

Arch. Pol. Fish.	Archives of Polish Fisheries	Vol. 16	Fasc. 1	21-36	2008
---------------------	---------------------------------	---------	---------	-------	------

CONCENTRATIONS OF Cd, Pb, Zn, AND Cu IN ROACH, *RUTILUS RUTILIS* (L.) FROM THE LOWER REACHES OF THE ODER RIVER, AND THEIR CORRELATION WITH CONCENTRATIONS OF HEAVY METALS IN BOTTOM SEDIMENTS COLLECTED IN THE SAME AREA

*Izabela Bochenek**, *Mikołaj Protasowicki**, *Ewa Brucka-Jastrzębska***

*Department of Toxicology, Agricultural University of Szczecin, Poland

**Department of Physiology, University of Szczecin, Poland

ABSTRACT. The aim of this research was to investigate the type of relationships between the concentrations of heavy metals in bottom sediments and in selected roach, *Rutilus rutilus* (L.), organs. The material studied included kidney, liver, gill, and muscle tissues of roach caught in selected areas of the Oder River. The contents of Cd, Pb, Zn, and Cu were analyzed in fish organs. The content of heavy metals in roach organs differed depending on the organ or, in some cases, on the feeding site. The concentration of heavy metals in bottom sediments also depended on the site of their collection. Positive mutual correlations between concentrations of selected metals in fish and bottom sediments were found. The contamination of bottom sediments in the lower reaches of the Oder River with Cd, Pb, Zn, and Cu was diverse and depended on the sampling area. The accumulation of metals in the organs of the studied fish varied and was positively correlated with the concentration of metals in sediments.

Key words: HEAVY METALS, SEDIMENTS, BIOAVAILABILITY, FISH, ROACH

INTRODUCTION

When analyzing the aquatic environment with reference to heavy metal concentrations, their toxicity, and bioavailability to aquatic organisms, it must be remembered that sediments are both carriers and potential sources of contaminants (Salomons and Förstner 1984, Calmano et al. 1990, Świdorska-Bróz 1993). The processes of exchange of selected xenobiotics between sediments and water are of crucial importance for the evaluation of the potential contamination of the environment and hydrobionts (Calmano et al. 1990, Głazewski 1991). An increase in heavy metal concentrations in water is directly linked to their content in sediments, and this

CORRESPONDING AUTHOR: Izabela Bochenek, Uniwersytet Szczeciński, Wydział Nauk Przyrodniczych, Zakład Fizjologii, ul. Sokoła 1/3, 71-691 Szczecin, Tel. +48 91 4494699; e-mail: zuniai@wp.pl

influences the amounts bioaccumulated in fish. Metals can penetrate fish via the gastrointestinal tract, skin, and gills, either directly assimilated from water, or indirectly with food through the gastrointestinal tract.

The diverse bioavailability of metals, reported by the majority of researchers, is conditioned by the character of the bonds between a metal and a sediment. The most mobile fractions are well known (Tesier et al. 1979, Helios-Rybicka 1992, Singh et al. 1996, Tack et al. 1996, Maiz et al. 1997, Quevauviller et al. 1997). It can be expected that there is a maximum correlation between these metal fractions and the content of metals in particular fish tissues.

The problem of metal speciation in bottom sediments, regarding their bioavailability to fish, is one of many aspects in studies of relationships within aquatic ecosystems. Only a part of the metals deposited in river sediments is available and can participate in the processes that affect the aquatic environment. It is known that metals bound via physical adsorption and chemisorption are in balance with sediment interstitial water, and may easily penetrate the aquatic environment. Knowledge of metal migration in unstable environmental conditions makes it possible to predict their potential uptake by plants and animals at a particular area. It also makes it possible to predict the interspecies differentiation in the content of trace metals (Miller et al. 1992). The aim of the present research was to investigate to what extent the concentrations of heavy metals in fish were correlated with their concentrations in the abiotic part of the environment (sediments).

MATERIALS AND METHODS

The study involved roach, *Rutilus rutilus* (L.) caught in May and June 2000, and data on concentrations of heavy metals in sediments present in exchangeable, carbonated, and total form. The data on heavy metals were collected in the same season and year as the fish analyzed. Five sites of sediment collection and roach sample collection, in the lower reaches of the Oder River, were selected (Fig. 1). A pool of 10 individuals from each area was analyzed. Prior to analysis, whole fish were kept in a freezer at -20°C . To perform analysis, fish organs were removed, and about 1 g samples were weighed to the nearest 0.001 g using a WSP 210 C^{-1} analytical balance. Cadmium, lead, copper, and zinc were determined in gills, livers, kidneys, and muscles. Heavy metal content in organs are presented in $\mu\text{g g}^{-1}$ dry weight (d.w.).

Mineralization was performed using a microwave system MDS 2000 with nitric (V) acid. Samples were placed in Teflon® containers and supplemented with 3 cm³ of HNO₃. Containers were twisted and samples mineralized in a microwave oven, according to the protocol presented in Table 1. After mineralization, samples were quantitatively transferred to polyethylene bottles and supplemented with deionized water up to 40 g. Lead and cadmium were determined using the Flameless Atomic Absorption Spectrometry method, with atomization in a graphite furnace (Perkin Elmer ZL 4110). Zinc and copper were determined using Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) (Jobin Yvon JY-24).

The data obtained were subjected to statistical treatment involving the analysis of variance (ANOVA) at the significance level of $P \leq 0.05$, and the comparison of Spearman's correlation coefficient. The analysis was conducted using Statistica 6.0 (StatSoft Inc.), and was based on the results obtained from all 10 individuals of each group.

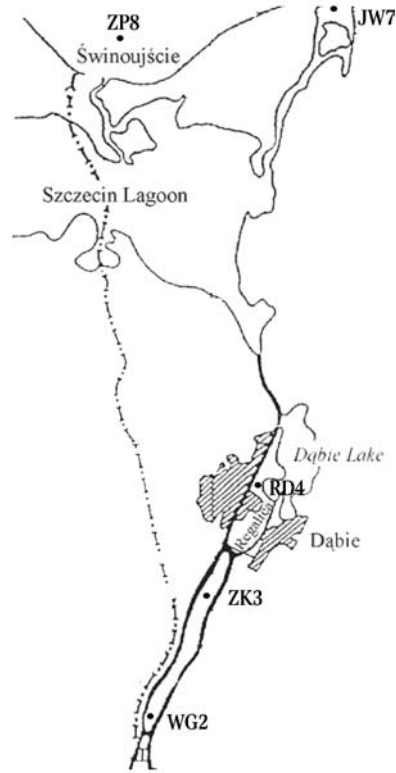


Fig. 1. Sites of sediment and roach samples collection. WG2 – the East Oder River in Gryfino, ZK3 – the West Oder River near the Krainka Island, RD4 – the East Oder River outlet to the Dąbie Lake, JW7 – the Wrzosowskie Lake, ZP8 – the Pomeranian Gulf.

TABLE 1

Microwave mineralization protocol applied for fish tissues in the MDS 2000 oven (application for 12 containers)

Level	I	II	III	IV	V
Power (%)	100	100	100	100	100
Pressure (psi)	20	40	85	135	175
Time (min)	10	10	10	10	5

RESULTS

Concentrations of heavy metals in bottom sediments depended on the site of their collection. The highest values of heavy metals content were noted at WG2, and the lowest value was noted at JW7 (Table 2).

TABLE 2

The average concentrations of heavy metals ($\mu\text{g g}^{-1}$ d.w.) bound in sediments in various chemical fractions

Sediments	Elements/Area				
	WG2	ZK3	RD4	JW7	ZP8
Cd					
Exchangeable fraction	1.84	0.18	1.88	0.77	0.30
Carbonate fraction	0.01	N.D.	0.02	0.01	0.01
Total concentration	27.98	8.59	18.85	1.86	3.08
Pb					
Exchangeable fraction	1.08	0.62	1.27	0.20	0.19
Carbonate fraction	1.58	1.67	1.97	0.00	0.00
Total concentration	306.40	200.90	213.60	80.10	119.20
Zn					
Exchangeable fraction	118.9	19.9	111.5	51.9	10.8
Carbonate fraction	444.4	242.6	350.2	74.3	67.6
Total concentration	1890.0	1478.0	1482.0	513.0	513.0
Cu					
Exchangeable fraction	N.D.	N.D.	N.D.	N.D.	N.D.
Carbonate fraction	1.11	0.18	1.11	1.78	0.35
Total concentration	295.80	128.60	197.10	54.10	59.20

*N.D. – not detectable, d.w. – dry weight

The average concentration of heavy metals in particular roach organs differed depending on the organ and, in some cases, on the feeding site. The highest average of cadmium content in roach was found in muscle at the ZP8 station ($0.325 \mu\text{g Cd g}^{-1}$ d.w.; Table 3). The highest average of lead and zinc were found in gills at JW7 ($0.254 \mu\text{g Pb g}^{-1}$ d.w.; Table 4) and WG2 ($384.1 \mu\text{g Zn g}^{-1}$ d.w.; Table 5), while the highest copper content was found in liver at WG2 ($30.21 \mu\text{g Cu g}^{-1}$ d.w.; Table 6).

TABLE 3

Concentrations (mean \pm SD) of cadmium ($\mu\text{g g}^{-1}$ d.w.) in organs of roach caught in the lower reaches of the Oder River

Tissues	Area				
	WG2	ZK3	RD4	JW7	ZP8
Muscles	0.008 \pm 0.002	0.007 \pm 0.002	0.002 \pm 0.001	0.002 \pm 0.001	0.325 \pm 0.012
Kidney	0.118 \pm 0.015	0.231 \pm 0.022	0.112 \pm 0.020	0.152 \pm 0.055	0.255 \pm 0.032
Liver	0.021 \pm 0.005	0.029 \pm 0.008	0.024 \pm 0.021	0.045 \pm 0.031	0.095 \pm 0.031
Gills	0.011 \pm 0.008	0.021 \pm 0.011	0.005 \pm 0.001	0.028 \pm 0.021	0.035 \pm 0.008

TABLE 4

Concentrations (mean \pm SD) of lead ($\mu\text{g g}^{-1}$ d.w.) in organs of roach caught in the lower reaches of the Oder River

Tissues	Area				
	WG2	ZK3	RD4	JW7	ZP8
	mean \pm SD	mean \pm SD	mean \pm SD	mean \pm SD	mean \pm SD
Muscles	0.003 \pm 0.001	0.041 \pm 0.008	0.001 \pm 0.000	0.004 \pm 0.002	0.002 \pm 0.001
Kidney	0.110 \pm 0.012	0.006 \pm 0.011	0.054 \pm 0.009	0.022 \pm 0.009	0.145 \pm 0.038
Liver	0.135 \pm 0.048	0.051 \pm 0.005	0.021 \pm 0.010	0.125 \pm 0.018	0.098 \pm 0.015
Gills	0.251 \pm 0.074	0.210 \pm 0.011	0.007 \pm 0.004	0.254 \pm 0.045	0.185 \pm 0.045

TABLE 5

Concentrations (mean \pm SD) of zinc ($\mu\text{g g}^{-1}$ d.w.) in organs of roach caught in the lower reaches of the Oder River

Tissues	Area				
	WG2	ZK3	RD4	JW7	ZP8
	mean \pm SD	mean \pm SD	mean \pm SD	mean \pm SD	mean \pm SD
Muscles	21.8 \pm 5.2	8.1 \pm 1.2	5.8 \pm 1.1	10.1 \pm 2.2	7.5 \pm 2.0
Kidney	350.8 \pm 25.1	251.3 \pm 74.2	202.5 \pm 45.0	264.1 \pm 87.5	175.5 \pm 74.2
Liver	140.1 \pm 54.5	25.9 \pm 7.8	38.4 \pm 5.7	59.5 \pm 8.1	42.5 \pm 8.3
Gills	384.1 \pm 58.8	48.1 \pm 11.1	87.5 \pm 8.1	147.8 \pm 14.1	65.5 \pm 9.1

TABLE 6

Concentrations (mean \pm SD) of copper ($\mu\text{g g}^{-1}$ d.w.) in organs of roach caught in the lower reaches of the Oder River

Tissues	Area				
	WG2	ZK3	RD4	JW7	ZP8
	mean \pm SD	mean \pm SD	mean \pm SD	mean \pm SD	mean \pm SD
Muscles	2.38 \pm 0.92	0.37 \pm 0.02	0.14 \pm 0.03	0.42 \pm 0.07	0.32 \pm 0.12
Kidney	1.48 \pm 0.15	1.15 \pm 0.42	1.12 \pm 0.24	2.32 \pm 0.35	0.75 \pm 0.24
Liver	30.21 \pm 3.45	3.19 \pm 0.48	7.54 \pm 1.40	7.25 \pm 0.93	6.97 \pm 0.87
Gills	0.81 \pm 0.34	0.78 \pm 0.91	0.25 \pm 0.24	0.88 \pm 0.42	0.58 \pm 0.18

TABLE 7

Correlation between Cd, Pb, Zn and Cu concentrations in sediments and roach tissues

Sediments concentration of element in		Kidney	Muscle	Gills	Liver
Cd	Exchangeable fraction	-0.619*	-0.452*	-0.482*	-0.493*
	Carbonate fraction	-0.120	0.426*	-0.035	0.357*
	Total concentration	-0.424*	-0.428*	-0.503*	-0.564*
Pb	Exchangeable fraction	-0.097	-0.709*	-0.206	-0.277
	Carbonate fraction	-0.140	-0.520*	-0.162	-0.384*
	Total concentration	0.201	-0.595*	0.014	0.022
Zn	Exchangeable fraction	0.367*	0.434*	0.626*	0.569*
	Carbonate fraction	0.423*	0.468*	0.597*	0.504*
	Total concentration	0.433*	0.421*	0.513*	0.404*
Cu	Exchangeable fraction	-	-	-	-
	Carbonate fraction	0.663*	0.184	0.227	0.226
	Total concentration	-0.176	0.656*	-0.044	0.742*

(-) The concentration of Cu in this fraction was below the detection limit/lack of data to conduct statistical analysis

* significant correlation $P \leq 0.05$

Correlation coefficients obtained in the studies show mutual relations between the concentrations of heavy metals in sediments and in fish (Table 7). Cadmium concentrations in roach kidneys, muscles, gills, and livers were correlated with its concentration in the exchangeable fraction, and with its total concentration in sediments, whereas cadmium concentrations in roach muscles and liver also correlated with its carbonated fraction of sediments. Statistically significant correlation coefficients were also revealed for relationships between lead concentration in fish muscles and lead concentrations in all analyzed fractions of sediments. Lead concentration in livers was correlated with its concentrations in the carbonated fraction of sediments. Statistically significant correlation coefficients between zinc concentration in kidneys, muscles, gills, and livers, and its concentrations in all analyzed fractions of sediments were observed. Statistically significant correlation coefficients were also recorded for copper. Correlations were found between copper concentrations in roach kidneys and in the carbonated fraction of sediments, as well as between its concentrations in roach muscles and livers and total concentrations in sediments. Correlation coefficients for lead and cadmium had negative values, whereas for zinc and copper the values were positive.

DISCUSSION

Heavy metals are inorganic contaminants widespread in the aquatic environment. Water pollution results in contamination of aquatic organisms and bottom sediments (Frenet 1981, Migula 1993, Świdorska-Bróz 1993, Dojlido 1995). Regarding the risk of elevated metal amounts to organisms, much attention is paid to cadmium, lead, zinc, and copper. Metal concentrations in sediments can be influenced by variations in sediment texture, composition of sediment, reduction/oxidation reactions, and adsorption/desorption processes (Luoma et al. 1997).

With regard to the results obtained in the present study, it must be taken into account that the bioavailability of trace metals is influenced by the physiological and ecological properties of organisms, the form of dissolved trace elements, the chemical and physical properties of the water, and the trace metal speciation in sediments (Jenne and Luoma 1977). Each element has specific properties which determine its behavior in the environment. Depending on the physico-chemical conditions of the environment, the element may be present in various chemical forms (Van Leeuwen 1999, Lee et al. 2000, O'Day et al. 2000).

Entering the aquatic environment, a majority of metals becomes bound to sediments, as a result of physicochemical and biological equilibriums and they settle relatively quickly (Szefer and Szefer 1991, Pempkowiak and Szefer 1992). Only a part of the metals present in river sediments can participate in short-term chemical processes and are bioavailable (Salomons and Förstner 1984). In suitable conditions, this heavy metal fraction may undergo quick desorption (Förstner et al. 1986, Szponar 1991, Luoma et al. 1997).

Numerous studies have been conducted on relationships between a chemical ability to release metals from solids and their uptake by biota, e.g. exchangeable metal fractions dissolved in water are frequently regarded as directly available for plants (Kurek et al. 1998). Having entered an organism, metals are not distributed equally, but accumulate in particular organs, which was confirmed by the present research. In fish, metals accumulate mainly in kidneys, liver, intestinal epithelium, and, to a lesser extent, in other organs as well (Protasowicki 1989, Migula 1991). Heavy metals are also supposed to be bound by the surface of gills, affecting the proper functioning of the organ (Wagh et al. 1985, Morsy and Protasowicki 1990).

Metals dissolved in water (Me^{2+} , inorganic compounds, and low molecular organic compounds) are absorbed via diffusion, active transport, and facilitated transport through gills and gastrointestinal tracts, whereas forms connected with ligands i.e. bound metals, suspensions, detritus, metal oxides, are absorbed through endocytosis (Migula 1991). In general, respiratory and gastrointestinal tracts, as well as skin, are the main paths of metal uptake by aquatic organisms. However, absorption via the gastrointestinal tract and skin is significantly limited. Heavy metals in free-ionic forms are hardly absorbed from the gastrointestinal tract, whereas their organic compounds are absorbed completely (Hall et al. 1997).

The content of the elements in a particular fish organ depends on their distribution pattern in the organism, and on the role the organ plays in the processes of their absorption and elimination. This regularity was reflected in the current results. The highest concentration of cadmium was observed in kidneys, being target organs in fish and other vertebrates. Relatively high concentrations of cadmium in gills suggested that this element was absorbed by the respiratory system and accumulated in kidneys as metallothionein. Metallothioneins bind metals such as zinc, copper, mercury, cadmium, and silver. The proteins are responsible for maintaining a balance between copper and zinc concentrations, and protect the organism from the toxic effect of cadmium and mercury, which are inhibitors of metallothioneins.

Metal distribution in fish depends on the metal properties and physicochemical factors. It is known, that the effects of toxicants on organisms depend on their concentration, dose, duration of exposure, and route of exposure. The rate of their transformation and elimination is essential for the biological effects they induce. In the initial stage of distribution, the main role is played by the minute heart volume, which conditions the rate of the distribution of the substance in the organism, and the velocity of blood flow through the organs. During the first several minutes post-absorption, the largest amount of the substance reaches the heart, liver, and kidney. Toxic effect is a result of mutual interactions of three factors: the organism, the toxicant, and the external environment. During both intoxication and detoxification, substances are transferred throughout the fish. In studies on fish intoxication with a sublethal cadmium dose ($10 \mu\text{g kg}^{-1}$ body weight), Brucka-Jastrzębska and Protasowicki (2004a) observed diverse cadmium concentrations in various organs of carp, decreasing in the order: kidney > liver > skin > gills > mid-posterior part of alimentary tract > anterior part of alimentary tract > muscles.

Cadmium concentration in roach muscle was relatively low, except for the fish from the Pomeranian Bay (ZP8), where the concentrations were significantly higher. This may indicate local, temporary contamination of waters with this metal. At the same time, cadmium concentration in fish muscles was higher than in kidneys. These observations support suggestions that, in this case, excretion of the metal from fish organisms was slower than its accumulation. Apart from a target tissue, affected by a toxic substance, there are also places responsible for its absorption, metabolic activation and detoxification, and elimination. The research of Brucka-Jastrzębska and Protasowicki (2004a, b), on cadmium and nickel toxicity to carp, revealed that sublethal doses of these metals produced no detectable toxic effects. However, following cadmium or nickel intoxication, a decline in fish activity occurred, resulting probably from shock, and from the processes of distribution and accumulation of cadmium and nickel in the organism. Such reactions, occurring during acute metal poisoning, were also reported by Prost (1994). According to Rice and Harrison (1978), the decline in metabolic activity of an organism, resulting from metal accumulation in tissues, also contributes to a decrease in the metabolic rate of muscle cells. This may occur because of a decline in metabolic energy, which is necessary for enzymatic processes accompanying detoxification. Brucka-Jastrzębska and Protasowicki (2004a) report that intraperitoneal cadmium intoxication of carp induced an increase of metabolic rate within the organs responsible for detoxification (kidney and liver), simultaneously reducing the energetic expenses in the other organs. Also Heath (1990) informs that exposure to cadmium increased oxygen demand of *in vitro* cultured liver and gill cells.

The extent of accumulation and elimination of metals from various organs is diverse. In the study by Sreedevi et al. (1992) a 4-day exposure of carp to nickel aquatic solutions of concentrations from 20 to 70 mg dm⁻³, resulted in the highest accumulation of the element in the gills, and the lowest in the liver, muscles, and kidney. *Clarias batrachus* (L.) exposed to nickel for 4 days, absorbed most of the metal in the kidney > liver > gills > intestines (Ray et al. 1990). Bream, *Abramis brama* (L.), from the Vistula River accumulated mercury mostly in the liver, intestines, heart, and gills (Kołacz et al. 1996). European catfish accumulated mercury and lead mainly in the liver and gonads (Svobodova et al. 1997). Windom et al. (1987) suggest that the extent of metal accumulation in the muscles is influenced significantly by the size and

age of fish, as well as by the degree of toxicity of chemicals affecting the organism. In the current study the highest cadmium concentrations were found in the kidneys, gills, muscles, and livers of roach caught in the Pomeranian Bay (ZP8).

The highest lead concentrations in fish were found in the gills, which indicates that the element was absorbed via the respiratory tract. High lead concentrations were also reported in the kidneys and livers. The fact that lead concentrations were higher in the muscles than in the kidneys, may lead to the conclusion that accumulation was overbalanced by detoxification. In the examined roach, the highest copper concentrations were detected in the liver, where it is stored. It was also observed that the level of copper concentration in fish livers and muscles was influenced by the catch site. Zinc, similarly to copper, is an essential element for living organisms; yet numerous studies have proved that fish are very sensitive to zinc compounds (Atchinson et al. 1987). Fish absorb zinc compounds mainly via the gastrointestinal tract, and the liver is an accumulating organ. In the present study, the highest zinc concentrations were observed in the kidneys. Based on the correlation coefficients calculated (Table 7), some relationships between heavy metal concentrations in fish organs and sediments have been demonstrated. Correlation coefficients, calculated for relations between concentrations of metals in analyzed fish organs and their concentrations in the exchangeable and carbonate fractions of bottom sediments, are considered particularly relevant.

The highest correlation coefficient, obtained for cadmium in roach kidneys and the sediment fraction I, was negative and statistically significant. The relationship was so clearly seen, because the kidneys are the main organs where cadmium is accumulated. The kidneys specialize in the elimination of toxicants from the organism, and renal dysfunctions decrease the blood purification rate. In the case of heavy metals, processes of redistribution also occur, slowing down metal excretion. The biological half-life of cadmium ranges from several months to several years, depending on the type of exposure. During the process of distribution to tissues, metals either bind to tissue proteins, or are further transported to cells. Having reached the liver, cadmium binds to thiol groups in metallothionein, and in this form is excreted with body fluids from the organism. Stimulation of metallothionein synthesis, which is involved in detoxification, reduces concentrations of chemicals circulating in the fish. Each toxicant is simultaneously present in both central and tissue compartments in two

fractions – bound to protein (the inactive fraction) and unbound (the free – active fraction). The substances bound to serum proteins may undergo processes of biotransformation and tubular excretion in kidneys. Much research demonstrates that amounts of metals accumulated in the organisms of freshwater and marine fish are very diverse (Protasowicki 1989, 1991, Sharif et al. 1991, Brucka-Jastrzębska and Protasowicki 2004a).

The negative correlation coefficient, calculated for relationships between cadmium concentrations in roach gills and in the exchangeable fraction of sediments, also turned out to be statistically significant. Similarly, cadmium concentrations in fish gills correlated negatively with its total concentrations in sediments. Cadmium bioavailability is related to the presence of its soluble forms. It must be remembered that sediment and water compositions are mutually dependent and undergo constant changes. Cadmium usually remains briefly in water, because it easily precipitates as carbonates, or adsorbs on suspension and bottom sediments. Therefore an increase in cadmium concentration in sediments would be accompanied by a decrease in its concentration in water (unless pollutants are introduced), resulting in a reduction of this biohazard for living organisms. However, it must be remembered that, in favorable conditions, cadmium may be desorbed from sediments (Alabaster 1980, Salomons and Förstner 1984).

Another element which revealed statistically significant correlation coefficients was lead. Significant negative correlations were observed between lead concentrations in roach muscles and in exchangeable or carbonated fractions of sediments, as well as the total concentration of lead in sediments. This surprising phenomenon may be explained in the same way as in the case of cadmium. Additionally, it is well known that in the case of a deficiency of dissolved complex compounds (and at pH > 6.0 lead is completely adsorbed in sediments), its bioavailability is minimal, and it does not pose a serious direct hazard to fish.

Relationships between zinc concentrations in fish organs and sediments from the areas where the fish were caught were statistically significant in all cases. Positive, statistically significant correlation coefficients occurred between copper concentrations in fish kidneys and in the carbonated fraction of sediments, as well as between concentrations of copper and zinc in fish tissues and sediments.

A majority of fish organs from polluted areas were characterized by an increased content of zinc and copper, if compared to fish from less contaminated areas. Industrial sewage and substances applied in agricultural production are the main sources of water contamination with copper (Kabata-Pendias and Pendias 1999). In the case of the lower reaches of the Oder River, contaminants also inflow from the upper reaches of the river, from the vicinity of Głogów (Copper Smelting-Mining Combine). When the maximum saturation of sediments with copper occurs and its concentration in water is still increasing, the amount of its bioavailable forms also increases. The bioavailability of metals is also significantly dependent on water hardness, because, in hard waters, copper precipitates as insoluble, hardly available carbonates and hydroxides (Alabaster 1980). High copper concentrations in fish livers observed during the present research can be explained logically by the fact that copper is a component of many enzymes and easily forms bindings between various proteins, especially between low-molecular weight proteins containing significant amounts of the thiol groups (Kabata-Pendias and Pendias 1999). An example of such a protein is metallothionein, which has a great capacity to bind copper and other metals (Olsson and Houx 1986). To explain these phenomena, detailed studies are necessary which would include many factors and changes occurring in the environment at a given time. It would also be important to investigate absorption, metabolism, and excretion of a given xenobiotic from a fish body.

Sediment can be considered as a heterogeneous mixture of dissimilar particles. Solid phases, interacting with dissolved constituents in natural waters, consist of a variety of components including clay minerals, carbonates, quartz, feldspar, and organic solids (Calmano et al. 1990). Organic surfaces adsorbing metals may be formed from organisms such as bacteria and algae, through the dying of plant and animal material, through aggregation of organic compounds of low molecular weight, and through sorption of organic compounds of low molecular weight to clay substrates and metal oxides (Davis and Gloor 1981).

Metals can be bound to sediments in several ways. They can adsorb on the surface of suspensions, associate with carbonates, bind to iron and manganese oxides, form insoluble sulfides (amorphous or crystalline), accumulate in living and inanimate organic matter, or be built in the crystalline structure of aluminosilicates (Tessier et al. 1979). In river sediments, metals are mainly bound to clay minerals, carbonates,

feldspar, and organic substances. Relatively high amounts of metals are associated with clay minerals and heavy minerals (Helios-Rybicka 1986, Helios-Rybicka and Kyzioł 1991). Contaminants, including metals, are accumulated in sediments continuously. The dating of sediments and analysis of metal concentrations make possible an estimation of the period when their accumulation rate increased (Pempkowiak and Ciszewski 1990, Sobczyński et al. 1996).

The evaluation of the influence of physicochemical conditions in the aquatic environment on the level of metal accumulation in sediments and fish from analyzed areas is complex and, therefore, difficult. Certainly in 1998, and maybe even in 1999, as a consequence of a catastrophic flood in 1997, the waters of the Oder River carried large amounts of contaminants including heavy metals. However constant self-purification processes, due to outwashing the sediment fine-grained fraction, probably reduced the primary level of contamination by the year 2000. Time and the course of self-purification processes were influenced by the conditions in the lower reaches of the Oder River. These processes could also be the reason why direct correlations between concentrations of metals in fish tissues and sediments were difficult to observe. It must be highlighted that the correlations obtained in the studies apply only to a particular area and a given period of time, and may change because of various external factors.

The results do not provide data on the direct influence of contaminations deposited in sediments, but may indirectly provide information about e.g. the velocity of self-purification processes, or the progress of self-purification during the period of the study. Observed correlations cannot be direct because metals deposited in sediments are not available for the aquatic organisms until they are released and transferred to the solution, due to changes in environmental conditions.

REFERENCES

- Alabaster J.S. 1980 – Water quality criteria for freshwater fish – Butterworths, London.
- Atchison G.J., Henry M.G., Sandheinrich M.B. 1987 – Effects of metals on fish behaviour: a review – Environ. Biol. Fish. 18: 11-25.
- Brucka-Jastrzębska E., Protasowicki M. 2004a – Elimination dynamics of cadmium, administered by a single intraperitoneal injection in common carp *Cyprinus carpio* L. – Acta Ichthyol. Piscat. 34: 167-180.
- Brucka-Jastrzębska E., Protasowicki M. 2004b – Elimination dynamics of nickel, administered by a single intraperitoneal injection in common carp *Cyprinus carpio* L. – Acta Ichthyol. Piscat. 34: 181-192.

- Calmano W., Förstner U. 1982 – Chemical extraction of heavy metals in polluted river sediments in Central Europe – *Sci. Tot. Environ* 28: 77-90.
- Davis J.A., Gloor R. 1981 – Adsorption of dissolved organics in lake water environments by aluminium oxide: Effect of molecular weight – *Environ. Sci. Technol.* 15: 1223-1227.
- Dojlido J.R. 1995 – The chemistry of surface waters – *Wyd. Ekonomia i Środowisko, Białystok*, 342 p. (in Polish)
- Förstner U., Ahlf W., Calmano W., Kersten M., Salomons W. 1986 – Mobility of heavy metals in dredged harbor sediments – In: *Sediments and Water Interactions* (Ed.) P.G. Sly, Springer, New York: 311-380.
- Frenet M. 1981 – The distribution of mercury, cadmium and lead between water and suspended matter in Loire estuary as a function of hydrological regime – *Wat. Res.* 15: 1343-1350.
- Głazewski R. 1991 – Chemical forms of Zn, Pb, and Cu in superficial sediments of Długie Lake in Olsztyn – In: *Toxic substances in the environment* (Eds.) A. Smoczyńska, Z. Drabent, L. Smoczyński, University of Technology and Agriculture, Olsztyn: 11-17 (in Polish).
- Hall B.D., Bodaly R.A., Fudge R.J.P., Rudd J.W.M., Rosenberg D.M. 1997 – Food as the dominant pathway of methylmercury uptake by fish – *Water Air Soil Pollut.* 100: 13-24.
- Heath A. G. 1990 – *Water pollution and fish physiology* – CRC Press Boca Raton Ann Arbor, Boston.
- Helios-Rybicka E. 1986 – The role of minerals and loamy rocks in binding heavy metals in river sediments of the Upper Vistula – *Zesz. Nauk. AGH, Geologia* 32, Kraków, 122 p. (in Polish).
- Helios-Rybicka E. 1992 – Heavy metal partitioning in polluted river and sea sediments: clay minerals effects – *Miner Petrogr. Acta* 35-A: 297-305.
- Helios-Rybicka E., Kyzioł J. 1991 – The role of minerals and the clay rocks in bond of heavy metals in water environment – *Zesz. Nauk. AGH, Sozologia i Sozotechnika* 31: 45-67.
- Jenne E.A., Luoma S.N. 1977 – Form of trace elements in solis, sediments, and associated waters: an overview of their determination and biological availability – In: *Biological implications of metals in the environment* (Eds.) H. Drucker, R.E. Wildung, Conf-750929 National Technical Information Service, Springfield, Virginia: 110-143.
- Kabata-Pendias A., Pendias H. 1999 – *The biogeochemistry of trace elements* – *Wyd. Nauk. PWN, Warszawa* (in Polish).
- Kończak R., Dobrzański Z., Bodak E. 1996 – The bioaccumulation of Cd, Pb, and Hg in animal tissue – *Med. Weter.* 52: 686-692 (in Polish).
- Kurek E., Suchonek W., Słomka A., Jaroszu J. 1998 – Bioavailability of Cd and Zn contained in sewage sludge – In: *Proc. of 2nd International Conference Trace Elements Effects on Organisms and Environment*. (Eds.) P. Migula, B. Doleżyn, M. Nakonieczny – Cieszyn 23-26 June 1998, Katowice: 47-51.
- Lee B.G., Lee J.S., Luoma S.N., Choi H.J., Koh Ch.H. 2000 – Influence of acid volatile sulfide and metal concentrations on metal bioavailability to marine invertebrates in contaminated sediments – *Environ. Sci. Technol.* 34: 4517-4523.
- Luoma S.N., Hornberger M., Cain D.J., Brown C., Lee B.-G., Axtmann E.V. 1997 – Fate, bioavailability and effects of metals in rivers and estuaries: Role of sediments – *Proc. of the U.S. Geological Survey (USGS) Sediment Workshop, February*, 4-7.
- Maiz L., Esnaola M.V., Milan E. 1997 – Evaluation of heavy metal availability in contaminated soils by a short sequential extraction procedure – *Sci. Total Environ.* 206: 107-115.
- Migula P. 1991 – Strategies of adaptation by invertebrates to environments polluted with heavy metals – *Biotechnologia* 3-4: 49-62 (in Polish).
- Migula P. 1993 – When heavy metals are harmful – *Biblioteczka Fundacji Ekologicznej „Silesia“*, Katowice (in Polish).

- Miller P.A., Munkittrick K.R., Dixon D.G. 1992 – Relationship between concentration of copper and zinc in water, sediment, benthic invertebrates, and tissues of white sucker (*Catostomus commersoni*) at metal-contaminated sites – Can. J. Fish. Aquat. Sci. 49: 978-984.
- Morsy G., Protasowicki M. 1990 – Cadmium bioaccumulation and its effects on some hematological and histological aspects in carp, *Cyprinus carpio* L. at selected temperatures – Acta Ichthyol. Piscat. 20: 105-116.
- O'Day P.A., Caroll S.A., Randall S., Martinelli R.E., Anderson S.L., Jelinski J., Knezovich J.P. 2000 – Metal speciation and bioavailability in contaminated estuary sediments, Alameda Naval Air Station, California – Environ. Sci. Technol. 34: 3665-3673.
- Olsson P.E., Haux C. 1986 – Increased hepatic methallothionein content correlates to cadmium accumulation in environmentally exposed perch (*Perca fluviatilis*) – Aquat. Toxicol. 9: 231-242.
- Pempkowiak J., Ciszewski P. 1990 – The concentration of selected heavy metals in the water and bottom sediments of the Bay of Puck – Arch. Ochr. Środ. 1-2: 153-163 (in Polish).
- Pempkowiak J., Szefer P. 1992 – Concentration, origin and sources of heavy metals in the Southern Baltic – Bull. Sea Fish. Inst. 1(125): 29-32.
- Prost M. 1994 – Fish diseases – Polskie Towarzystwo Nauk Weterynaryjnych, Wydanie III, Lublin 551 p. (in Polish).
- Protasowicki M. 1989 – The bioaccumulation of cadmium in selected organs of the carp (*Cyprinus carpio* L.) in the case of various means of intoxication – Symp. Biochemia stosowana w naukach rolniczych, Szczecin (in Polish).
- Protasowicki M. 1991 – The distribution of magnesium in fish organs and its dysfunction in conditions of cadmium poisoning. Magnesium in the biological environment – Materiały konferencji PTMag., Szczecin: 24-26 (in Polish).
- Quevauviller Ph., Rauret G., Lopez-Sanchez J.F., Rubio R., Ure A., Muntau H. 1997 – Certification of trace metal extractable contents in a sediment reference material (CRM 601) following a three-step sequential extraction procedure – Sci. Total Environ. 205: 223-234.
- Ray D., Banerjee K., Chatterjee M. 1990 – Bioaccumulation of nickel and vanadium in tissues of the Catfish *claris batrachus* – J. Inorg. Biochem. 38: 169-173.
- Rice D.W., Harrison F.L. 1978 – Copper sensitivity of pacific herring, *Clupea harengus pallasi*, during its early life history – Fish Bull 76: 347-356.
- Salomons W., Förstner U. 1984 – Metals in the hydrocycle – Springer-Verlag, Berlin.
- Sharif A.K., Mustafa A.L.I., Amin M.N., Safiullah S. 1991 – Trace element concentrations in tropical marine fish from the Bay of Bengal – Sci. Total Environ. 138: 223-234.
- Singh S.P., Tack F.M.G., Verloo M. 1996 – Extractability and bioavailability of heavy metals in dredged sediment derived surface soils – Chem. Spec. Biol. 8: 105-110.
- Sobczyński T., Zerbe J., Elbanowska H., Sajewska K., Siepak J. 1996 – The chemical examination of bottom sediments of lakes in the National Park of Wielkopolska, from the point of view of anthropogenic stress – Ekol. Tech. 4 (5/6): 17-22 (in Polish).
- Sreedevi P., Sivaramakrishna B., Suresh A., Radhakrishnaiah K. 1992 – Effect of nickel on some aspects of the gill and kidney of the freshwater fish, *Cyprinus carpio* L. – Environ. Pollut. 77: 59-63.
- Svobodova Z., Groch L., Flajshans M., Vykusova B., Machova J. 1997 – The effect of longterm therapeutic bath of malachite green on common carp (*Cyprinus carpio* L.) – Acta Vet. Brno 66: 111-117.
- Świdarska-Bróz M. 1993 – Micro-pollution in a water environment – Politechnika Wroclawska, Wroclaw (in Polish).
- Szefer P., Szefer K. 1991 – Concentration and discrimination factors for Cd, Pb, Zn and Cu in benthos of Puck Bay, Baltic sea – Sci. Tot. Environ. 5: 127-133.

- Szponar Z. 1991 – The mechanism and kinetics of the sorption of copper (II), zinc (II), cadmium (II), and lead (II) on the granulometric fractions of the bottom sediment of the Gdańsk Deep – In: Toxic substances in the environment (Eds.) A. Smoczyńska, Z. Drabent, L. Smoczyński, University of Technology and Agriculture, Olsztyn: 63-65 (in Polish).
- Tack F., Vossius H., Verloo M. 1996 – A comparison between sediment metal fractions obtained from sequential extraction and estimated from single extractions – Intern. J. Environ. Anal. Chem. 63: 61-66.
- Tessier A., Campbell P., Bisson M. 1979 – Sequential extraction procedure for the speciation of particulate trace metals – Anal. Chem. 51: 844-851.
- Van Leeuwen H.P. 1999 – Metal speciation dynamics and bioavailability: inert and labile complexes – Environ. Sci. Technol. 33: 3743-3748.
- Wagh S.B., Shareef K., Shaikh S. 1985 – Acute toxicity of cadmium sulphate, zinc sulphate, and copper sulphate to *Barbus ticto*. Effects on oxygen consumption and gill histology – J. Environ. Biol. 16: 287-293.
- Windom H., Stein D., Sheldon R., Smith J.R. 1987 – Comparison of trace metal concentrations in muscle tissue of a benthopelagic fish (*Coryphaenoides armatus*) from the Atlantic and Pacific Ocean – Deep-Sea Research 34: 213-220.

Received – 24 September 2007

Accepted – 04 April 2008

STRESZCZENIE

STĘŻENIA Cd, Pb, Zn, Cu U PŁOCI, *RUTILUS RUTILUS* (L), POZYSKANYCH Z DOLNEGO ODCINKA ODRY, I ICH KORELACJE ZE STĘŻENIAMI METALI CIĘŻKICH W OSADACH DENNYCH Z TYCH SAMYCH OBSZARÓW

Celem badań było określenie relacji pomiędzy stężeniami metali ciężkich w osadach dennych a ich stężeniami w wybranych organach płoci, *Rutilus rutilus* (L.). Materiał badawczy stanowiły tkanki nerek, wątroby, skrzel i mięśni płoci złowionych w wybranych rejonach rzeki Odry (rys. 1).

Stwierdzono znaczne zróżnicowanie koncentracji metali ciężkich na analizowanych stanowiskach (tab. 2). Koncentracje metali ciężkich w osadach dennych w dolnym odcinku Odry były największe, a w rejonie Jeziora Wrzosowskiego najmniejsze. Otrzymane wyniki wskazują na zróżnicowanie w kumulacji metali ciężkich w zależności od narządu i miejsca żerowania ryb (tab. 3-6). Największą zawartość kadmu stwierdzono u płoci złowionych w Zatoce Pomorskiej, a ołowiu, cynku i miedzi u ryb pochodzących z dolnej Odry. Największe koncentracje ołowiu notowano w skrzelach, kadmu i cynku w nerkach, natomiast miedzi w wątrobie. Stwierdzono istotne zależności między stężeniami wybranych metali w rybach a ich stężeniem w osadach dennych (tab. 7).