

Baltic Coastal Zone No. 11	
(83-101) 2007	Institute of Biology and Environmental Protection Pomeranian Academy Słupsk

HEAVY METALS MIGRATION IN THE SYSTEM: NEAR-BOTTOM WATER – INTERSTITIAL WATER – BOTTOM SEDIMENT IN GARDNO LAKE

Jan Trojanowski, Czesława Trojanowska, Czesław Jańczak

*Department of Environmental Chemistry, Pomeranian Academy,
ul. Arciszewskiego 22b, 76-200 Słupsk, Poland
e-mail: trojanowski@pap.edu.pl*

Abstract

The study of heavy metals concentration in the estuarine lake Gardno water and bottom sediments showed that the river Łupawa and periodic inputs of sea water exert decisive influence on forming of the water stores and bottom sediments quality in this lake. The largest concentrations of Cd, Cu, Mn, Pb and Zn were observed at river mouth into the lake region (Cd – 0.26, Cu – 3.71, Mn – 94.3, Pb – 10.01, Zn – 16.26 $\mu\text{g dm}^{-3}$) and the lowest at water outflow from the lake region (Cd – 0.13, Cu – 1.81, Mn – 53.8, Pb – 8.86, Zn – 8.05 $\mu\text{g dm}^{-3}$). Average concentrations of those metals in the lake water, suspension and bottom sediment form the following row: Mn>Zn>Pb>Cu>Cd. The contents of analysed metals were the highest in interstitial water, smaller in near-bottom water and the smallest in surface water. Average content of metals in near-bottom suspension was about 30% higher than that in surface suspension, but enrichment factors of those metals in suspensions do not show essential statistic differences. This probably results from continual mixing of water masses by wind. The migration coefficients indicated that bottom sediments of lake Gardno have large accumulation properties of heavy metals.

Key words: Heavy metals, near-bottom water, interstitial water, bottom sediment, lake

INTRODUCTION

Heavy metals are one of the most important factors among many others in biosphere pollution. Great interest for heavy metals results mainly from the serious dangers which are created by the present increase of their quantities. After exceeding a definite barrier of their concentration they start to act inhibitedly or quite toxicly on growth and metabolic processes of animal and plant organisms (Lampert and Sommer 1996, Schintu et al. 1989, Starmach et al. 1996, Pawlik-Skowrońska 2001). According to Kostecki (2000) and Tamura et al. (2001) higher concentration of heavy metals become inhibitor of biological processes such as organic carbon oxidation, nitrification and denitrification.

They finally get to the water environment in their biogeochemical cycles. Total heavy metal content in polluted water is composed of water soluble species. Metals quantity, lifted species heavy metals ions by suspension and those precipitated into bottom sediment. Those contents depend on some details of physico-chemical properties of natural waters (eg. redox potential, hardness of water) and specific given metals properties (Borg 1983, Förstner and Wittmann 1985, Abou-Mesalam 2002) and in some cases even on biological activity of algae (Golimowski et al. 1990, Widianarko et al. 2000). The first part of metal's ions is adsorbed by suspension form. The second part appears in water soluble form. It contains both simple ions and complex ions with organic and inorganic ligands. The third part appears in colloidal form. The humus compounds play essential role for heavy metals migration (Tao et al. 2003). Their functional groups carboxylic, keton, amine, fenolic and thiolic bind metal ions into organic complexes and chelates (Sposito 1986). Benes and coworkers (1976) showed that humus substances remove copper, zinc, cobalt and mercury ions from water space. Contents of soluble metals in water make frequently little percentage of their total contents in suspended matter and bottom sediments (Fytianos et al. 1986, Marsden and Rainbow 2004). Considerable part of those metals transfers to bottom sediments. Higher levels of those metals are observed in bottom sediments and suspensions. Their levels in the water soluble form are lower. Some quantities of them can be moved again from sediments into the water by bottom microorganisms, plants and fauna (Benes et al. 1982, Marsden and Rainbow 2004). Metal accumulation into sediments coexists with the leaching process of metal ions process from deposited metals in bottom sediment to interstitial water existing between sediment pores and demersal-bottom water.

The aim of our research has been:

- determination of five heavy metals accumulation in bottom sediment, suspension, surface and demersal water of coastal area of the Gardno Lake;
- discovery of studied metals origin in water, suspension and bottom sediments of lakes ecosystem;
- determination of directions of those metals' flow between the analysed forms.

RESEARCH REGION

The Gardno Lake is the second as regards largeness in relation to area (2468.1 ha) of coastal lake in Poland. It is situated in the Słowiński seaside region in the central part of the Polish coast. The lake belongs to polymictic lakes which do not have great depth (Trojanowski 2003). Average depth equals 1.3 m and maximum depth is 2.6 m. Gardno lake is separated from shore of Baltic Sea by 0.8-2.0 km of sandy land band forming spit with different hills of sandy moraine covered by pine forests. Swamps, marshes and peat bogs surround the lake from south-west and east site. The lake largest water affluent is the Łupawa River. It delivers 81% of the water quantity to the lake during a year (Cyberski and Jędrasik 2003). It flows from the east site of the lake. Only a small difference of water level between the Gardno lake and Baltic Sea which amounts to about 24 cm is usually observed. This facilitates dou-

ble-sited water replacement between lake and sea rather than the short river mouth to the Baltic Sea. Total water masses in the Gardno Lake exchange average 9.2 times during the year.

The bottom of the lake is almost flat and covered by large quantities of shudges and sediments. Only small areas of the bottom have hard ground of sandy lake. So it is mainly in the north-east region of the lake and also quite near Kamienna island in the centre of the lake. Other small rivers such as: Bagiennica, Grabownica and Broda flow into the Gardno Lake as well. The lake is joined with greater Łebsko Lake of about 8 km long channel from its north-east side.

MATERIALS AND METHODS

Water samples used for our research were taken once a month during 2002-2003 using special Ruttner sampler from three chosen areas of the Gardno Lake and from the Łupawa River 200 m before its mouth to this lake (Fig. 1). Collected water samples from the surface and demersal layer of water were brought into polyethylene bottles. At laboratory water samples were filtered using Milipore membrane (0.40 μm diameter pores). Bottom sediment samples were taken carefully using Kajak sampler in three seasons of 2001 (in April, July and October) from selected areas. Bottom sediments were divided into 5 cm layers and kept at low temperature.

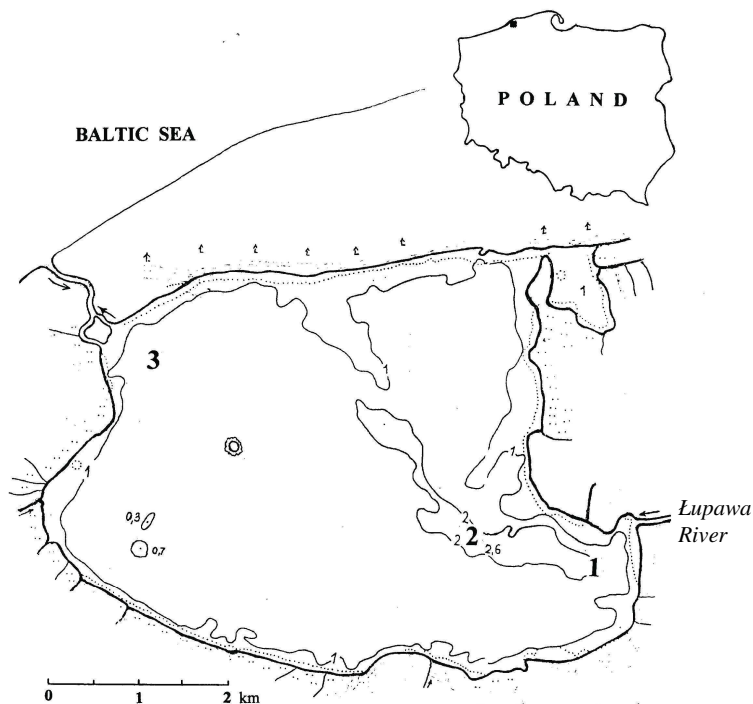


Fig. 1. Location of sampling stations in the lake Gardno and river Łupawa

Interstitial water samples were separated by filtration of fresh sediment samples by mill net and preserved in frozen state at -10°C during a maximum period of months in order to make all chemical analyses. On the contrary suspensions were separated from water by filtration through hard paper filter. Such separated suspensions were dried at $+60^{\circ}\text{C}$ on paper filters to constant mass and stored in exsiccator. Total suspension contents were determined by gravimetric methods.

Atmospheric falls were collected in suitable containers. They were emptied with frequency once a month.

Bottom sediment samples were dried at room temperature and afterwards at 105°C to constant mass. Well dried sediment samples were crushed and chemically analysed.

The approximate value of organic matter was determined as a loss of mass after ignition. Before ignition at 550°C , samples of suspensions and sediments were weighed. The content of iron, organic carbon and silica in sediments were carried out according to Januszkiewicz (1978) method. Iron was determined using a complexometric method applying orto-phenantrolin reagent. Organic carbon – by the dichromate method. Silica and undissolved residue in sediments were determined by application of mixture of nitric (V) and hydrochloric acids by 3:1 proportion.

Heavy metals analyses in water samples water and suspension were carried out according to Neugebauer and Bolafek method (1984). Water samples were concentrated ten times by evaporation before chemical analysis. The content of heavy metals was determined by wet mineralization of studied samples in the mixture of nitric (V) and perchloric (VII) acids. The dry residue, after evaporation of water, was dissolved in 10 cm^3 of 0.1 M HCl solution. Cadmium, manganese, zinc, lead and copper concentrations were determined from such prepared solution by flame technique of atomic absorption spectrometry. The wave length, slot width, current intensity of lamp and other parameters were adjusted in each case according to manufacturers recommendations. For the control version activity of apparatus were applied two reference materials SCP Science EnviroMAT™ & AgroMAT™ ES-H-1 Ground Water and EU-H-1 Waste Water [39]. Was also applied the research method recovering early prepared central pattern of metal subject the same treatment like sample. Lead and manganese concentrations in reference samples were higher with 7.4% than average obtained by other certificating laboratories. For copper, cadmium and zinc the differences were 4.3%, 3.8% and 4.6% respectively. It was also used for the recover of earlier prepared middle standard of the metal subjected to the same preparation like the sample. Magnitude of the recover for the lead was in 98.3%, for manganese – 99.3%, for copper – 98.8%, for cadmium – 94.3% and for zinc in 99.4%. Heavy metals concentration were given in $\mu\text{g dm}^{-3}$ for water and in $\mu\text{g g}^{-1}$ for suspension and sediment samples (per gram of dry mass).

Our experimental analytical results were applied to primary statistical calculations obtaining an average value of (\bar{x}), standard deviation of (S_x), coefficient of variation of (V_x) and amplitude range ($x - \text{min}, \text{max}$). Comparison of our experimental average heavy metal concentrations were done using t-Student test.

72 surface and demersal water samples, 72 suspension samples, 18 interstitial water samples and 90 bottom sediment samples were analysed.

Enrichment coefficients were calculated taking into account these experimental trace elements concentration values for the studied lake's ecosystem in order to discover those metals' origin. Enrichment coefficient was calculated using formula 1 (Szefer 1989)

$$EF = (C_{me}/C_{Fe})_s : (C_{me}/C_{Fe})_{Ec} \quad (1)$$

where:

C_{me} – concentration of given metal

C_{Fe} – iron concentration

s – concentration in the studied compartment

Ec – average concentration in crust the earth

Enrichment coefficients of heavy metals concentration in surface water were calculated as well. Kwapuliński et al. (1993) estimated migration of those metals from bottom sediments to dimersal and interstitial waters and participation of atmospheric falls and bottom sediments in forming metal contents in the bottom water.

RESULTS AND DISCUSSION

Among the studied metals, manganese was prevailed metal in the Gardno Lake waters. Its average content in water was equal $72.9 \mu\text{g dm}^{-3}$ and was almost four times higher in interstitial water (Tab. 1). Metals concentrations differed statistically one from another. Average concentrations of metals in the lake water in summer and autumn seasons form series $\text{Mn} > \text{Zn} > \text{Pb} > \text{Cu} > \text{Cd}$. Hłyńczak et al. (1998) observed similar trend in Głębokie Lake. Zinc and lead contents were six times lower in comparison to manganese ones. Whereas the average content of copper was $2.63 \mu\text{g dm}^{-3}$ and cadmium only $0.21 \mu\text{g dm}^{-3}$. Gardno Lake waters contain more zinc and lead quantities than those in Puck Bay (Pempkowiak and Ciszewski 1990). Average lead and zinc concentrations in Gardno Lake waters amounted to 9.81 and $13.25 \mu\text{g dm}^{-3}$, respectively (Tab. 1). Lead concentration in Gardno Lake waters is eight times higher than that in Puck Bay. Zinc was only three times higher. Copper, cadmium and zinc concentrations in Gardno Lake waters indicate the first class of purity for such kind natural water reservoir. They are comparable or slightly lower than those obtained earlier for Majcz and Inulec lakes waters (Królak 1997) and estuarines waters (Turner and Millward 2000). Similar levels of those metals were given for Dobczyce water reservoir by Szarek-Gwiazda (1998) and for estuarine water by Wright and Worrall (2001). But concentrations of manganese and lead are considerable higher in Gardno Lake water. The lead concentration for Dobczyce reservoir water was three times lower than observed by us in Gardno Lake waters. Manganese concentration was almost two times lower in Dobczyce reservoir. Concentrations of those two metals are two times higher in Gardno Lake waters than in Majcz and Inulec lakes. Taking into consideration more polluted Głębokie Lake with classless purity waters and data given by Hłyńczak et al. (1998) level of zinc is three times lower and lead content is even four times lower in Gardno Lake water. Generally, we can state that heavy metal concentrations are not high in water of Gardno Lake but exceptions are manganese and lead.

Table 1

The content of heavy metals ($\mu\text{g dm}^{-3}$) in the Gardno Lake water (x^* – average value of respective species water, x' – average value of deep water, S_x – standard deviation)

Metals	Water	Stations			Min.	Max.	x^*	x'	S_x
		1	2	3					
Pb	surface	9.17	8.80	7.04	2.65	11.57	8.34	9.81	2.32
	near-bottom	10.86	12.29	10.68	2.16	14.30	11.28		1.84
	interstitial	26.80	29.51	23.46	10.09	50.67	26.59		5.83
Mn	surface	81.9	60.0	46.2	16.2	100.0	62.5	72.9	16
	near-bottom	106.8	81.9	61.4	18.7	151.9	83.4		23
	interstitial	323.7	295.0	219.4	88.1	442.5	279.4		57
Cu	surface	2.45	1.83	1.07	0.88	6.97	1.78	2.63	0.28
	near-bottom	4.98	2.87	2.55	0.63	8.24	3.47		0.34
	interstitial	13.32	10.97	6.04	2.51	30.07	10.11		2.03
Cd	surface	0.20	0.19	0.12	0.04	0.42	0.17	0.21	0.03
	near-bottom	0.32	0.28	0.15	0.05	0.57	0.25		0.03
	interstitial	1.14	1.12	0.53	0.18	1.66	0.93		0.08
Zn	surface	12.61	13.62	7.94	2.51	20.31	11.41	13.25	1.12
	near-bottom	19.91	16.38	8.96	2.72	35.46	15.08		3.15
	interstitial	51.91	44.28	20.50	11.47	79.19	39.04		10.26

Heavy metals' contents in surface and demersal Gardno Lake water were statistically different at stations 1, 2 and 3 (Tab. 1). The investigated metals' contents of surface waters from stations 1 and 2 were quite similar. Statistically essential differences were observed only between stations 1 and 2 for manganese and copper concentration. The concentrations of those two metals were about 35% higher at the Łupawa River mouth (st. 1) than at station 2. It was not surprising that the lowest metal concentration was observed at station 3 where the strongest sea water penetration takes place. Periodic inputs of sea water into the Gardno Lake dilute lake water and decrease heavy metals' concentration in it. Many authors (Trojanowski et al. 1991, Mudryk et al. 1999, Wright and Worrall 2001, Windom and Nienchesk 2003) have mentioned a similar phenomenon. It was noted that heavy metals' concentrations were higher with increasing distance from the sea. The highest concentrations of the examined metals were observed at station 1 (Łupawa River mouth into the lake). It is evident that Łupawa River waters are the main source of heavy metals in Gardno Lake. Average heavy metals' concentrations in Łupawa river amounted to $51 \mu\text{g dm}^{-3}$ for zinc, $13.2 \mu\text{g dm}^{-3}$ for lead, $84.5 \mu\text{g dm}^{-3}$ for manganese, $1.1 \mu\text{g dm}^{-3}$ for copper, and $0.5 \mu\text{g dm}^{-3}$ for cadmium.

Metals' concentrations in near-bottom water were higher than in surface water. The highest statistical essential differences were observed in Mn, Cu and Cd concentrations, and essentially lower for the other two metals. It means that atmospheric fallout has essential role in supplying Pb and Cd of Gardno Lake water. In the case of

Cu its concentration in near-bottom water was two times higher than in surface layer water. Heavy metals' content in demersal water was three times lower than their content in interstitial water. Transition of these ions from interstitial water to demersal water is evident (Tab. 1). Studies by Tovar-Sanchezi et al. (2006) and Otero and Macias (2002) confirm this conclusion.

Content of prevailed majority of the examined metals in interstitial water changed in similar way as in lake water. Their average concentrations differ statistically between particular stations. The highest difference of the examined heavy metals' concentrations are noticed between two stations (1 and 2) and the third one (Tab. 1). The highest concentration of the examined metals was observed most often in Łupawa River mouth into the lake (st. 1). The lowest one was observed at flow of water from the lake region (st. 3). The most diversified values were observed for copper, cadmium and zinc. Their concentrations at station 1 were more than two times higher than at station 3. Only in the lead case, concentrations in interstitial water were similar on all investigated regions – average $26.6 \mu\text{g dm}^{-3}$. Generally these rather high heavy metals' concentrations in this part of water results from its close contact with bottom sediments where released metals ions are penetrated first to interstitial water. Similar results were obtained by Koschinsky et al. (2003).

On the other hand the suspension concentration introduced with Łupawa River waters amounted average to 15.6 mg dm^{-3} (Fig. 2). Suspension concentrations were lower in April and May (12.4 mg dm^{-3}) in comparison to those in autumn period (19.3 mg dm^{-3}). Average heavy metals concentrations in suspensions introduced by Łupawa River waters to Gardno Lake were statistically different and amounted to $53.1 \mu\text{g g}^{-1}$ for zinc, $36.5 \mu\text{g g}^{-1}$ for lead, $144.2 \mu\text{g g}^{-1}$ for manganese, $0.8 \mu\text{g g}^{-1}$ for cadmium and $5.1 \mu\text{g g}^{-1}$ for copper (Fig. 3).

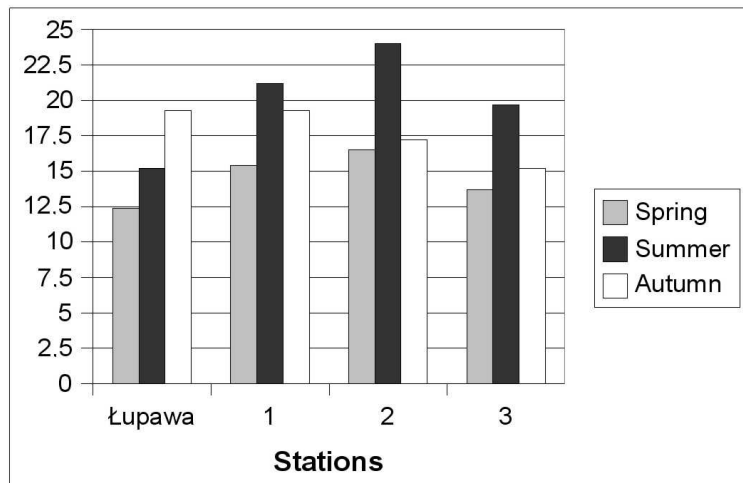


Fig. 2. Concentration of suspension (in mg dm^{-3}) in water of the lake Gardno and river Łupawa

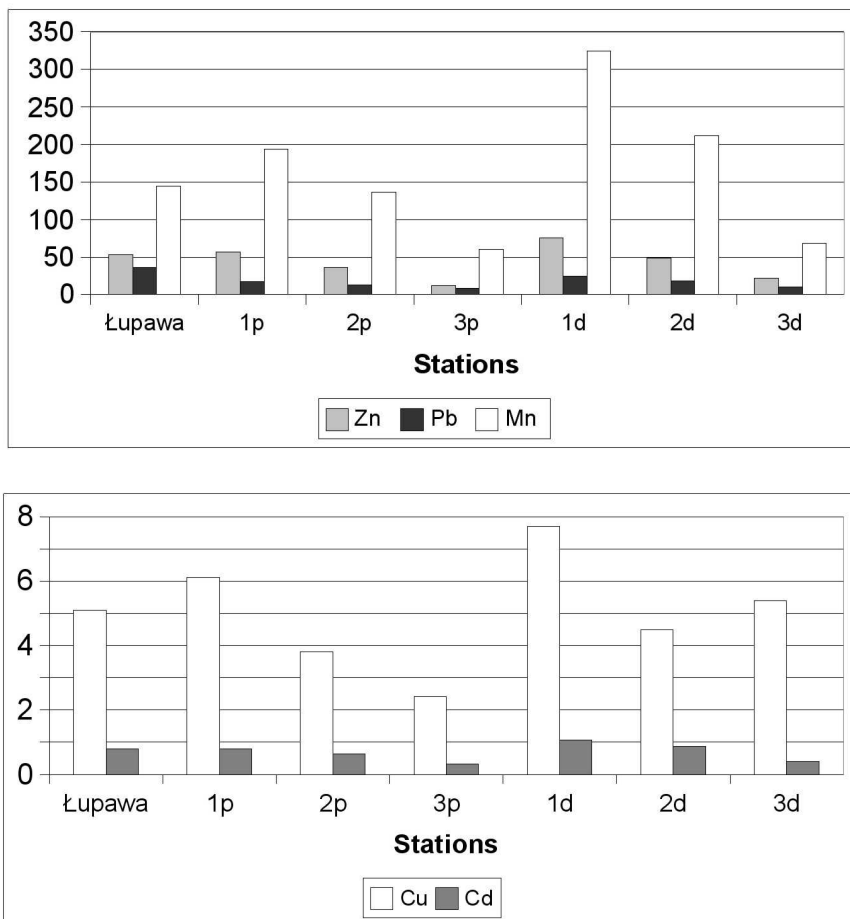


Fig. 3. The content of heavy metals (in $\mu\text{g g}^{-1}$ d.w.) in suspensions from the lake Gardno and river Łupawa water (1p, 2p, 3p – surface water, 1d, 2d, 3d – near-bottom water)

Suspension concentration in Gardno Lake waters was generally higher in comparison with that from Łupawa River. Its average concentration amounted to 18.0 mg dm^{-3} (Fig. 2) with oscillations from the lowest value to 10.8 mg dm^{-3} (st. 3) to 29.4 mg dm^{-3} (st. 2). Average studied metals' content in Gardno Lake suspensions differed statistically and amounted in its surface layer to $0.59 \mu\text{g g}^{-1}$ for Cd, $4.1 \mu\text{g g}^{-1}$ for Cu, $35.1 \mu\text{g g}^{-1}$ for Zn, $130 \mu\text{g g}^{-1}$ for Mn, $12.7 \mu\text{g g}^{-1}$ for Pb (Fig. 3). Average concentrations of those metals in suspensions increased as follows: $\text{Cd} < \text{Cu} < \text{Pb} < \text{Zn} < \text{Mn}$. That sequence was the same as in water. Analogous sequence was observed by Bojanowski and Koszałka (1976) investigating Wisła River and An and Campbell (2003) investigating Lake Texoma. Slightly different sequence was observed

by Brzezińska et al. (1984) in south part of the Baltic Sea. Average examined metals concentrations in surface lake suspension were lower than those in Łupawa River. Not in all lake regions, suspensions are characterized by lower metals concentrations. For example in station 1 region, zinc content in suspension was 6% higher than that in the river, manganese – about 26% and copper – about 17%. Cadmium concentration was the same and amounted to $0.8 \mu\text{g g}^{-1}$. Increased heavy metals' content in the station results from many years alluvion sedimentation of material from the river containing heavy metals ions absorbed on suspensions.

Examined metals' concentrations in suspensions from demersal water and from surface layer water were statistically different. Average metals content in near bottom suspension was about 30% higher than in surface suspension (Fig. 3). The lowest differences were observed at station 3 between the surface and demersal waters, particularly in the case of manganese, concentration of which amounted to $60.6 \pm 15.3 \mu\text{g g}^{-1}$ in surface suspension and $68.2 \pm 17.4 \mu\text{g g}^{-1}$ in demersal suspension.

Concentration coefficients of examined metals in suspensions are given in table 2.

Table 2
Concentration coefficients (K_d) for manganese, lead, zinc, copper and cadmium in suspended matter of the Gardno Lake (A – surface layer, B – near-bottom layer, x^* – average value).

Metal	Layer	Station 8			x^*
		1	2	3	
Mn	A	1.8	1.6	1.2	1.5
	B	2.2	1.5	0.9	1.5
Pb	A	2.7	2.3	1.3	2.1
	B	3.0	2.6	1.1	2.2
Zn	A	2.5	2.1	2.3	2.3
	B	1.5	1.6	2.1	1.7
Cu	A	4.0	3.3	2.7	3.3
	B	3.3	3.1	2.7	3.0
Cd	A	4.5	2.7	1.5	2.9
	B	3.8	3.0	2.4	3.1

They oscillated between 0.9 and 4.5. Their average values do not reveal essential statistical differences between them for near bottom and surface sediments with exception of those observed at station 1. This results from a little bit different chemical composition of suspension from those layers. Surface water suspension is mainly of river and atmospheric fall origin with high quantities of terrigenous matter. Whereas near bottom suspension contains died organic matter in addition. The lowest concentration metal coefficients were observed at station 3 with exception of zinc. The differences among them were very small for surface and near bottom layers suspensions. This results from not great depth of the lake – in this region amounted to 0.8 m – therefore the differences between physico-chemical properties of suspension from both layers are not high, particularly taking into account continuous mixing by wind. Decrease of average metal enrichment factors for suspensions in

surface water follows in such sequence $\text{Cu} > \text{Cd} > \text{Zn} > \text{Pb} > \text{Mn}$. The similar sequence was observed for sea water (Bolałek et al. 1988). For demersal water, the sequence was statistically different: $\text{Cd} > \text{Cu} > \text{Pb} > \text{Zn} > \text{Mn}$. Manganese showed the lowest concentration coefficients both for suspensions from demersal and surface waters. Obtained values of these coefficients are several dozen lower than analogous coefficients observed in south Baltic waters (Brzezińska et al. 1984).

Atmospheric fall influence on heavy metals content in water as well. They contain dusts with heavy metals and introduce them immediately to water reservoirs. From the other hand the atmospheric falls intensify surface water flow and surface water run-off from drainage area. Average heavy metal concentrations in atmospheric falls in the Gardno Lake region amounted to $5.08 \mu\text{gPb dm}^{-3}$, $0.30 \mu\text{gCd dm}^{-3}$, $11.15 \mu\text{gZn dm}^{-3}$, $1.62 \mu\text{gCu dm}^{-3}$.

Chemical composition of bottom sediments characteristic for Gardno Lake was significant differentiated. Bottom sediments near Łupawa river mouth into lake (st. 1) and bottom sediments from the deepest region of the lake (st. 2) were characterized by the highest contents of organic matter (Tab. 3, Trojanowski 2003) and higher sorption capacity (Sokołowska 2000). The highest concentration of organic matter was observed at station 2. It amounted to average 37.8% and the lowest 15.4% at station 3. It is evidence of higher level of their degradation process at the last station. The concentration of organic matter in sediments does not exceed 5% in pure water reservoir (Starmach et al. 1976). According to Stagenberg classification of all bottom sediments of the Gardno Lake belong to silica type suspensions, because they have more than 50% of silica concentration, despite of their high organic matter content.

Table 3

Chemical characteristics (in%) of bottom sediments in the lake Gardno (x^* – average value, S_x – standard deviation)

Components	Stations			x^*	S_x
	1	2	3		
Org. mat.	23.0	37.8	15.4	25.4	2.1
C_{org}	12.7	22.2	8.9	14.6	2.8
T-P	0.186	0.214	0.119	0.193	0.03
T-N	1.098	1.540	0.761	1.134	0.27
CO_2	1.33	0.22	0.55	0.70	0.16
Ca	1.69	0.28	0.69	0.89	0.12
Mg	0.24	0.11	0.19	0.18	0.12
Fe	0.56	0.94	0.21	0.57	0.09
Al	1.98	1.68	2.87	2.17	0.08
SiO_2	68.6	57.2	78.9	68.2	5.1

Concentrations of heavy metals in bottom sediments of Gardno Lake is differentiated not only horizontally but also in vertical profile (Tab. 4). Average concentrations of these metals differed statistically between upper layer 0-10 cm and deeper layers 10-20 cm. The upper layer of sediments with thickness of 0-10 cm contained the bi-

ggest quantity of these trace metals. Concentration dropped strongly below this 10 cm and was about three times lower in comparison to that in upper layer. This indicates that in exchange processes on interface bottom sediment-water participate mainly metals from 10 cm upper layer sediments.

Table 4

The content of manganese, lead, zinc, copper and cadmium in bottom sediments of the Gardno Lake (x^* – average value, x' – average value 0-10 cm layer, S_x – standard deviation, V_x – index of variation)

Metals	Layers (cm)	Stations			Min.	Max.	x^*	x'	S_x	V_x (%)
		1	2	3						
Mn	0-5	345	256	85	41	461	229	226	80	34.9
	05-10	361	227	84	40	472	224		95	42.4
	10-15	106	90	37	13	176	77		27	35.1
	15-20	45	25	20	4	72	29		9	31.0
Pb	0-5	36.2	23.9	17.1	7.4	61.6	25.7	24.0	3.1	12.0
	05-10	29.1	21.3	16.1	6.3	58.5	22.2		2.9	13.1
	10-15	7.8	8.0	5.7	0.8	20.3	7.2		1.2	16.7
	15-20	6.0	8.8	5.3	1.0	15.8	6.7		1.5	22.4
Zn	0-5	81.4	60.0	27.6	7.5	113.4	56.3	55.5	14.6	25.9
	05-10	82.6	56.2	25.2	8.1	120.6	54.7		12.0	21.9
	10-15	6.3	3.8	7.9	0.8	18.8	6.0		1.1	18.3
	15-20	5.0	3.4	8.6	0.5	16.8	5.7		0.9	15.8
Cu	0-5	9.9	5.2	5.8	0.7	20.3	7.0	7.4	2.9	41.4
	05-10	10.5	5.7	6.9	0.8	18.8	7.7		3.0	38.9
	10-15	3.5	3.0	2.6	0.1	10.4	3.0		0.9	30.0
	15-20	2.9	7.3	2.4	0.2	10.1	4.2		1.4	33.3
Cd	0-5	1.36	0.93	0.61	0.12	2.25	0.97	1.00	0.13	14.4
	05-10	1.45	1.02	0.63	0.10	2.09	1.03		0.12	12.4
	10-15	0.41	0.32	0.37	0.06	1.04	0.37		0.03	8.1
	15-20	0.32	0.41	0.27	0.05	0.96	0.33		0.03	9.1

Analysed metals' content in studied sediments showed essential statistical differences among investigated lake regions (Tab. 4). Sediments from station 1 near the Łupawa River mouth have significantly higher metal concentrations. They amounted to the average of $226 \mu\text{g Mn g}^{-1}$, $55.5 \mu\text{g Zn g}^{-1}$, $24 \mu\text{g Pb g}^{-1}$, $7.4 \mu\text{g Cu g}^{-1}$, $1.0 \mu\text{g Cd g}^{-1}$ and were four times higher for Mn and almost three times for Zn, two times for Pb and Cd, and one and a half times for Cu than those in lake region near river mouth into the sea (st. 3).

Composition differences of bottom sediments can be explained by water mass transport into the sea direction and by sedimentation of easy precipitated suspensions as well as by progressive settlement of finer solid particles river mouth into

lake, that's why the higher values of metals concentrations were observed at station 1. Lake bottom sediments are slowly dislocated to deeper lake parts (Alarn et al. 2001, An and Kampbell 2003). In relation to that at station 2 high metal concentrations in bottom sediments about 30% lower than those at station 1 for Mn, Pb and Zn and about 50% lower for two other metals were noticed. Besides that higher levels of chloride ions have influence on heavy metal contents in bottom sediments at station 3. Leaching of heavy metals from suspension takes place by periodical supply of the sea water into lake. Significant chloride concentration accelerates desorption of heavy metal ions from bottom sediments into water space forming double chemical species.

Metal contents in bottom sediments of the Gardno Lake were similar in comparison to those for other lakes (Bojakowska and Sokołowska 1997, An and Kampbell 2003). The highest difference was observed for manganese. Its average content in the investigated lake, amounted to $226 \mu\text{g g}^{-1}$ and was almost three times lower than given earlier by Bojakowska and Sokołowska (1997) for other lakes. The average Zn, Pb and Cu values were about 30% lower. Only Cd concentration is 20% higher. The concentrations of Cd and Pb were the same in Piaseczno water reservoir and in Authie Bay water in France (Billon et al. 2002), Cu content was six times lower and Mn content was two times lower.

To indicate metals origin in bottom sediments in the Gardno Lake enrichment coefficients (EF) for particular metals were determined according to Szefer (1989). Those coefficients were given in table 5. According to this method for antropogenic origin of those heavy metals, their enrichment coefficients are higher than 10. The EF below 3 indicated their natural origin. Pb, Zn and Mn should be included to the first group of origin but already Cd to the second one. Enrichment factors for Pb and Zn in sediments oscillated between 86 and 326 and for Mn between 16 and 42. EF values for Cu oscillated from 2 to 9 and depended on the place of taking the samples, those differences can be attributed to variable Cu levels in environment. The higher values noted for sediments at station 1 show local Cu pollution source of lake and bottom sediments by Łupawa River.

In order to evaluate the pollution of the Gardno Lake by those metals the enrichment coefficients were calculated for demersal water – reference water, demersal water – interstitial water and demersal water – bottom sediment systems according to formula:

$$FF_o = \frac{C_{me}/C_{Mn} \text{ demersal water}}{C_{me}/C_{Mn} \text{ reference water}} \quad (2)$$

EF_o – enrichment coefficient in regards to reference water

EF_m – enrichment coefficient in regards to intermolecular water

EF_s – enrichment coefficient in regards to bottom sediment water

Table 5
Enrichment coefficients of heavy metals in near-bottom water in respect to their content in reference water (EF_o) and interstitial water (EF_m) and bottom sediments (EF_d) and general enrichment coefficients of heavy metals in bottom sediments (EF) in the Gardno Lake

Metals	Near-bottom water			Bottom sediments
	EF_o	EF_m	EF_d	EF
Cu	2.75	1.19	1.09	5.6
Pb	6.79	1.31	1.25	227
Zn	9.10	1.42	1.27	212
Cd	1.49	0.91	0.68	0.30
Mn				38.2

Mn was used as a normalized metal, which occurred in great quantities, and it showed no synergism effect in respect to Pb, Cu, Zn and Cd. Table 5 contains the demersal water enrichment coefficients. According to the presented data in this table heavy metal enrichment factors demersal water were middle in Gardno Lake in respect to water from pure regions (Kabata-Pendias and Pendias 1979). Enrichment coefficients do not exceed 10 value. Zn shows the highest EF_o value – 9.10 and Pb – 6.79 and the lowest one Cd – 1.49. Considerably lower enrichment coefficient values were observed for interstitial waters (EF_m from 0.91 to 1.42) and for bottom sediments (EF_s from 0.68 to 1.27). It is worth to note that in the Cd case those two values are lower than 1.0. It may mean that Cd migration from interstitial water and bottom sediments to near-bottom water occur only in small degree whereas first of all Cd transfer takes place from water to sediment. Determinated heavy metal migration coefficients between bottom sediment and interstitial and demersal waters confirm such conclusion. Those coefficients were determined according to Tracy formula (Kwapuliński et al. 1993):

$$\alpha = \frac{1}{C_w} \left(\frac{F}{h} - \frac{\Delta C}{t} \right) (10^{-3} \text{ year}^{-1}) \quad (3)$$

Where:

C_w – metal content in investigated fractions of reservoirs ($\mu\text{g g}^{-1}$)

F – total atmospheric precipitation to the lake according to data of Regional Environmental Protection Agency in Słupsk ($\text{mg m}^{-3} \text{ year}^{-1}$)

h – reservoir depth where samples were taken

ΔC – metal concentration difference between its maximal and minimal values in fraction from which metal was given

Δt – number of days suitable to ΔC expressed by fraction: number of days/365.

All calculated coefficients of the studied metals' removals from bottom sediment to demersal water or to interstitial water have negative values (Tab. 6). That means that migration from bottom sediment to demersal water occur only in insignificant lower

degree. Whereas migration in the opposite direction have dominant significance, that is confirmed by calculated coefficients for reverse direction. All those coefficients had positive values. The comparison of those values certify, that cadmium was the most sorbed metal by sediment. The migration speed of other metals from demersal water to sediment was similar.

Table 6

Migration coefficients (α) of heavy metals in system near-bottom water – interstitial water – bottom sediments of the Gardno Lake

Metals	Migration metals			
	from bottom sediment to near-bottom water	from near-bottom water to bottom sediment	from bottom sediment to interstitial water	from interstitial water to bottom sediment
Pb	-3 000	0.065	-504	0.014
Cu	-2 932	0.066	-74	0.071
Cd	-5 000	1.320	-3 080	1.210
Zn	-7 896	0.074	-3 008	0.070

The partition of metal migration from atmospheric fall and from the bottom sediments to demersal water was calculated on the basis of graphic analysis of equation given by Kwapuliński et al. (1993)

$$\frac{C_d}{C_s} = k_1 \frac{C_f}{C_s} + k_2 \quad (4)$$

Where:

C_d – average metal concentration in demersal water ($\mu\text{g dm}^{-3}$)

C_s – average metal concentration in interstitial water ($\mu\text{g dm}^{-3}$)

C_f – average metal concentration in atmospheric fall ($\mu\text{g dm}^{-3}$)

k_1 – factor of atmospheric fall part

k_2 – factor of bottom sediment part

Factor partition values presented in table 7 show cadmium supremacy of partition of demersal water contamination by the metal from bottom sediment over that one from atmospheric fall. That results from trace cadmium content in atmospheric fall. Cadmium atmospheric fall on lake area amounted only to $0.24 \text{ mg m}^{-2} \text{ year}^{-1}$ in examined period according to Regional Environmental Protection Agency in Słupsk. The greatest cadmium supply to demersal water occurs in summer both from bottom sediments and from atmospheric falls. Values of those coefficients for all other metals are slightly higher. Greater partition into Pb, Cu and Zn enrichment of demersal water takes place in spring and autumn. Whereas bottom sediments are the greatest source of those three metals in demersal water in summer period.

Table 7
Coefficients of participation of atmospheric precipitations (k_1) and bottom sediments (k_2) to form heavy metals content in near-bottom water of the Gardno Lake

Metals	Season	k_1	k_2
Cd	spring	0.11	0.16
	summer	0.18	0.22
	autumn	0.15	0.19
Pb	spring	0.40	0.21
	summer	0.14	0.32
	autumn	0.51	0.20
Cu	spring	0.85	0.12
	summer	0.19	0.22
	autumn	0.64	0.21
Zn	spring	0.56	0.18
	summer	0.12	0.30
	autumn	0.42	0.24

CONCLUSIONS

1. Low value of lead, zinc, copper, cadmium and manganese concentrations in water and bottom sediments of the Gardno Lake indicated the lack of large pollution sources from industrial sewage supplies.
2. The Łupawa River and periodic inputs of sea water have the most decisive influence on the forming of the water stores and bottom sediments quality in Gardno Lake. In connection with that the largest studied metals concentrations were observed at river mouth into the lake region and the lowest at water out-flow from the lake region.
3. Average studied metals concentrations in lake water, in suspensions and bottom sediments form the following row: $Mn > Zn > Pb > Cu > Cd$. That indicates that biochemical equilibrium appears between those lake systems.
4. Heavy metals concentrations in studied lake water are greater than in the Baltic Sea water.
5. The contents of the analysed metals in particular kinds of water decreased in the following way: interstitial water $>$ demersal water $>$ surface water.
6. Average content of studied metals in near bottom suspension was about 30% higher than in surface suspension. Whereas enrichment factors of those metals in suspensions do not show essential statistic difference with exception zinc, what indicates the similar chemical character of all kind suspensions. That results probably from continual mixing of water masses by wind.
7. Decrease of average metal enrichment factors in suspensions from surface water was arranged in the following way: $Cu > Cd > Zn > Pb > Mn$ and in suspensions from demersal water: $Cu > Cd > Pb > Zn > Mn$.

8. Bottom sediments of Gardno Lake characterize high accumulation properties of heavy metal. Positive values of migration coefficients from demersal water to sediment and high lead and zinc enrichment factors of sediments indicate on that conclusion.
9. The highest concentration of the studied metals occur in upper 0-10 cm layer of sediment. Lead, zinc and manganese in those sediments are mainly of anthropological origin, but cadmium – of natural one. Wheares copper origin is dependent on sample collection regions.
10. Tendency of heavy metal migration from water space to interstitial water and to bottom sediments exists evidently in the Gardno Lake.
11. Bottom sediments and atmospheric precipitations take part in enrichment of demersal water with in Pb, Zn and Cu in Gardno Lake. Atmospheric precipitations have prevailed influence during spring and autumn but bottom sediments have such influence during summer.

REFERENCES

- Abou-Mesalam M. M., 2002. Retention behaviour of nickel, copper, cadmium and zinc ions from aqueous solutions on silico-titanate and silico-antimonate used as inorganic ion exchange materials. *Rad. Nucl. Chem.*, 259, 479-484.
- Alam M.G. M., Tanaka A., Stagnitti F., Allinson G., Maekawa T., 2001. Observations on the effects of cage carp culture on water and sediment metal concentrations in lake Kasumigura, Japan. *Ecotox. Environ. Safety*, 48, 107-115.
- An Y.-J., Kampbell D. H., 2003. Total, dissolved, and bioavailable metals at Lake Texoma marinas. *Envir. Poll.*, 122, 253-259.
- Beck J. N., Ramelow G. J., Thompson R. S., Mueller C. S., Werbe C. L., 1990. Heavy metal content of sediment in the Calasieu River/Lake Complex, Luisiane. *Hydrobiologia*, 192, 149-165.
- Benes P., Gjessing E. T., Steinnes E., 1976. Interactions between humus and trace elements in fresh water. *Water Res.*, 10, 32-48.
- Benes P., Gjessing E. T., Steinnes E., 1982. Role of bacterial extracellular polymers in metal uptake in pure bacterial culture and activated sludge. I. Effect of metal concentration. *Water Res.*, 16, 66-73.
- Billon G., Ouddane B., Recourt P., Boughriet A., 2002. Depth variability and some geochemical characteristics of Fe, Mn, Ca, Mg, Sr, S, P, Cd and Zn in Anoxic sediments from Authie Bay (Northern France). *Estu., Coast. Shelf Sci.*, 55, 167-181.
- Bojakowska I., Sokołowska G., 1997. Akumulacja pierwiastków śladowych w osadach jeziornych w zależności od strefy ich sedymentacji. (Accumulation of vestigial elements according to the zone of their sedimentation). *Przegląd Geol.*, 45, 482-508, (in Polish).
- Bojanowski R., Koszałka T., 1976. Pierwiastki śladowe w wodach Wisły. (Vestigial elements in water of Wisła River). *Stud. i Mat. Oceanol.* 14, *Chemia Morza*, 2, 199-216, (in Polish).
- Bołałek J., Neugebauer E., Nowacki J., 1988. Miedź, ołów, kadm i cynk w powierzchniowej i przydennej wodzie Zatoki Gdańskiej w 1985 i 1986 roku. (Copper, lead, cadmium and zinc in surface and near-bottom water of Gdańsk Bay). *Studia i Mater. Oceanol.* 54, *Chemia Morza*, 8, 109-129, (in Polish).
- Borg H., 1983. Trace metals in Swedish natural fresh waters. *Hydrobiologia*, 101, 27-34.

- Brzezińska A., Trzosińska A., Żmijewska W., Wódkiewicz L., 1984. Trace metals in suspended matter and surficial bottom sediments from the Southern Baltic. *Oceanologia*, 18, 59-77.
- Cyberski J., Jędrasik J., 2003. Wymiana i cyrkulacja wód w jeziorze Gardno. W: Jezioro Gardno. (xchange and circulation in Gardno Lake waters. In: Gardno Lake. (Ed.) Z. Mudryk). PAP, Słupsk, 35-64, (in Polish).
- Förstner U., Wittmann G. T. W., 1985. Metal pollution in the aquatic environment. Springer-Verlag, Berlin-Heidelberg-New York-Tokyo, 486-503.
- Fytianos K., Samanidou V., Angelidis K., 1986. Comparative study of heavy metals pollution in various rivers and lakes of northern Greece. *Ambio*, 15, 42-44.
- Golimowski J., Merks A. G. A., Valenta P., 1990. Trends in heavy metal in dissolved and particulate phase in the Dutch Rhine-Meuse (maas) Delta. *Sci. Total Environ.*, 92, 113-127.
- Hłyńczak A. J., Baranowska-Bosiacka I., Janeczko A., 1998. Występowanie niektórych metali ciężkich w wybranych zbiornikach wodnych Szczecina. (Occurrence of some heavy metals in selected water reservoirs of Szczecin). *Arch. Ochr. Środ.*, 24, 1, 57-67, (in Polish).
- Januszkiewicz T., 1978. Studia nad metodyką analizy chemicznej składu współczesnych osadów dennych jezior. (Studies on the method of chemical analysis of the recent lake sediments). *Zesz. Nauk Roln. Techn. Olsztyn*, 8, 187, 3-30, (in Polish).
- Kabata-Pendias A., Pendias H., 1979. Pierwiastki śladowe w środowisku biologicznym. (Trace elements in biological environment). Wyd. Geologiczne, Warszawa, (in Polish).
- Koschinsky A., Winkler A., Fritsche U., 2003. Importance of different types of marine particles for the scavenging of heavy metals in the deep-sea bottom water. *Appl. Geochem.*, 18, 693-710.
- Kostecki M., 2000. Zawartość metali ciężkich w mięsie i wątrobie niektórych gatunków ryb z antropogenicznego zbiornika Dzierżno Duże (woj. Śląskie). (Contents of heavy metals in meat and liver of some fish species from reservoir of Dzierżno Duże (Śląsk province)). *Arch. Ochr. Środ.*, 26, 109-125, (in Polish).
- Kostecki M., Leśniak M., Stenzel M., 1993. Metale ciężkie w kanałach odwadniających teren wyrobisk popiaskowych KPP "Szczakowa". (Heavy metals in drain channels area of sand excavation in KPP "Szczakowa"). *Arch. Ochr. Środ.*, 1-2, 46-58, (in Polish).
- Królak E., 1997. The content of heavy metals in *Dreissena polymorpha* (Pall.) in lakes Majecz and Inulec, Masurien Lakeland. *Pol. Arch. Hydrobiol.*, 44, 4, 477-486.
- Kwapuliński J., Wiechuła D., Bazgier M., Anders B., Pyka M., Loska K., Szilman E., 1993. Migracja niklu w układzie woda przydenna – woda międzycząsteczkowa – osad denny. W: Chrom, nikiel i glin w środowisku, problemy ekologiczne i metodyczne. (Migration of nickel in system near-bottom water – interstitial water – bottom sediment. In: Chromium, nickel and aluminium in environmental, ecological and methodical problems). Kom. Nauk. przy Prezydium PAN "Człowiek i Środowisko", *Zesz. Nauk.*, 5, 177-181, (in Polish).
- Lampert W., Sommer U., 1996. Ekologia wód śródlądowych. (Ecology of the inland waters). PWN, Warszawa, (in Polish).
- Marsden I. D., Rainbow P. S., 2004. Does the accumulation of trace metals in crustaceans affect their ecology – the amphipod example? *Marine Chemistry*, 83, 121-130.
- Mudryk Z., Donderski W., Skórczewski P., Walczak M., 1999. Neustonic and planktonic bacteria isolated from brackish lake Gardno. *Pol. Arch. Hydrobiol.*, 46, 121-131.
- Neugebauer E., Bolałek J., 1984. Wstępne wyniki badań nad zawartością miedzi, kadmu, ołowiu i kobaltu w wodach Zatoki Puckiej. (Preliminary results of investigations for contents of copper, cadm, lead and cobalt in Puck Bay water). *Zesz. Nauk. Uniwer. Gdańsk., Oceanografia*, 10, 26-35, (in Polish).

- Otero X. L., Macias F., 2002. Spatial and seasonal variation in heavy metals in interstitial water of salt marsh soils. *Environ. Poll.*, 120, 183-190.
- Pacyna J., 1991. Source receptor relationship for atmospheric trace elements in Europe. *Acise Precipit.*, 35, 101-110.
- Pawlik-Skowrońska B., 2001. Phytochelatin production in freshwater algae *Stigeoclonium* in response to heavy metals contained in mining water; effects of some environmental factors. *Aqua. Toxic.*, 52, 241-249.
- Pempkowiak J., 1991. Enrichment factors of heavy metals in the Baltic sediments dated with ²¹⁰Pb and ¹³⁷Cs. *Environ. Inter.*, 17, 421-428.
- Pempkowiak J., Ciszewski P., 1990. Stężenie wybranych metali ciężkich w wodzie i osadach dennych Zatoki Puckiej. (Concentration of selected heavy metals in water and bottom sediments of Puck Bay). *Arch. Ochr. Środ.*, 1-2, 153-163, (in Polish).
- Schintu M., Sechi N., Sarritzu G., Contu A., 1989. Reservoir sediments as potential source of heavy metals in drinking water. *Water Sci. And Technol.*, 12, 21-38.
- Sokołowska I., 2000. Właściwości sorpcyjne osadów dennych jeziora Gardno. (Sorption properties of bottom sediments in Gardno Lake). Praca magisterska. Zakład Chemii Środowiskowej, PAP, Słupsk, (in Polish).
- Sposito G., 1986. Sorption of trace metals by humic materials in soils and natural waters. *Critical Rev. Environ. Contamin. And Toxicol.*, 2, 4-22.
- Starmach K., Wróbel S., Pasternak K., 1996. Hydrobiologia. Limnologia. (Hydrobiology. Limnology). PWN, Warszawa, (in Polish).
- Szarek-Gwiazda E., 1998. Horizontal vertical and seasonal distribution of heavy metals in the water of a stratified dam reservoir (Dobczyce Reservoir, southern Poland). *Acta Hydrobiol.*, 40, 2, 113-120.
- Szefer P., 1989. Rozmieszczenie i potencjalne źródła pochodzenia wybranych pierwiastków metalicznych w ekosystemie południowego Bałtyku. (Distribution and potential sources of selected metal elements in southern Baltic ecosystem). (The paper qualifying for assistant-professor-ship), Akademia Medyczna w Gdańsku, Gdańsk, (in Polish).
- Tamura H., Mita K., Tanaka A., Ito M., 2001. Mechanism of hydroxylation of metal oxide surfaces. *J. Col. Inter. Sci.*, 243, 202-207.
- Tao Z. Y., Guo Zh. J., Dong W. M., 2003. Use of ion exchange for the determination of stability constants of metal-humic substance complexes. *J. Rad. Nucl. Chem.*, 256, 575-580.
- Tovar-Sanchez A., Huerta-Diaz M. A., Negro J. J., Bravo M. A., Sañudo-Wilhelmy S. A., 2006. Metal contamination in interstitial waters of Doñana Park. *J. Envir. Manag.*, 78, 286-293.
- Trojanowski J., 2003. Usytuowanie i ogólna charakterystyka jeziora. W: Jezioro Gardno (Situation and general characteristics of the lake. In: Gardno Lake. (Ed.) Z. Mudryk). PAP, Słupsk, 9-14, (in Polish).
- Trojanowski J., Trojanowska C., Korzeniewski K., 1991. Trophic state of coastal lakes. *Pol. Arch. Hydrobiol.*, 38, 23-34.
- Turner A., Millward G. E., 2000. Particle dynamics and trace metal reactivity in estuarine plumes. *Estuar., Coast. Shelf Sci.*, 50, 761-774.
- Widianarko B., Van Gestel C. A. M., Varweij R. A., Van Straalen N. M., 2000. Associations between trace metals in sediment, water, and Guppy, *Poecilia reticulata* (Peters), from urban streams of Semarang, Indonesia. *Ecotox. Environ. Safety*, 46, 101-107.
- Windom K., Nienchisk L., 2003. Analysis and evaluation of heavy metal uptake and release by insoluble starch xanthate in aqueous environment. *Water Sci. Techn.*, 44, 161-168.
- Wright J., Worrall F., 2001. The effects of river flow on water quality in estuarine impoundments. *Physics and Chemistry of the Earth, Part B: Hydrol., Oceans and Atmosph.*, 26, 741-746.

MIGRACJA METALI CIĘŻKICH W UKŁADZIE: WODA PRZYDENNA – WODA IŁOWA – OSAD DENNY JEZIORA GARDNO**Streszczenie**

W latach 2002-2003 przeprowadzono badania nad koncentracją metali ciężkich w wodzie i osadach dennych estuariowego jeziora Gardno. Wykazano, że przepływająca przez to jezioro rzeka Łupawa i okresowe wlewy wody morskiej mają istotny wpływ na zawartość Mn, Zn, Cu, Pb i Cd w wodzie i osadach dennych tego jeziora. Największą koncentrację tych metali obserwowano w rejonie ujścia Łupawy do jeziora (Cd – 0,26, Cu – 3,71, Mn – 94,3, Pb – 10,01, Zn – 16,26 $\mu\text{g dm}^{-3}$), a najmniejszą w rejonie wypływu tej rzeki z jeziora (Cd – 0,13, Cu – 1,81, Mn – 53,8, Pb – 8,86, Zn – 8,05 $\mu\text{g dm}^{-3}$). Przeciętna zawartość tych metali w wodzie, zawiesinach i osadzie dennym układała się w następującej kolejności Mn>Zn>Pb>Cu>Cd. Ich stężenia były najwyższe w wodzie iłowej, mniejsze w wodzie przydennej, a najmniejsze w wodzie powierzchniowej. Przeciętna zawartość analizowanych metali w zawieszynie przydennej była o około 30% większa niż w zawieszynie powierzchniowej. Wyznaczone współczynniki wzbogacenia wskazują, że Pb, Zn i Mn w osadach dennych badanego jeziora są głównie pochodzenia antropogenicznego, natomiast Cd pochodzenia naturalnego. Pochodzenie Cu zależne jest od rejonu jeziora. Osady dennie jeziora Gardno charakteryzują się dużymi zdolnościami kumulacji metali ciężkich. Dlatego też w tym jeziorze obserwuje się głównie migrację badanych metali z toni wodnej do wody iłowej i osadów dennych. Udział we wzbogacaniu wody przydennej w Pb, Zn i Cu mają zarówno osady dennie, jak i opady atmosferyczne. Wiosną i jesienią decydujący wpływ mają opady atmosferyczne, a latem osady dennie.