these elements in the organs and food of all analysed fish species was presented in Fig. 2 and 3. Cadmium and lead accumulate in different ratio in the liver and kidney. In some cases the contents of these elements in the muscles were comparable or even higher than the concentration in the liver and kidney. However, in all species the contents of cadmium and lead were higher in the gills than in the muscles. It proves that the respiratory system is the main way of acquisition of these metals by fishes. Cadmium accumulated much better in alimentary tracts than in muscles, and that is why this way of cadmium accumulation may also be significant. It confirms the results of the earlier study, which revealed that for fishes, the most accessible form of cadmium is Cd<sup>2+</sup>, and of lead Pb<sup>2+</sup> and PbOH<sup>+</sup>. Cadmium ions are taken in by fishes both through the alimentary tracts and through gills, while lead mainly through the respiratory system (Spry and Wiener 1991). Protasowicki and Chodyniecki (1992) studied the accumulation of cadmium from the alimentary tract of carp. The element was provided in specially prepared gelatin pills. The authors proved a very high increase of cadmium contents in the organs responsible for

absorption and excretion processes, i.e. the alimentary tract, liver, and kidney. When this element was put in the water, the acquisition occurred mainly through the gills (Protasowicki and Chodyniecki 1988).

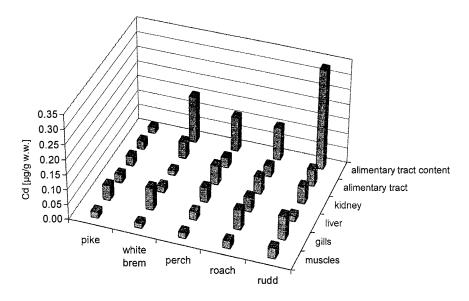


Fig. 2. Cadmium content in fishes

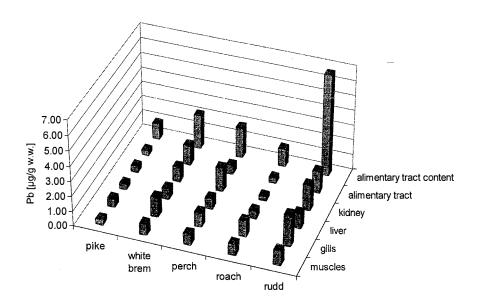


Fig. 3. Lead content in fishes

The ranges of concentrations, average values, and standard deviations of cadmium and lead contents selected plant species from Świdwie Lake are shown in Tab. 3. The results show extensive variability of samples taken from the analysed species. The wide ranges of analysed metals occurrence prove that, and what is connected with it, relatively high standard deviations from mean values. Leaves, stems, and roots of cattail and reed samples were analysed separately. The highest amounts of the metals were found in the roots, much less—in the leaves and stems (Tab. 3). This kind of metal distribution is typical for macrophytes and was observed by Mungur et al. (1995), Sawidis et al. (1995), Wójcik (1995). It proves that the roots are a good indicator of changes in the contents of metals in plants. Content of cadmium was significantly higher in cattail, while the amount of lead was statistically equal in both species, that is why the level of these elements in plants from the lake ought to be monitored by analysis of roots of cattail.

 $\label{eq:Table 3} Table \, 3$  Cadmium and lead occurrence [µg/g d.w.] in Świdwie Lake plants

Material		Cd		Pb	
	n	Range	Mean ±SD)	Range	Mean ±SD)
Bladderwort	20	0.02-0.49	$0.12 \pm 0.10$ )	< 0.04–3.7	$0.8 \pm 0.9$ )
Duckweed	8	< 0.01-0.03	$0.07 \pm 0.05$ )	< 0.04-0.8	$0.4 \pm 0.4$ )
Cattail:					
leaves	20	< 0.01-0.10	$0.03 \pm 0.03$	< 0.04-2.0	$0.5 \pm 0.5$ )
stems	20	< 0.01-0.03	$0.01 \pm 0.01$	< 0.04-0.4	$0.1 \pm 0.1$ )
roots	20	0.18-1.19	$0.58 \pm 0.24$ )	1.6–17.4	6.4 ±4.2)
Reed:		0			
leaves	20	< 0.01–0.05	$0.02 \pm 0.02$ )	< 0.04-0.8	$0.2 \pm 0.2$ )
stems	20	< 0.01-0.19	$0.03 \pm 0.04$ )	< 0.04-0.9	$0.2 \pm 0.2$
roots	20	< 0.01-0.72	$0.35 \pm 0.19$ )	1.0-17.4	5.8 ±4.3)

SD, standard deviation

Kabata-Pendias and Pendias (1993) state, that the normal (physiological) content of cadmium in above-ground parts of the plants from non-polluted areas is between 0.05 and 0.2 μg/g d.w., while the excessive (toxic) concentration is between 5 and 30 μg/g d.w. The respective amounts of lead are from 5 to 10 μg/g d.w. and from 30 to 300 μg/g d.w. The measured concentration of cadmium and lead in the leaves of cattail and reed from Świdwie Lake can be regarded as a natural. Also the content of the metals found both in other parts of analysed marcophytes and in duckweed should be considered as low. They are comparable, and often lower than the concentration measured by other researchers in the same species or types of plants (Nuorteva et al. 1986; Warda et al. 1993; Sawidis et al. 1995; Wójcik 1995; Samecka-Cymerman and Kempers 1996). No data were found concerning metal concentration in bladderwort but the measured contents were characteristic for the species of submerged water plants taken from non-polluted waters

(Nuorteva et al. 1986; Dobicki et al. 1990; Warda et al. 1993). In the areas under the direct influence of pollution from highways Mungur et al. (1995) found maximum of 905 µgPb/g d.w. in submerged parts of reed and 264 µgPb/g d.w. in above-water parts. To compare, the maximum amount of lead in the roots of the same species from Świdwie Lake was 17.4 μg/g d.w., while in the leaves 0.84 μg/g. d.w. In Kerkeni Lake in Macedonia (Sawidis et al. 1995) the concentration of cadmium in sediment was approximate to the concentration stated in the sediments of Świdwie Lake, but in spite of this, the content of this element in roots of Phragmites australis was almost 10 times higher than in plants from Świdwie Lake. Marek (1990) noticed a much lower level of lead content in the sediments of fish ponds in the catchment area of the Barycz River than in Świdwie Lake, while the contents of this element in the tissues of reed and cattail there were comparable. These data show that the bioavailability of these metals varies greatly. In our study the low accessibility of lead and cadmium for plants in the conditions of Świdwie Lake was shown. It is proved by the fact that in spite of very high contents of lead and much elevated amounts of cadmium in the top layer of bottom sediments, the level of these elements in plants was not high.

#### CONCLUSIONS

- 1. Proved in the majority of the core samples the higher content of the heavy metals in top layers of sediments in comparison with the deeper layers deposited earlier shows that the sources of pollution with these elements in the lake are anthropogenic.
- 2. The contents of lead recorded in the upper layers of the sediments can be regarded as a typical for polluted waters.
- The main way of the cadmium supply to the lake is the Gunica River. The source of cadmium is the catchment area of the river and the southern part of the catchment area of the lake.
- 4. Regular distribution of lead in the upper layers of the sediments and its high concentration in the rain water shows that the atmosphere is the main source of this element in the lake, while the supply through the river and canal waters plays a minor role.
- 5. The distribution and small concentration of cadmium and lead in the organs, muscle tissue and food of the fishes, and the low level of the contents of these elements in the selected plant species suggest that lead and cadmium occurring in biotic elements of the environment of the lake are barely accessible for the organisms studied.

6. Taking into account the accumulation levels of heavy metals, it can be concluded that the rudd *Scardinius erythrophtalmus* L. and roots of cattail *Typha angustifolia* can be very useful as indicatory organisms for monitoring the changing levels of cadmium and lead.

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## KADM I OŁÓW W RYBACH I WYBRANYCH ELEMENTACH EKOSYSTEMU JEZIORA ŚWIDWIE

#### **STRESZCZENIE**

Badano pionowe rozmieszczenie kadmu i ołowiu w osadach, ich zawartość w wodach powierzchniowych i opadowych; w narządach (skrzela, wątroba, nerki, mięśnie, przewód pokarmowy) i treści przewodów pokarmowych płoci, krapia, wzdręgi, okonia i szczupaka; w rzęsie wodnej i pływaczu zwyczajnym; a także liściach, łodygach i korzeniach trzciny pospolitej oraz pałki wodnej. Poziom oraz rozmieszczenie analizowanych metali w osadach jeziora wskazują na antropogeniczne pochodzenie tych pierwiastków. Rozmieszczenie kadmu i ołowiu w narządach i treści przewodów pokarmowych ryb, a zwłaszcza wykazany niski ich poziom w rybach i roślinach pozwala sądzić, że pierwiastki te, związane z abiotycznymi składnikami środowiska, jeziora są mało dostępne dla organizmów. Analiza wyników badań pozwala sądzić że, najlepszymi bioindykatorami przydatnymi w ocenie stopnia zanieczyszczenia ekosystemu jeziora kadmem i ołowiem są: wzdręga Scardinius erythrophtalmus L. oraz korzenie pałki wąskolistnej Typha angustifolia.

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