

HEAVY METALS IN SURFACE MICROLAYER IN WATER
OF LAKE GARDNO

JAN TROJANOWSKI*, JÓZEF ANTONOWICZ

Department of Environmental Chemistry, Pomeranian University,
Arciszewskiego str. 22, 76-200 Słupsk, POLAND

*Corresponding author e-mail: trojanowski@apsl.edu.pl

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Abstract: In the present paper we show results of our research on the contents of selected heavy metals in the surface and subsurface water layers of the estuarine lake Gardno. Obtained results show that there are substantial differences between concentrations of lead, copper and zinc in surface microlayer and subsurface waters. We observed that the surface microlayer is capable of accumulating much higher amounts of these metals than the subsurface waters. Analysis of seasonal changes in heavy metal concentrations in surface microlayers and subsurface waters shows some periodicity of these changes.

INTRODUCTION

The surface microlayer is a thin layer, of several hundred μm found in the contact interface between water and the atmosphere [8, 10, 41]. This layer covers 3/4 of the Earth surface. It represents a significant part of water environment creating independent subecosystems on the boundary of the atmosphere-hydrosphere exchange. It is sometimes named "the last millimeter of ocean" [31]. It is created on the surface in all water ecosystems. This surface microlayer in a water reservoir is a specific chemical and physical environment, different from subsurface water. It constitutes a unique ecotone in relation to its physical, chemical and biological manageability [1, 27, 28], markedly different from subsurface water [4]. This monomolecular surface water layer is a common boundary layer with an enormous importance to the two phases: water and the atmosphere [10, 30]. For this reason it becomes variable in time and in space in terms of exchange processes [2, 11, 41]. Exchange of substance and energy is a very important process in the biogeochemical element cycles. The exchange process between the atmosphere and hydrosphere plays a key role in the water environment and determines global radiation balance [12, 31, 42]. This exchange takes place thanks to the same biological, chemical and radiational transformations in two environments [11, 15].

Apart from physical factors, the microorganism metabolic activity in the water surface microlayer also influences its chemical composition [9, 46]. Research on water ecosystems shows a clear difference in concentrations of different substances between the surface microlayer and subsurface water. Usually concentrations of individual water

ingredients in the microlayer are higher than in water depths [1, 2, 9, 10, 15, 30, 36], and the same is true also for metal concentrations [6, 8, 23, 33, 34]. Hardy *et al.* [16] analyzed the influence of such factors as chemical microlayer composition, transport and forms of metals as well as the time spent in the microlayer on the actual levels of metals in the microlayer. Possible enrichment mechanisms in surface microlayer water in the case of metals were discussed by Liss [26]. Special attention needs to be paid to metal transport by air bubbles, containing on their surface active material which can bind metal ions from water, to metal association by insoluble organic forms and binding of metals from water and from air in metalorganic complexes. It has an essential influence on the vital condition of organisms. High levels of heavy metals found in the surface microlayer are toxic not only to neuston organisms, but also to larval fish and fry as well as other water organisms, which take food from the surface layer water. In many cases, as for example in the case of pelagic fish, their spawn develops directly in the surface microlayer [46]. The goal of the conducted research was to investigate seasonal changes in climax metal selection in the surface microlayer of Lake Gardno in terms of water salinity.

MATERIAL AND METHODS

Lake Gardno is situated in the Słowiński National Park, in the middle part of the Baltic coast (Fig. 1).

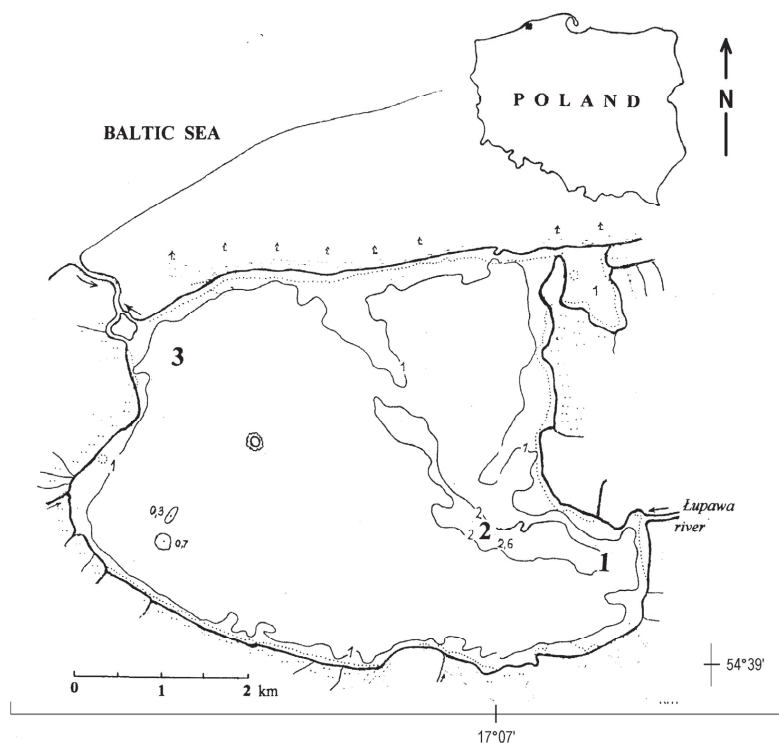


Fig. 1. Lake Gardno, northern Poland, with locations of sampling stations

This shallow lake (mean depth 1.3 m) is a full mixing lake [43, 44, 45]. Lake Gardno is the second estuary lake in Poland as regards surface [40]. From the Baltic coastline the lake is separated by a narrow land strip up to 2 km wide. Water is supplied by the Łupawa River, which discharges to Gardno in its south-eastern part (Fig. 1), and as well as by many little tributaries. The difference of water levels between the lake and the sea is not large (about 26 cm), it facilitates exchange of water by the estuary section of the Łupawa to the sea. In the north-eastern part of the lake this section is in the channel form, about 10 m wide, to join it with the sea [44].

Samples of surface microlayer and subsurface water in Lake Gardno were taken from three places (Fig. 1) once a month, from March 1999 to October 2000. Two sampling techniques were applied: glass plate [18] and polyethylene Garrett net [14]. Both methods differed in the thickness of microlayer sample collection. Samples of the thinnest microlayer (90–120 μm) were taken using a glass plate and were named Film (F), while those of the layer collected with a Garrett net at a depth of 200–320 μm were denoted as Garrett Film (FG). Samples of subsurface water (SUB) were taken from a depth of about 15 cm with use of polyethylene containers. Volume of water sample was divided into 3 sub-samples, thickened at 70°C and mineralized with HNO_3 *trace pure* and HClO_4 *trace pure* (ratio of acids 5 : 1). Mineralization was carried out in a Maxidiges MX 350 Prolabo microwave mineralizer coupled with a microcomputer designed to control the program of power and time of mineralization [35, 47]. After a full sample oxidation standardization to the constant volume of demineralized water was performed samples were kept in a laboratory refrigerator at a temperature of 4°C until measurement time [19, 32].

Determination of zinc was conducted in an Atomic Absorption Spectrophotometer Carl-Zeiss Jena AAS3 in oxy-acetylene flame. Analyses were conducted at a wavelength of 213.9 nm [5, 50]. Assays of copper and lead were also performed with an Atomic Absorption Spectrophotometer Carl-Zeiss Jena AAS3, but this time with an attachment of an EA3 electromagnetic atomizer and automatic sample feeding. Analyses were conducted at a wavelength of 217.0 nm for lead and 324.8 nm for copper, respectively [5, 50]. The Work programme for the electromagnetic atomizer was established according to: [7, 13, 49]. For the selected series of 30 sub-samples Pb and Cu assays were conducted using two apparatuses: GBC Avanta Σ with an attachment of a GBC GF 3000 graphite furnace and of a PAR 3000 auto sampler (Medical University in Gdańsk) as well as a Carl-Zeiss Jena AAS3 apparatus. However, for Zn assays an AAS Philips Pu 9100 apparatus working in the flame version (Medical University in Gdańsk) and a Carl-Zeiss Jena AAS3 apparatus were used. For the purpose of verification of results two reference materials were used, i.e. SCP Science EnviroMAT™ & AgroMAT™ ES-H-1 Ground Water and EU-H-1 Waste Water [39]. Analytical methods recovering previously prepared central pattern of metal subjected to the same treatment as samples were applied. Lead concentration in the reference sample was higher by 8.6% than the average reported by other certifying laboratories. For copper and zinc these differences were 4.3% and 4.6%, respectively. It was used also to recover the previously prepared middle standard of the metal subjected to the same preparation as the sample. Magnitude of the recovery for lead was 91.3%–109.3%, for copper it was 92.3%–104.3 % and for zinc it was 95.4%–105.3 %, respectively.

For chlorine ions argentometry was applied according to Standard Methods [37]. Enrichment factors of water surface microlayers for heavy metals in relation to subsurface water was calculated using equations:

For film: $EF_F = C_F/C_{SUB}$
 For Garret film: $EF_{FG} = C_{FG}/C_{SUB}$
 where C_F , C_{FG} , C_{SUB} – concentration of heavy metals in relation to water layer [15].
 Pearson's correlation coefficient was calculated using the "Statistica" program [38].

RESULTS

In the period from March 1999 to October 2000 the concentrations of three heavy metals (Cu, Zn, Pb) were analyzed in surface water microlayers and subsurface water in Lake Gardno. Table 1 presents medium concentrations of copper in both microlayers and in subsurface water in individual sampling stations on the lake.

Table 1. Mean concentrations recorded for Cu, Pb, and Zn ($\mu\text{g dm}^{-3}$) in individual analyzed layers and respective calculated enrichment factors

Cu	F	FG	SUB	$EF_{F/SUB}$	$EF_{FG/SUB}$
1	34.8	19.6	14.5	5.43	2.86
2	33.6	11.4	6.1	8.43	3.19
3	56.9	21.0	13.9	8.49	3.57
Pb					
1	41.8	24.9	8.5	4.92	2.93
2	31.5	22.9	8.6	3.66	2.66
3	46.6	34.9	8.8	5.3	3.97
Zn					
1	26.3	24.4	13.7	1.92	1.78
2	30.3	26.4	12.7	2.39	2.08
3	38.1	30.5	13.3	2.86	2.29

The highest concentration of copper (mean $56.9 \mu\text{g dm}^{-3}$) was observed in film at position 3 (F, Fig. 2D), which was exposed the most to the effect of sea water.

Medium concentration of chlorine ions in this area amounted to 730 mg dm^{-3} [43] and was five times higher than at location 1, on which water from Lake Gardno is influenced by the ground factor, because water from the Łupawa River flows into the lake there. However, the copper content in Garrett's film water (FG) and from the subsurface at location 1 was the same as at location 3 (FG and SUB) and amounted to 20 and $21 \mu\text{g dm}^{-3}$ (Garrett's film) and $14 \mu\text{g dm}^{-3}$ (subsurface). The lowest level of copper was observed in water at location 2, which was characterized by the biggest depth. The copper content in this microlayer (FG) and subsurface water (SUB) at location 2 was nearly two times lower than at the other locations (Table 2, Fig. 2 E–F).

In the case of lead (Fig. 3) a similar distribution of its concentration in the analyzed water layers was found as it was found for copper.

The highest concentration of lead was found at location 3 (F – 46.6 , FG – 34.9 , SUB – $8.8 \mu\text{g dm}^{-3}$), the lowest at location 2 (F – 31.5 , FG – 22.9 , SUB – $8.6 \mu\text{g dm}^{-3}$, Tab 2). We need to stress here a much higher lead concentration in Garrett's film at location 3 ($34.9 \mu\text{g dm}^{-3}$) than that in Garret's film at location 1 ($24.9 \mu\text{g dm}^{-3}$), i.e. by about $10 \mu\text{g dm}^{-3}$. In the case of copper, its concentration at location 3 was higher by merely about $2.6 \mu\text{g dm}^{-3}$.

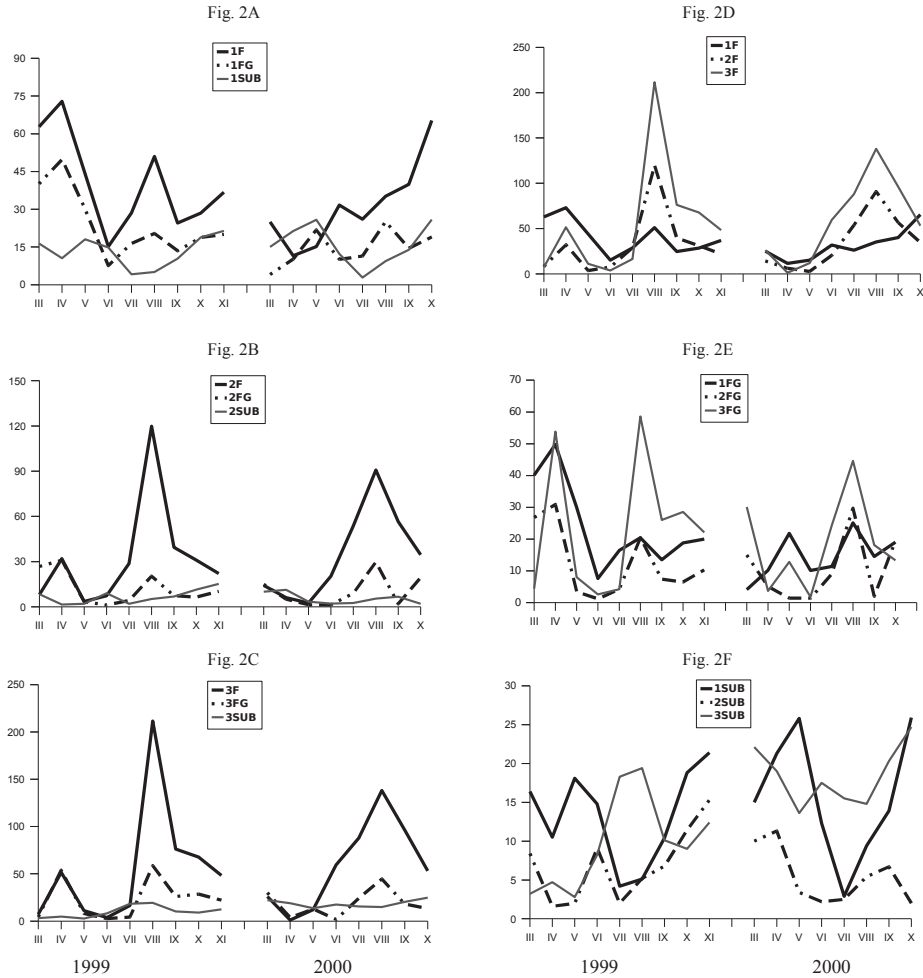


Fig. 2. Seasonal dynamic of copper concentration change ($\mu\text{g Cu dm}^{-3}$) in surface microlayer and subsurface water of Gardno lake in 1991 (III-XI) and 2000 (III-X) year

The concentration of this metal in subsurface water at all analyzed locations was similar and amounted to about $8.6 \mu\text{g dm}^{-3}$ (Tab. 1).

In both water surface microlayers (F and FG) a progressive increase in zinc concentration was observed going from location 1 to location 3 (Tab. 1, Fig. 4), that is as in the case of an increasing concentration of chlorine ions.

In the case of zinc concentration at location 3, it amounted to F – 38.1, FG – 30.5, SUB – $13.3 \mu\text{g dm}^{-3}$, at position 1 to F – 26.3, FG – 24.4, SUB – $13.7 \mu\text{g dm}^{-3}$, respectively. This metal concentration in subsurface water, similarly to lead, was similar at all the locations and amounted to about $13 \mu\text{g dm}^{-3}$.

In all cases the concentrations of analyzed metals was often highest in film, i.e. the thinnest microlayers ($105 \pm 15 \mu\text{m}$). A multiple of concentration in film and in Garrett film with relation to subsurface water is reflected in values of enrichment factor in Table 1.

Table 2. Values of enrichment factors for film and Garrett film recorded for Cu, Pb, Zn at Lake Gardno sampling locations

	EF _{F/SUB}	EF _{FG/SUB}	EF _{F/SUB}	EF _{FG/SUB}	EF _{F/SUB}	EF _{FG/SUB}
Cu	st. 1		st. 2		st. 3	
Mean	3.54	1.84	8.64	3.23	4.45	2.08
Minimum	0.54	0.27	0.54	0.13	0.06	0.10
Maximum	10.00	4.74	23.04	19.31	10.94	11.45
Mean from 3 locations					5.54	2.38
	EF _{F/SUB}	EF _{FG/SUB}	EF _{F/SUB}	EF _{FG/SUB}	EF _{F/SUB}	EF _{FG/SUB}
Pb	st. 1		st. 2		st. 3	
Mean	5.01	2.86	3.72	3.12	4.80	3.71
Minimum	1.09	0.54	1.33	0.55	0.53	0.69
Maximum	17.05	7.92	10.60	13.80	19.61	12.68
Mean from 3 locations					4.51	3.23
	EF _{F/SUB}	EF _{FG/SUB}	EF _{F/SUB}	EF _{FG/SUB}	EF _{F/SUB}	EF _{FG/SUB}
Zn	st. 1		st. 2		st. 3	
Mean	2.43	2.07	1.52	1.36	2.10	1.68
Minimum	0.72	0.53	0.50	0.39	0.33	0.14
Maximum	10.10	8.45	3.30	2.53	5.69	3.69
Mean from 3 locations					2.01	1.70

This factor for copper in film (EF_F) ranged from 0.06 (location 3) to 23.04 (location 2), and in Garrett film (EF_{FG}) from 0.10 (location 3) to 19.31 (location 2). The highest value of these factors was observed at location 2 and amounted for film to a mean of 8.64 and for Garrett film to 3.23 (Table 2). In Garrett film the difference between respective factors was considerably smaller than in film. It seems that the reason for this difference is the copper source which is accumulated in microlayers. Most probably this element originates mainly from the atmosphere, because enrichment factors for film at location 2 are almost three times bigger than for Garrett film, at location 1 and 3 two times bigger (Tab. 2). What is more, correlation factors for copper contents in the depths of water and contents in film, at locations 1 and 2 were statistically non-significant, which showed that the main source of this metal in studies on microlayers in this area should be searched for elsewhere – most probably in the atmosphere (Tab. 3).

Table 3. Pearson's correlation coefficient (n = 17). Bold-face print showed statistically significant correlations

	Cu		Pb		Zn	
	1F	1FG	1F	1FG	1F	1FG
1PW	-0.03	0.03	0.15	0.41	0.71	0.87
	2F	2FG	2F	2FG	2F	2FG
2PW	-0.17	-0.09	0.42	0.07	0.45	0.60
	3F	3FG	3F	3FG	3F	3FG
3PW	0.3	0.02	0.19	-0.09	0.41	0.36

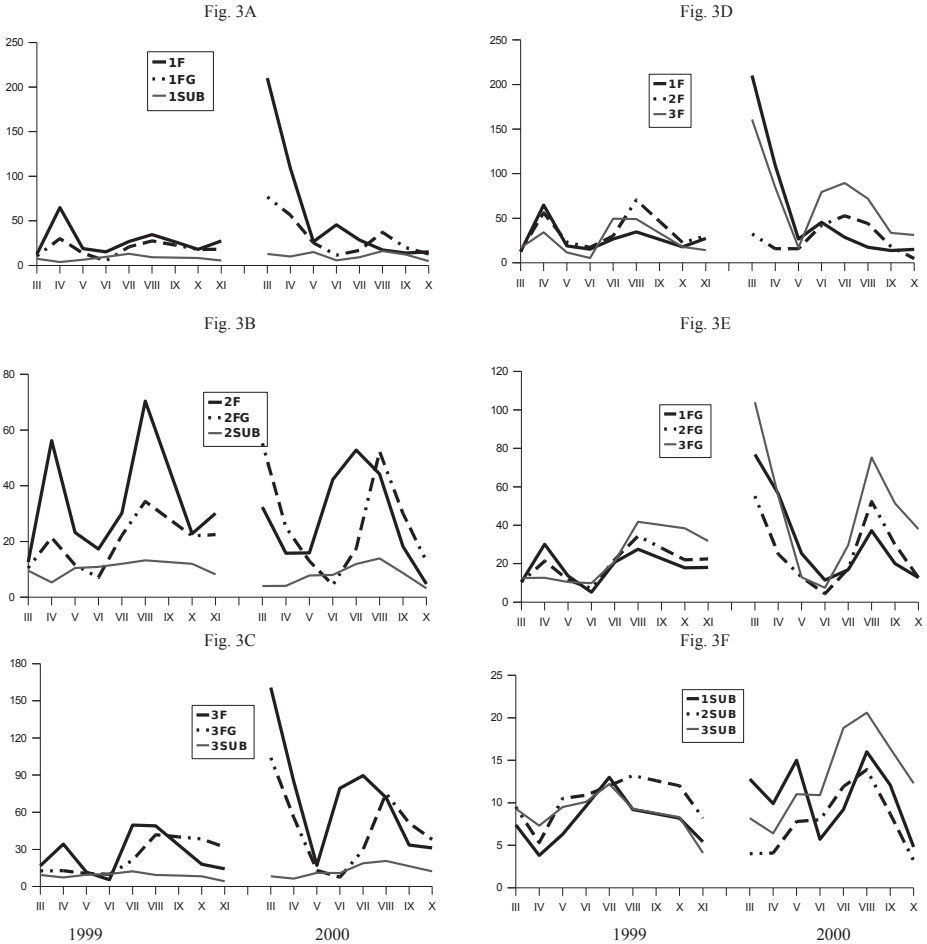


Fig. 3. Seasonal dynamic of lead concentration change ($\mu\text{g Pb dm}^{-3}$) in surface microlayer and subsurface water of Gardno lake in 1999 (III-XI) and 2000 (III-X) year

It is confirmed by the lowest concentration of copper in subsurface water at location 2, but all the same the concentration in film is similar to that at location 1. Only at location 3 the value of the correlation coefficient of 0.30 indicates that in sea water an essential influence on copper accumulation in surface microlayers is also played by its concentration in deep water.

In 84% of cases the enrichment factor of film for copper was bigger than for Garrett film. This result showed that the thinner microlayer has a much bigger ability to accumulate copper than the thicker microlayers.

The enrichment factors of surface microlayer water in the case of lead ranged from 0.53 in film (location 3), to 19.61 (location 3), but in Garrett film they ranged from 0.54 (location 1) to 13.80 (location 3, table 2). The mean difference in their value was much

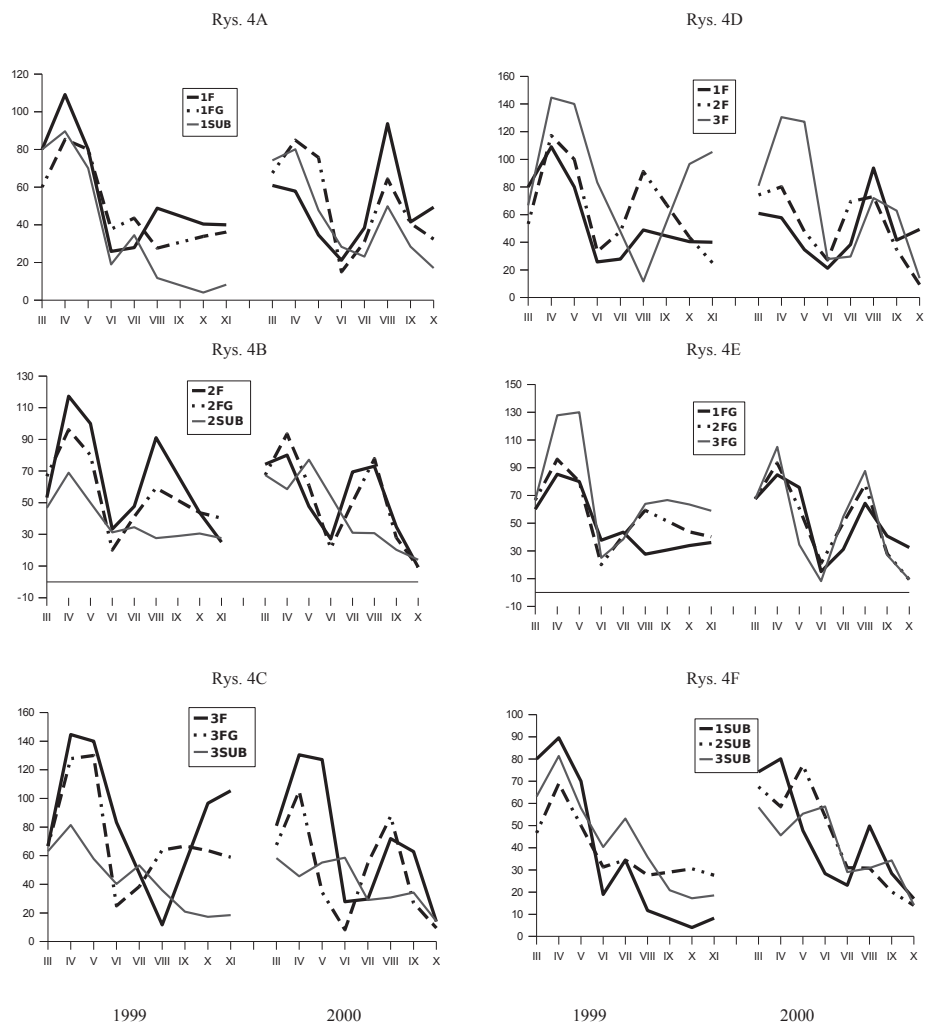


Fig. 4. Seasonal dynamic of zinc concentration change ($\mu\text{g Zn dm}^{-3}$) in surface microlayer and subsurface water of Gardno lake in 1999 (III-XI) and 2000 (III-X) year

smaller than in the case of copper, for film the mean values at locations 1 and 3 were comparable. However, the lowest enrichment factor was observed at location 2, in contrast to that of copper. In the case of Garrett film the mean enrichment factors recorded at individual samplings stations were much closer than in film.

Calculated linear correlation coefficients for lead were usually positive. At the second location for line F and location 1 for microlayer FG a low correlation coefficient was recorded. It suggests a much bigger influence of subsurface water on lead accumulation in the microlayer than that of copper. Only at location 3 this influence was negligible.

Frequency of higher lead concentrations in the surface microlayer than in subsurface water was much higher than in the case of copper and exceeded 88% and for film 100%. The frequency of cases when lead concentration in film was higher than in Garrett film

was 61%. The lowest frequency (88%) was observed for zinc. Zinc was characterized by the smallest enrichment factors at location 2, which was comparable for both microlayers and for film it amounted to 1.52, while for Garrett film it was 1.36 (Tab. 2). The highest value of these factors was observed at location 1 (2.43 for film and 2.07 for Garrett film). Frequency of cases in which $EF > 1$ for film and Garrett film amounted to 88% at location 1, 94% at location 2 and about 80% at location 3, respectively.

At the level of significance $p = 0.05$ and $n = 17$ the correlation coefficient for the content of zinc in the surface microlayer in water of Lake Gardno and the content of this metal in the subsurface microlayer showed a significant value (Tab. 3). It indicates that zinc accumulating in microlayers comes mainly from water depths.

The changes in copper concentration in the analyses of surface layers of water in Lake Gardno in the course of a year are presented in Figure 2. Completely different changes in proportions were observed at location 1 than at locations 2 and 3 (Figs. A–C). At location 1 the highest copper concentration was observed in March and April 1999 (about $68 \mu\text{g dm}^{-3}$ in film and $45 \mu\text{g dm}^{-3}$ in Garrett film) while in October 2000 it was 65 and $19 \mu\text{g dm}^{-3}$, respectively. In 1999 from spring to autumn declining trends were observed in contents of this metal in microlayers (in film from 62 in March to $37 \mu\text{g dm}^{-3}$ in November), and in 2000 there was an increasing trend (from 25 to $65 \mu\text{g dm}^{-3}$). However, at locations 2 and 3 the highest copper concentration in microlayers always occurred in the summer period, reaching its maximum in August. Particularly high concentrations were observed for film at location 3, about the highest concentration of chlorine ions (mean 730 mg dm^{-3}), in which the highest was observed in 1999 (about $211 \mu\text{g dm}^{-3}$). In August 1999 and 2000 valuables of enrichment factors for this microlayer adopted the highest values (about 10). Figures 2A–C showed clearly the influence of land and marine factors on copper concentrations in investigated surface microlayer waters. Both film (Fig. 2D) and Garrett film (Fig. 2E) in terms of copper concentrations in the summer season showed the lowest values at location 1, in the area of the Lupawa River gate region, so in this area the lowest Cl^- ion concentration was found (mean 83 mg dm^{-3}). However, the highest concentration of this metal was observed at location 3, in the sea water gate zone, thus the highest concentration of chlorine ions (mean 730 mg dm^{-3}). Results for sea water changed conditions in surface microlayers, were conducive to accumulation of considerable copper amounts. Probably the reason for such a situation is connected with neuston marine organisms, which have a bigger ability to accumulate heavy metals.

Figure 2F shows changes of copper concentration in subsurface water at individual locations. In the investigated period this concentration in this water layer changed in the smallest range from 1.6 to $25.9 \mu\text{g dm}^{-3}$. Regularity of these changes in the course of a year may not be identified. Also significant differences were observed between locations. Only in the case of location 1 the highest concentration of this metal in spring and autumn may be explained by the biggest water quantity being brought to the lake in that time by the Lupawa River. It may be stated that in most cases the lowest copper concentrations in subsurface water were observed in the summer period (locations 1 and 2) or towards the end of spring (location 3). A probable reason for this was the utilization of copper by water organisms as an element essential to vegetation and it may also result from its intensified migration to surface microlayers of water.

Changes of copper concentration in Garrett film in this lake were similar to those in film. They are characterized by two concentration maximums, one of them occurring in

spring and the other in summer. Often the concentration of this metal in film is much more higher than in Garrett film. Similarly to subsurface water, minimal copper concentrations in both microlayers were observed in May and June, and sometimes in April.

Lead contents in surface microlayers of Gardno waters changed showing two maximums – in spring and summer (Figs. 3A–F). In the analyzed summer period the maximum was found in August. In June the lowest lead concentration was observed in May 2000 (Fig. 3D). We need to stress here much higher concentrations of this metal in microlayers in spring 2000, especially at locations 1 and 3. At location 1 the spring maximum in film was five times bigger than in the summer, while at position 3 it was two times bigger.

Similarly to copper, also lead concentration in microlayers depended on the location where samples were taken. In the summer period both in film and Garrett film the lowest concentration of this metal was observed at location 1, while the highest at location 3 (Fig. 3D–E). Probably in this case the reason was also the difference in properties of sea water and those of fresh water.

Seasonal changes of lead concentration in individual surface water layers are shown in Figures 3D–F. They take a similar course in lake grounds and are characterized by two maximum concentrations, occurring in spring and summer.

Figure 4 shows seasonal changes in zinc contents in surface microlayers and subsurface water in Lake Gardno. In all cases a declining trend was observed for the concentration of this metal in the course of a year. Dynamics of changes were similar of for copper and lead. They were characterized by two maximums – in spring and summer. In the case of zinc, the spring maximum was much bigger than the summer one. It is particularly visible in Garrett film in 1999, when zinc concentration in summer at individual locations was almost two times bigger than in the summer. In the case of Garrett film the same relationship may be observed as for lead and copper, the highest concentration of zinc in summer being recorded at location 3, while the lowest at location 1 (Fig. 4E). Such relationships were not observed in film (Fig. 4D). However, this relationship was much more evident in spring both in film and in Garrett film. Zinc content in spring in microlayers from location 3 was much higher than at other locations. The biggest difference was noticed in spring 2000 (Fig. 4D), when zinc concentration in film from location 3 in April amounted to about $145 \mu\text{g dm}^{-3}$, from location 2 to $117 \mu\text{g dm}^{-3}$ and from location 1 to $109 \mu\text{g dm}^{-3}$. Thus, the influence of sea water on zinc concentration in microlayers was marked more clearly in spring than in summer.

The levels of zinc concentration in subsurface water are much bigger than those of copper and lead. The concentration ranged from 4.0 to $89.6 \mu\text{g dm}^{-3}$ (Fig. 4). In this case two maximums – spring and summer, were also observed. The course of these changes was similar to the seasonal changes in zinc concentration in subsurface water and in surface water at locations 1 and 2, which suggests that the main source of this metal in microlayers in a major part of the lake is its content in subsurface water.

DISCUSSION

Heavy metals accumulate generally in surface microlayers, yielding correlation coefficients from 1 to 100 [46]. Such a big discrepancy in enrichment factors obtained results from the type of analyzed metals, the adopted sampling technique and manageability of a given water region [17, 28, 46]. To date analyses of heavy metals contained in surface

lake water microlayers have been rare, so comparable material concerns mainly sea water. When comparing empirical values discussed in this study, those presented in Table 4, reported by Cross *et al.* [3], Hardy *et al.* [16], Hong and Lin [21], Migon and Nicolas [29], we may observe that mean enrichment factors recorded in sea and ocean waters are much higher than those for fresh water.

Table 4. Enrichment factors of surface microlayer for selected heavy metals recorded in salt water according to literature date

Region	Year	Metal	EF	References
Puget Sound, Washington	1982–1983	Cu	10–16	16
		Pb	26–65	
		Zn	14–29	
Chesapeake Bay	1986	Cu	8	17
		Pb	43	
		Zn	2,6	
Xiamen Bay, China	1987	Cu	1–2.61	21
Mediterranean Sea	1994	Pb	19	29

The accumulation of heavy metals in surface water microlayers results from physical properties of this specific subecosystem and from collection of different chemicals and microorganisms conducive to accumulation. Physical properties include the force of surface tension, adhesive force, convection of matter from deep waters and the bottom, passive transport with air bubbles. An additional type of heavy metal accumulation in the microlayer is their binding by microsuspension (colloidal system), e.g. high quality of protein, carbon hydrate and other substances, which are also collected in this subecosystem. Also neuston organisms can produce organic components, which can yield the chelation effect for heavy metals dissolved in the surface microlayer [46]. Hunter and Liss [22] and Lion and Lacke [24] suggested that dissolving metals can be included in the complexes of ions metals with organic ligands and in this form can exist in the surface microlayer. On the other hand, a fundamental source of enrichment of the microlayer with elements is rainfall, which consists of dusts and aerosols getting into microlayers thanks to gravity. In the presented studies the enrichment of surface microlayers in waters of Lake Gardno by rainfall plays the biggest role in the case of copper and lead, where obtained correlation coefficients were low (Tab. 3). In the case of lead, except for the area with a considerable effect of sea water (location 3), its concentration in deep waters is also essential. Positive correlation coefficients for zinc, recorded in this study, showed that the analyzed surface microlayers were fed with this metal by subsurface water.

In the presented results we can notice that Zn, Pb, Cu are accumulated in major quantities in the thinner microlayer (film) at each of the discussed locations (Figs. 2–4). Also Falkowska [11] showed that heavy metals and other inorganic matter are found in higher concentrations in the microlayer partly due to a closer exchange zone, i.e. the air–water interphase. This effect is caused by better collineation of inorganic matter to remain in the thinner surface layer. In the thick layer which was sampled using the Garret net we can find a higher accumulation of phytoneuston and heterotrophic bacteria than in deep waters, which facilitates the binding of heavy metals in organic combinations with live neuston cells [22, 24, 46].

The concentrations of analyzed heavy metals in terms of their contents can be ordered as follows: Zn > Pb > Cu. This statement is true both in the situation observed in subsurface water and in the analyzed surface microlayers and is consistent with the findings for sea ecosystems reported by Hardy *et al.* [17] and Lion [25].

Observed seasonal dynamics of heavy metal concentrations change in subsurface water. The correlation observed in the case of Pb and Zn indicated the influence of subsurface water on the accumulation of these metals in surface microlayers. In the case of Cu, in surface microlayers very high concentrations in September and much lower in early spring can be observed. In that time in subsurface water decreasing concentrations of these elements may usually be observed (Fig. 2). It correlates with changes observed in microlayers in the spring period (March–May) and July–August for Pb and Zn (Figs. 3 and 4). In the case of Zn and Pb one can notice a drop of concentrations in all investigated layers during May–June and after the autumn period (Figs. 3B and 4B). Scarce scientific papers analyzed seasonal changes of assayed values in surface microlayers, especially for heavy metals. In land ecosystems Hlibricht-Illkowska [20] analyzed biogenic substances in surface microlayers. Similar study was conducted in the Bay of Gdansk by Falkowska [11], who came to a conclusion that seasonal changes showed a significant temporary fluctuation, but we may find their maximum and minimum concentrations of chemical matter in close periods. When investigating such dynamism we should take into consideration the fact that the ecological situation in lakes changes each year. In the same month but different years different meteorological conditions are found, which significantly affects live organisms, thus affecting also the circulation of matter, including heavy metals analyzed in the presented study. Changes of Zn and Cu concentrations, as elements in specific quantities essential for life, are connected with the migration of neuston microorganisms [31]. Also Pb, although harmful for neuston organisms, will be included in cell structures [24, 46].

Seasonal dynamics in discussed heavy metal contents in the surface microlayers is a physical property resultant of this specific subecosystem, because they are essential for substance storage in this ecoton. On the other hand, the property of accumulation frequent for microneuston organisms, which include heavy metals in their organism and connected with permanent migration within daily and seasonal periods, will influence changes in their concentrations in subsurface water. The third element is precipitation, which influences this microlayer bringing in its load. In this case the dynamic of observing changes in the surface microlayer is not always consistent with changes observed in subsurface water.

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METALE CIĘŻKIE W MIKROWARSTWIE POWIERZCHNIOWEJ WODY JEZIORA GARDNO

W prezentowanej pracy są przedstawione wyniki analizy stężenia metali ciężkich w powierzchniowej i podpowierzchniowej warstwie wody estuariowego jeziora Gardno. Uzyskane wyniki wskazują, że są znaczące różnice między stężeniem ołowiu, miedzi i cynku w mikrowarstwie powierzchniowej wody a ich stężeniem w warstwie wody podpowierzchniowej. Zaobserwowano, że mikrowarstwa powierzchniowa ma zdolność do akumulowania znacznie wyższych ilości tych metali niż woda podpowierzchniowa. Analiza zmian sezonowych fluktuacji koncentracji metali ciężkich w mikrowarstwie powierzchniowej i podpowierzchniowej wody wskazuje na periodyczny charakter tych zmian.