

Baltic Coastal Zone No. 12	
(5-19) 2008	Institute of Biology and Environmental Protection Pomeranian Academy Słupsk

QUANTITY OF SELECTED PHYSICAL AND CHEMICAL PARAMETERS IN SURFACE MICROLAYERS AND SUBSURFACE WATER ON THE EXAMPLE OF THREE LAKES

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Abstract

For the period of 4 years, in quarter-time cycle, samples had been taken from surface microlayers and subsurface water of the lakes: Gardno, Jasiień and Dołgie Wielkie, by two techniques (Garret net and glass plate). In each talked over layers we have analyzed contents of calcium, general alkalinity, conductance and water reaction (pH). We have also determined the ability of surface microlayer to accumulate these components and we have compared it to subsurface water ability and verified whether this ability depends on the kind of the lake.

Key words: surface microlayer, lake, alkalinity, pH value, calcium, conductivity

INTRODUCTION

Knowledge about surface microlayer we owe a lot to the broad see scientific studies and relatively not-numerous researches of inland environment. Surface microlayer is several hundred μm thin layer that occurs in the contact water with atmosphere (Estep et al. 1985, Falkowska 1996, Trojanowski et al. 2001). This layer constitutes insignificant part of water environment and makes self-contained ecoton on the border of atmosphere and hydrosphere exchanging (MacIntyre 1974, Norkrans 1980). It forms itself on the surface of all water ecological systems. The surface microlayer of water containers is a special chemical and physical environment, completely different from the subsurface water. Stability of the layer is among other things determined by adhesion forces which form as a result molecular attraction on the border of two mediums: water and air. The surface tension causes physical stability of the layer. This monomolecular surface layer is a common border layer that has an enormous significance for both phases: water and atmosphere (Norkrans 1980, Falkowska 1996). Through this layer occur replacement processes changing in time and place (Falkowska 1996, Trojanowski et al. 2001, Maki and Remsen 1989). Mass

and energy exchanging is a very important process in biogeochemical circulation of chemical elements. Exchange processes between atmosphere and hydrosphere have an essential role in water environment (Norkrans 1980, Falkowska 1996, Trojanowski et al. 2001). The exchange takes place thanks to biological, chemical and radiation processes that occurs simultaneously in depths of water and atmosphere and transport processes in both mediums (Falkowska 1996). The surface microlayer influences the gas exchange (Quinn and Otto 1971, Liss 1977) and transport mechanisms from water column to the atmosphere and *vice versa* (Norkrans 1980). Dissolved substances and microorganisms reach the microlayer thanks to simple diffusion assimilated with gas bubbles. Next they are transported to this unique zone by diffusion, floated along with gas bubbles, convection movement, lifting of bottoms and subsurface water. Simultaneously the microlayer is supplied by rainfall with dust and aerosols (Garrett 1967, Jarvis 1967, Duce et al. 1976, Norkrans 1980, Lion and Leckie 1981, Falkowska 1996). All above processes lead to accumulate the majority of chemical substances and microorganisms (Norkrans 1980). During this exchange there also occurs accumulation process of different substances in surface microlayer of water environment. Literature reports underline its susceptibility to cumulate greater amounts of chemical substances and microorganisms. Concentration of these substances in surface microlayer is usually higher than the one in subsurface water (Norkrans 1980). It was found, among other things, that there was clearly higher concentration of heavy metals (Duce et al. 1972, Piotrowicz et al. 1972, Lion et al. 1979, Elzerman and Armstrong 1979, Lion and Leckie 1981, Maki and Hermansson 1994), different forms of phosphorus and nitrogen (Estep and Remsen 1985, Trojanowski et al. 2001, Mudryk et al. 2002, Falkowska 2001, Falkowska 1999, Maki and Remsen 1989), sulfur compounds (Yang et al. 2005), pesticides (Chernyak et al. 1996, Southwood et al. 1999), fatty acids, esters, alcohols (Garrett 1967, Lion and Leckie 1981, Kozarec et al. 2003), proteins (Lion and Leckie, 1981) chlorophyll (phytoplankton) (Lion and Leckie 1981, Falkowska 1999) and microorganisms (Estep et al. 1985, Maki and Remsen 1989, Mudryk et al. 1999). The majority of chemical substances is cumulating in surface microlayer and often reaches repeatedly higher concentration than in the bottom. For example, heavy metals reach concentration even 100 times higher than in subsurface water, especially in sea water (Wurld and Obbard 2004). The concentration of biogenic substances in surface microlayer of lakes and ponds reservoirs is several times higher comparing to subsurface water (Estep et al. 1985, Trojanowski et al. 2001). However not all substances at observed hydro-chemical parameters have ability to accumulate in surface microlayer. Observing this fact, we have decided to answer the question whether general alkaline, conductivity, pH and calcium concentration can have higher values in the surface microlayer in comparison to subsurface water and arrangement whether properties of surface microlayer can be dependent on the kind of a lake.

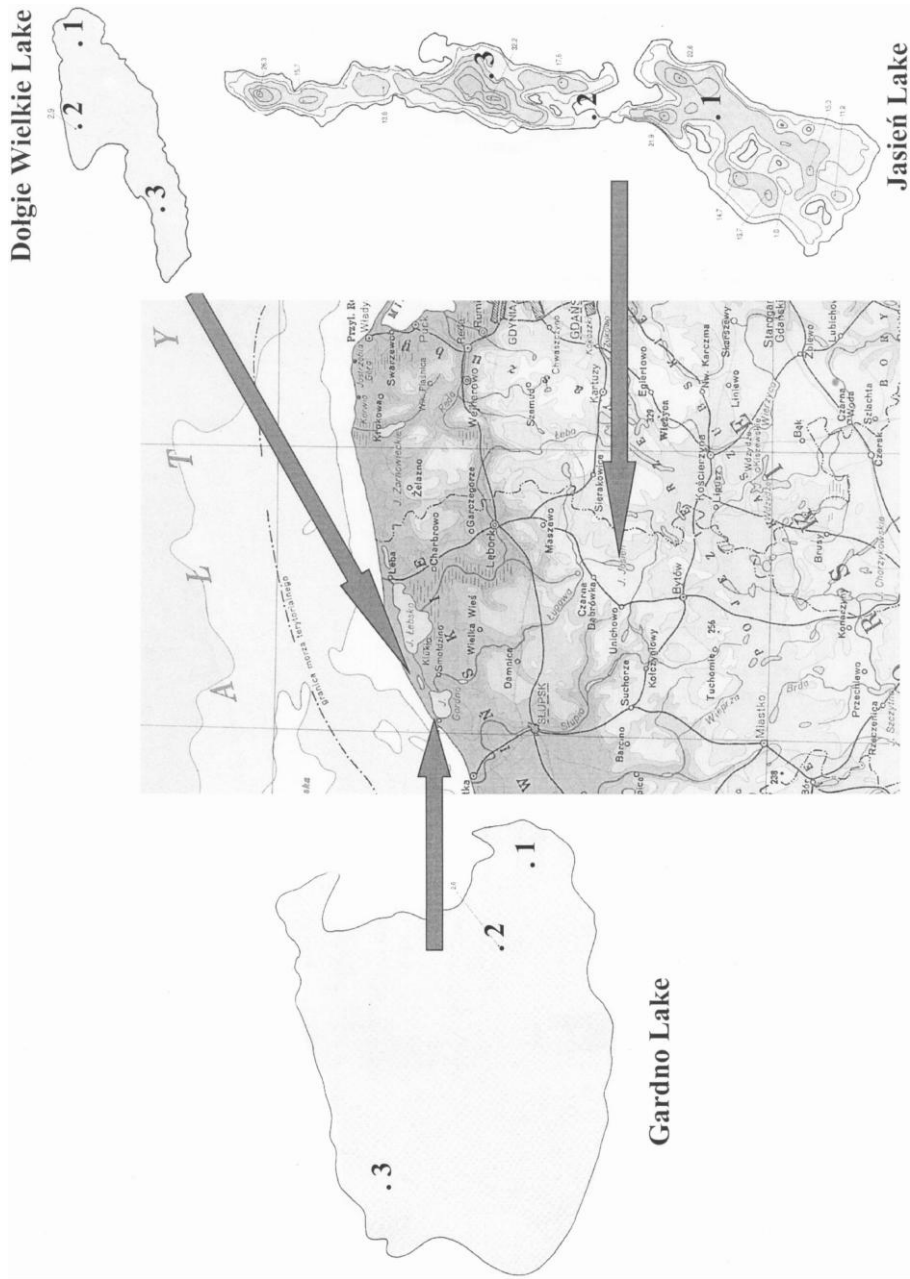


Fig. 1. Investigated lakes with marked sampling locations

MATERIALS AND METHODS

Samples of water from surface microlayer were taken from inland lake Jasień, sea-side lake Dołgie Wielkie and estuary lake Gardno. Samples were taken during 4 years in quarter cycle from 1998 to 2002 (Gardno), 2000 to 2004 (Jasień and Dołgie Wielkie). Three sampling points were located in characteristic area of each lake (Fig. 1). It is worth to take attention that the first position on lake Gardno is situated near the estuary of lake Łupawa, the third position – near the canal having a dozen meters width and linking the lake with the Baltic Sea. The choice of positions on Gardno was dictated by the fact that sea water was mixing with the lake water through the canal end hence we had observed in the third position repeatedly higher concentration of chloride ions than in the zone of the Łupawa River influence (Trojanowski 2003a). Both lakes are connected by the Łupawa River. Morphometric features are shown in the table 1.

Table 1
Morphometrical information about measured lakes (Jańczak, 1997)

	Gardno	Dołgie Wielkie	Jasień	
			northern basin	southern basin
Surface [ha]	2 468.1	156.4	240.5	336.7
Mean depth [m]	1.3	1.4	9.1	7.5
Maximal depth [m]	2.6	2.9	32.2	22.6
Volume [m ³]	30 950.5	2 151.8	21 996.4	26 052.4
Maximal lenght [m]	6 850	2650	4690	3 100
Maximal width [m]	4 730	930	900	1 465
Total lenght of shore line including islands [m]	23 350	6 675	14 150	13 190
Above mean sea level [m]	0.3	1.5	112.6	112.6
Expansion of the shore line	1.33	1.51	2.03	2.57

In water samples there were measured: general alkaline (Standard Methods 1992); pH of water by electrometric method with digital pH-meter CP-315 Elmetron (PN-90 C-045540/01); electrical specific conductivity with digital conductometer CC-315 Elmetron and electrode (PN-EN 27888, 1999) and calcium concentration (Hermanowicz et al. 1999).

Samples of surface water were taken with the usage of three techniques:

1. Technique of glass plate (SM) – trial of surface water was taken at thickness 80-115 μm . In order to take water we used glass plate (dimension: 50×50 cm and thickness 3 mm). Glass plate was immersed in water at an angle of 45 degrees. After surface water stabilization a plate was removed with speed in the range be-

- tween 5 and 20 cm's⁻¹. The sample of water was taken out by a rubber wiper from both sides of the plate to a container (Harvey and Burzell 1972).
2. Technique of Net Garret (GM) – (Garrett 1965) the trial was taken at the surface microlayer of thickness 250-300 μm. There was used a polyethylene net at dimension of 75×75 cm and mesh diameter of 0.14 mm stretched on the hanger. The net was dipped in the water similarly as glass plate and next got out by the wiper to the container (Garrett 1965, Piotrowicz et al. 1972). The boat, from which the samples were taken, was drifting to avoid diluting of water from surface microlayer by expansion of material into subsurface layer (Estep and Remsen 1985).
 3. Subsurface water (PW) was taken from the depth of 20 cm by dipping closed container which was opened in the settled deep (Hermanowicz et al. 1999).

Statistical testing in this study was performed by applying Statistica software (Statsoft, Inc.). Type of variable distribution was determined by Kolmogorov-Smirnov test and it had allowed to choose the most appropriate test (parametrical or suitable non-parametrical) to further statistical analysis of taken material (STATISTICA PL 1997, Stanisiz 1998).

In case of normal distribution the results of the test according to Kolmogorov-Smirnov were negative and there were found logarithms of all compared data. Next it was investigated whether the distribution was normal. There was used one-factor analysis of variance (ANOVA) with the test of essential Tukey's difference describing which of all researched samples had had significant statistical differences or H-Kruskal-Wallis' test with non-parametrical equivalent ANOVA, when mean values had had distribution different from normal (STATISTICA PL 1997, Stanisiz 1998).

To compare two investigated environments – the water from surface microlayer and the subsurface water – there were EF factors calculated according to below formulas:

$$EF_{SM} = \frac{C_{SM}}{C_{PW}}$$

$$EF_{GM} = \frac{C_{GM}}{C_{PW}}$$

C_{SM} – amount of analyzed parameter in surface microlayer SM,

C_{GM} – amount of analyzed parameter in surface microlayer GM,

C_{PW} – amount of the same analyzed parameter in subsurface water (Estep et al. 1985, Guitart et al. 2004).

RESULTS

The mean concentration of calcium in Jasień Lake amounted to 54.6 μg/dm³ and was 3.5 times higher than in Dolgie Wielkie Lake, and only 22% higher than in Gardno Lake (44.9 μg/dm³) (Tab. 2). Thanks to t-Tukey's test (ANOVA, F = 110.10,

Table 2
 Calcium concentration [mg/dm^3] in surface microlayers and subsurface water of measured lakes taking test stands into consideration
 (x = mean, R = difference between maximal and minimal value, SD = standard deviation)

	Gardno				Dołgie Wielkie				Jasień			
	X	R	SD	EF	X	R	SD	EF	X	R	SD	EF
1SM	50.2	64.3	18.9	1.18	13.5	22.6	5.8	1.17	61.8	50.6	12.6	1.09
1GM	47.3	61.8	18.5	1.11	12.8	21.6	5.6	1.11	61.4	57.5	15.3	1.07
1PW	43.6	59.8	18.9		11.8	21.0	5.7		57.5	55.5	14.7	
2SM	52.4	65.9	20.4	1.22	14.4	26.9	6.9	1.22	59.9	54.5	14.8	1.12
2GM	48.9	76.0	22.1	1.10	13.3	26.2	6.9	1.11	57.7	50.1	13.8	1.08
2PW	44.8	70.2	21.2		12.1	24.2	6.5		53.6	43.4	12.6	
3SM	53.5	94.0	24.7	1.17	14.5	32.3	7.9	1.18	58.1	46.9	13.3	1.11
3GM	50.7	89.6	24.4	1.10	13.8	30.7	7.7	1.10	57.3	57.2	15.3	1.08
3PW	46.4	86.3	22.7		12.6	29.4	7.2		52.7	46.1	12.9	
mean SM	52.0			1.19	14.1			1.19	59.9			1.11
mean GM	49.0			1.10	13.3			1.11	58.8			1.08
mean PW	44.9				12.2				54.6			

Table 3
Quantity of alkalinity [mval/dm³] in surface microlayers and subsurface water of measured lakes taking test stands into consideration
(x = mean, R = difference between maximal and minimal value, SD = standard deviation)

	Gardno					Dołgie Wielkie					Jasień					
	X	R	SD	EF	X	R	SD	EF	X	R	SD	EF	X	R	SD	EF
ISM	2.59	0.80	0.24	0.97	0.80	0.98	0.33	1.03	2.34	0.58	0.15	1.04	2.34	0.58	0.15	1.04
IGM	2.73	0.78	0.22	1.02	0.79	1.20	0.33	1.01	2.32	0.51	0.13	1.04	2.32	0.51	0.13	1.04
IPW	2.68	0.72	0.23		0.79	1.12	0.33		2.24	0.46	0.13		2.24	0.46	0.13	
2SM	2.30	0.60	0.18	0.97	0.87	0.97	0.30	1.14	2.26	0.67	0.16	0.96	2.26	0.67	0.16	0.96
2GM	2.38	0.77	0.24	1.00	0.76	1.14	0.32	1.05	2.28	0.77	0.17	0.96	2.28	0.77	0.17	0.96
2PW	2.38	0.70	0.21		0.79	1.23	0.32		2.37	1.01	0.26		2.37	1.01	0.26	
3SM	2.35	0.80	0.27	0.92	0.89	1.60	0.43	1.09	2.30	0.67	0.15	1.03	2.30	0.67	0.15	1.03
3GM	2.52	1.00	0.36	0.99	0.94	1.58	0.44	1.12	2.29	0.68	0.16	1.03	2.29	0.68	0.16	1.03
3PW	2.59	1.20	0.38		0.84	1.18	0.37		2.22	0.64	0.16		2.22	0.64	0.16	
mean SM	2.41			0.94	0.85			1.09	2.30			1.01	2.30			1.01
mean GM	2.54			1.00	0.83			1.06	2.30			1.01	2.30			1.01
mean PW	2.55				0.81				2.28				2.28			

$n = 48$, $p < 0.001$) we can see that there were significant statistical differences between calcium concentration in PW layer and the others researched lakes. General alkaline average in subsurface water of the Gardno Lake was three times higher than in the Dołgie Wielkie Lake and only 12% higher than in the Jasiień Lake (Tab. 3). The Tukey test has proven that there are significant statistical differences in amount of general alkaline between all researched lakes in the PW layer (ANOVA $df = 126$, $F = 483.74$, $n = 48$, $p < 0.001$) and even differences between test stands in the PW layer of the Gardno Lake (ANOVA, $df = 30$, $F = 3.33$, $p < 0.05$). The highest mean value of electric conduction has been affirmed in Gardno. Average value of electric conduction in the subsurface water of Gardno has amounted to $450.8 \mu\text{S}$ at significant and statistical differences between tests stands (ANOVA, $df = 45$, $F = 12.08$, $p < 0.001$) from average $240.7 \mu\text{S}$ in the 1st position near the Łupawa River up to $688.9 \mu\text{S}$ in the 3rd position near the village Rowy (Tab. 4). Neighbouring the Dołgie Wielkie Lake has characterized itself with the water at $110.8 \mu\text{S}$ average electric conviction and the inland lake Jasiień – $243.4 \mu\text{S}$ (Tab. 4). The average electric conviction of the Gardno Lake has been three times higher than of Dołgie Wielkie and about 85% higher than Jasiień. Thanks to non-parametric ANOVA test by Kruskal-Wallis ($N = 144$, $H = 102.78$, $p < 0.001$, $n = 48$) there was established that there exist significant statistical differences between individual lakes in PW layer. Average pH in the subsurface water of the Gardno Lake (PW) has amounted to 7.53 (Tab. 5), in Dołgie Wielkie – 7.30 and in Jasiień – 7.91. The Tukey's test (ANOVA, $df = 126$, $F = 7.19$, $p < 0.01$, $n = 48$) has shown that there are differences between Jasiień and Dołgie Wielkie lakes.

Analysing factors EF obtained for SM and GM microlayers we have established that average factors EF_{SM} and EF_{GM} for calcium are similar between test stands within each lake limits. In both lakes Gardno and Dołgie Wielkie this factor has amounted to 1.19 and has been over 7% higher than in the Jasiień Lake (Tab. 2). In spite of apparently inconsiderable difference between EF_{SM} the Tukey's test (ANOVA, $df = 141$, $F = 7.02$, $p < 0.01$, $n = 48$) has shown significant differences with EF_{SM} factors between the Jasiień Lake and the other researched objects.

EF_{SM} and EF_{GM} factors calculated for the general alkalinity for both measured subsurface microlayers had reached value near 1 and only slightly had differenced between test stands on the premises of each lakes. The EF_{SM} factor was highest in lake Dołgie (1.09) and the lowest in lake Gardno (0.94). In the GM layer the situation was similar (like in the SM layer) and correspondingly for the Dołgie Wielkie Lake the EF factor amounted to 1.06, for lake Jasiień – 1.01, and lake Gardno – 1.00. Statistically significant differences of EF_{SM} factor calculated for general alkalinity of surface microlayer in investigated lakes were confirmed by applying of non-parametric Kruskal-Wallis' test ($N = 129$, $H = 16.09$, $p < 0.01$, $n = 48$).

Analysed subsurface water the most often had shown insignificantly higher conductance than microlayers of surface water and that is why obtained EF_{SM} and EF_{GM} factors had been near lower than the one. It is necessary to pay attention that enrichment factors in the Gardno Lake having sea features (stand no. 3) were lower: $EF_{\text{SM}} = 0.84$ and $EF_{\text{GM}} = 0.86$ (Tab. 4). During analyzing EF_{SM} factors obtained for individual lakes there had been established that they had been the highest for the Dołgie Lake ($EF_{\text{SM}} = 0.98$) and the lowest for the Gardno Lake ($EF_{\text{SM}} = 0.92$). In the

Table 4
Quantity of conductance [μS] in surface microlayers and subsurface water of measured lakes taking test stands into consideration
(x = mean, R = difference between maximal and minimal value, SD = standard deviation)

	Gardno			Dolgie Wielkie			Jasien					
	X	R	SD	EF	X	R	SD	EF	X	R	SD	EF
1SM	232.0	165.2	46.2	0.97	108.5	46.5	20.1	0.97	230.2	187.3	55.9	0.94
1GM	233.7	161.9	46.5	0.97	108.5	48.0	19.7	0.97	236.7	152.3	50.8	0.97
1PW	240.7	162.9	46.0		111.9	49.1	20.6		243.2	135.0	49.2	
2SM	401.7	1 448.0	345.7	0.94	108.4	77.9	24.5	0.98	232.4	168.3	52.3	0.95
2GM	408.6	1 503.0	360.6	0.95	109.4	74.7	24.3	0.99	234.5	156.3	51.6	0.96
2PW	422.6	1 435.7	339.0		111.1	80.8	25.5		243.2	144.1	52.1	
3SM	575.2	1 244.2	441.9	0.84	107.1	70.9	23.5	0.98	231.3	163.0	54.1	0.95
3GM	579.2	1 236.6	456.2	0.86	110.8	93.8	29.7	1.01	237.0	158.0	53.0	0.97
3PW	688.9	1 249.3	463.4		109.5	91.8	26.2		243.8	163.3	53.9	
mean SM	403.0			0.92	108.0			0.98	231.3			0.95
mean GM	407.2			0.93	109.6			0.99	236.1			0.97
mean PW	450.8				110.8				243.4			

Table 5
 Values of pH in surface microlayers and subsurface water of measured lakes taking test stands into consideration
 (x = mean, R = difference between maximal and minimal value, SD = standard deviation)

	Gardno						Dołgie Wielkie						Jasień					
	X	R	SD	EF	X	R	SD	R	SD	EF	X	R	SD	EF	X	R	SD	EF
1SM	7.39	1.44	0.45	0.99	7.52	5.28	1.22	5.28	1.22	1.04	7.82	1.28	0.31	0.98	7.82	1.28	0.31	0.98
1GM	7.42	1.34	0.41	0.99	7.33	4.76	1.19	4.76	1.19	1.01	7.74	1.44	0.33	0.97	7.74	1.44	0.33	0.97
1PW	7.48	1.56	0.46		7.24	4.20	1.00	4.20	1.00		8.03	2.73	0.64		8.03	2.73	0.64	
2SM	7.80	1.97	0.65	1.04	7.45	5.36	1.30	5.36	1.30	1.04	7.76	1.00	0.30	0.99	7.76	1.00	0.30	0.99
2GM	7.32	1.70	0.50	0.99	7.22	4.88	1.25	4.88	1.25	1.01	7.71	1.31	0.33	0.98	7.71	1.31	0.33	0.98
2PW	7.52	2.31	0.64		7.15	3.41	0.90	3.41	0.90		7.86	1.86	0.42		7.86	1.86	0.42	
3SM	7.39	1.64	0.57	0.97	7.59	5.10	1.32	5.10	1.32	1.01	7.83	1.44	0.38	1.00	7.83	1.44	0.38	1.00
3GM	7.53	1.70	0.50	0.99	7.47	4.68	1.26	4.68	1.26	1.00	7.75	1.36	0.37	0.99	7.75	1.36	0.37	0.99
3PW	7.60	1.70	0.58		7.51	5.23	1.38	5.23	1.38		7.83	1.40	0.36		7.83	1.40	0.36	
mean SM	7.53			1.00	7.52					1.03	7.80			0.99	7.80			0.99
mean GM	7.42			0.99	7.34					1.01	7.73			0.98	7.73			0.98
mean PW	7.53				7.30						7.91				7.91			

GM layer there had been similar situation. Thanks to non-parametric ANOVA Kruskal-Wallis' test ($N = 144$, $H = 8.72$, $p < 0.05$, $n = 48$) there had been established that there were statistical differences with values of EF_{SM} and EF_{GM} factors for conduction between measured lakes ($N = 144$, $H = 10.42$, $p < 0.01$, $n = 48$).

Average factors EF_{SM} and EF_{GM} obtained for pH of water amounted near to 1 in each lake and they had not been diversified too much within the lakes. The factor EF_{SM} was the highest in Dołgie Wielkie Lake ($EF = 1.03$), in Gardno Lake amounted to 1.00 and in Jasię Lake – 0.99 (Tab. 5). According to ANOVA Kruskal-Wallis' test ($d f = 129$, $H = 13.40$, $p < 0.01$, $n = 48$) the differences connected with EF_{SM} were statistically significant.

DISCUSSION

Quantities of all four analysed parameters obtained from lakes Gardno, Jasię and Dołgie Wielkie showed that EF_{SM} i EF_{GM} factors had amounted near to 1. As was mentioned before in introduction, majority of chemical substances were cumulated in subsurface microlayers several to even one hundred times more than in subsurface water (Wurld and Obbard 2004), on the other hand, analyzed parameters had not been cumulated in surface microlayers or had been slightly cumulated. Analogous conclusions were showed by Münster et al. (1998). In Finland lakes there were investigated numerous hydrochemical parameters and there were obtained samples of surface microlayer thanks to the technique of glass plate. There was established that pH in SM microlayer in Mekkojärvi Lake had shown EF_{SM} factor equal 1.08 and in lake Valkjärvi – 1.02, that is pH had been higher in microlayer than in subsurface water. These results can be acknowledged to these ones which were obtained in measured lakes Dołgie Wielkie and Gardno. On the other hand, there where factors amounted suitably: $EF_{SM} = 0.99$ and $EF_{GM} = 0.98$ in the layer of subsurface water concentration of H^+ ions had been higher in surface layer than subsurface water. Zhang et al. (2003) obtained similar results like in the Jasię Lake.

In case of conductance as well Münster et al. (1998) obtained enrichment factor near to 1, that is $EF_{SM} = 1.06$ in lake Mekkojärvi and $EF_{SM} = 1.03$ in Valkjärvi what corresponded to the result of this factor obtained in lakes Gardno, Dołgie Wielkie and Jasię as well to measures led in Norwegian lake Skjervatjern by Knulst et al. (1997).

In lakes with higher salinity like Gardno, conductance exactly correlates with amount of chloride ions which does not cumulate in surface layer (Mudryk et al. 2002). That is why $EF_{SM} = 0.84$ and $EF_{GM} = 0.86$ factors in Gardno reach the lowest value in the 3rd position (Tab. 4). In this test stand concentration of chloride ions is several times higher than in the 1st position (Trojanowski and Trojanowska 1999, Trojanowski 2003b).

Wurld and Obbard (2004) maintain that conductance and pH of the subsurface water achieve values similar to these in surface water and layer of subsurface water. These factors influence the enrichment of the surface microlayer in other chemical substances, for example heavy metals. Probably general alkalinity and calcium concen-

tration as factors influencing pH should even influence the ability to cumulate substances like heavy metals in surface microlayer. Especially significant meaning has conductance. For example in water characterized by high conductance (ocean and sea water) EF_{SM} factors with heavy metals reach values even to 65 (Hardy et al. 1985, Hardy et al. 1990), on the other side in the lake water these factors reach values to 2-10 (Antonowicz and Trojanowski, in press).

Factors quantity of EF_{SM} and EF_{GM} in analyzed lakes oscillate about 1, however seemingly fine differences turn out statistical significant in followed cases:

- EF_{SM} in case of conductance, calcium enrichment and pH,
- EF_{GM} in case of conductance.

One of probable cause of obtaining the statistical differences with microlayer enrichment SM in these parameters can be different amount of these parameters in subsurface water. Moreover these parameters can directly have influence one on another like calcium concentration increase should cause pH increase in the direction of alkalinity, what is visible in case of Jasiień Lake where we can see both the highest value of pH and calcium concentration.

For the quite small enrichment of the surface microlayer in calcium in comparison to most of metals appeals its small content in the rain water. For example rain-water, tested in Pomerania, contains only 2.3 mg/dm^3 of calcium (Szefer and Szefer, 1986). Probably calcium reveals quite small ability to accumulation as in lake as in sea water what results obtained by Bigg et al. (2004) confirm.

REFERENCES

- Antonowicz J., Trojanowski J. Heavy metals in water microlayers of shallow estuarine Gardno Lake (in press).
- Atlas jezior Polski. (The atlas of Polish lakes). 1997. (Ed.) J. Jańczak, *Inst. of Meteor. and Water Man.*, Poznań, (in Polish).
- Bigg K., Leck C., Tranvik L., 2004. Particulates of the surface microlayer of open water in the central Arctic Ocean in summer. *Mar. Chem.*, 91, 131-141.
- Chernyak S., Rice C., McConnel L., 1996. Evidence of currently-used pesticides in air, ice, seawater and surface microlayer in the Bering and Chukchi Seas. *Mar. Poll. Bull.*, 32(5), 410-419.
- Duce R., Quinn J., Olney C., Piotrowicz S., Ray B., Wade T., 1972. Enrichment of heavy metals and organic compounds in the surface microlayer of Narragansett Bay, Rhode Island. *Science*, 176, 161-163.
- Duce R., Hoffman G., Ray B., Fletcher I., Wallace G., Fasching J., Piotrowicz S., Walsh P., Hoffman E., Miller J., Heffter J., 1976. Trace metals in the marine atmosphere: sources and fluxes. In: *Marine pollutant transfer*. (Eds.) H.L. Windom, R.A. Duce, Lexington Books, Lexington, 77-119.
- Elzerman A.W., Armstrong D.E., 1979. Enrichment of Zn, Cd, Pb and Cu in the surface microlayer of Lakes Michigan, Ontario and Mendota. *Limnol. Oceanogr.*, 24, 133-144.
- Estep K., Maki J., Danos S., Remson C., 1985. The retrieval of material from the surface microlayer with screen and plate samples and its implications for partitioning of material within the microlayer. *Freshw. Biol.*, 15, 15-19.
- Estep K., Remsen C., 1985. Influence of the surface microlayer on nutrients, chlorophyll and algal diversity of a small eutrophic bog pond. *Hydrobiol.*, 121, 203-213.

- Falkowska L., 1996. Mikrowarstwa powierzchniowa morza. (Sea surface microlayer). UG Gdańsk, (in Polish).
- Falkowska L., 1999. Sea surface microlayer: a field evaluation of teflon plate, glass plate and screen sampling techniques. Part 2. Dissolved and suspended matter. *Oceanol.*, 41(2), 56-63.
- Falkowska L., 2001. 12-hour cycle of matter transformation in the sea surface microlayer in the offshore watersea of the Gdańsk Basin (Baltic Sea) during spring. *Oceanol.*, 43(2), 201-222.
- Garrett W., 1965. Collection of slick forming materials from the sea surface. *Limnol. Oceanogr.*, 10, 602-605.
- Garrett W., 1967. The organic chemical composition of the sea surface. *Deep-Sea Res.*, 14, 221-227.
- Guitart C., Garcia-Flor N., Dachs J., Bayona J., Albaigas J., 2004. Evaluation of sampling devices for the determination of polycyclic aromatic hydrocarbons in surface microlayer coastal waters. *Mar. Poll. Bull.*, 48, 961-968.
- Hardy J., Apts C., Crecelius E., Bloom N., 1985. Seasurface microlayer metals enrichments in an urban and rural bay. *Est. Coast. Shelf Sci.*, 20, 299-312.
- Hardy J., Crecelius E., Antrim L., Kiesser S., Broadhurst V., 1990. Aquatic surface microlayer contamination in Chesapeake Bay. *Mar. Chem.*, 28, 333-351.
- Harvey G., Burzell L., 1972. A simple microlayer method for small samples. *Limnol. Oceanogr.*, 17, 156-157.
- Hermanowicz W., Dojlido J., Dożańska W., Koziorowski B., Zerbe J., 1999. Fizykochemiczne badanie wody i ścieków. (Physico-chemical studies on waters and waste waters). Arkady, Warszawa, (in Polish).
- Jarvis N., 1967. Adsorption of surface-active material at the sea-air interface. *Limnol. Oceanogr.*, 12, 213-221.
- Knulst J., Backlund P., Hessen D., Riise G., Södergren A., 1997. Response of surface microlayers to artificial acid precipitation in a meso-humic lake in Norway. *Wat. Res.*, 31(9), 2177-2186.
- Kozarac Z., Čosović B., Frka S., Möbius D., Hacke S., 2003. Complex methodological approach to the studies of natural microlayers at the air/water interface. *Colloids and Surfaces A: Physicochem. Eng. Aspects*, 219, 173-186.
- Lion L., Harvey R., Young L., Leckie J., 1979. Particulate matter. Its association with microorganisms and trace metals in an estuarine salt marsh microlayer. *Environ. Sci. Technol.*, 13, 1522-1525.
- Lion L., Leckie J., 1981. The biogeochemistry of the air-sea interface. *Ann. Rev. Earth Planet. Sci.*, 9(4), 49-86.
- Liss P., 1977. Effect of surface films on gas exchange across the air-sea interface. *Rapp. P.V. Reun. Cons. Int. Explor. Mer.*, 171, 120-124.
- MacIntyre F., 1974. The top milimeter of the ocean. *Sci. Am.*, 230, 62-77.
- Maki J., Remsen C., 1989. Examination of a freshwater surface microlayer for diel changes in the bacterioneuston. *Hydrobiol.*, 182, 25-34.
- Maki J., Hermansson M., 1994. The dynamics of surface microlayers in aquatic environments. The biology of particles in aquatic systems. In: *Biology of particles in aquatic systems*. (Ed.) R.S. Wotton, CRS Press, 7, 161-182.
- Mudryk Z., Donderski W., Skórczewski P., Walczak M., 1999. Neustonic and planktonic bacteria isolated from a brackish lake Gardno. *Pol. Arch. Hydrobiol.*, 46, 121-129.
- Mudryk Z., Trojanowski J., Antonowicz J., Skórczewski P., 2002. Chemical and bacteriological studies of surface and subsurface layers in estuarine lake Gardno. *Pol. J. Env. Stud.*, 12(2), 199-206.

- Münster U., Heikkinen E., Knulst J., 1998. Nutrient composition, microbial biomass and activity at the air-water interface of small boreal forest lakes. *Hydrobiol.*, 363, 261-270.
- Norkrans B., 1980. Surface microlayer in aquatic environments. *Adv. Microb. Ecol.*, 4, 51-85.
- Quinn J., Otto N., 1971. Carbon dioxide exchange at the air-sea interface: Flux augmentation by chemical reaction. *J. Geophys. Res.*, 76, 1539-1549.
- Piotrowicz S., Ray B., Hoffman G., Duce R., 1972. Trace metals enrichment in the seasurface microlayer. *J. Geophys. Res.*, 77, 5243.
- PN-90 C-045540/01, 2001. Badania pH, kwasowości i zasadowości. Woda i ścieki. Polska Norma. (Test for pH, acidity and alkalinity. Water and waste waters. Polish standard). *Pol. Comm. of Meas. and Qual. Norm.*, (in Polish).
- PN-EN 27888 (in agreement with ISO 7888:1985), 1999. Oznaczanie przewodności elektrycznej właściwej. Jakość wody. Polska Norma. (Determination of electrolytic conductivity. The quality of water. Polish standard). *Pol. Comm. of Meas. and Qual. Norm.*, (in Polish).
- Southwood J., Muir D., Mackay D., 1999. Modelling agrochemical dissipation in surface microlayers following aerial deposition. *Chemosphere*, 38(1), 121-141.
- Standard methods for the examination of water and wastewater 18th edition 1992. APHA, Washington.
- Stanisz A., 1998. Przystępny kurs statystyki w oparciu o program STATISTICA PL na przykładach z medycyny. (Statistics course based on medicine examples supported by STATISTICA PL software). *StatSoft Polska*, Kraków, (in Polish).
- STATISTICA PL, 1997. Podręcznik użytkownika. Tom 1: Ogólne konwencje i statystyki. (User's guide. Volume 1: General conventions and statistics). *StatSoft Polska*, (in Polish).
- Szefer P., Szefer K., 1986. Some metals and their possible sources in rain water of the southern Baltic coast, 1976 and 1978-1980. *Sci. Total Env.*, 57, 79-89.
- Trojanowski J., Trojanowska C., 1999. Ładunek zanieczyszczeń wprowadzany dopływami jezior Słowińskiego Parku Narodowego. (Pollution loads introduced by Słowiński National Park lake's tributaries). *Słupskie Pr. Mat.-Prz.*, PAP Słupsk, 12b, 93-104, (in Polish).
- Trojanowski J., Trojanowska C., Antonowicz J., 2001. Nitrogen and phosphorus in surface microlayers of estuarine, shallow lake (north Poland). *Ecohydrobiol. and hydrobiol.*, 1(4), 457-463.
- Trojanowski J., 2003a. Usytuowanie i ogólna charakterystyka jeziora. W: Jezioro Gardno. (The location and general characteristics of Gardno Lake. In: Gardno Lake). (Ed.) Z. Mudryk, PAP Słupsk, 456, 9-12, (in Polish).
- Trojanowski J., 2003b. Charakterystyka hydrochemiczna. W: Jezioro Gardno. (Hydrochemical characteristics. In: Gardno Lake). (Ed.) Z. Mudryk, PAP Słupsk. 456, 53-63, (in Polish).
- Yang G., Tsunogai S., Watanabe S., 2005. Biogenic sulfur distribution and cycling in the surface microlayer and subsurface water of Funka Bay and its adjacent area. *Cont. Shelf Res.*, 25, 557-570.
- Wurld O., Obbard J., 2004. A review of pollutants in the sea-surface microlayer (SML): a unique habitat for marine organisms. *Mar. Poll. Bull.*, 48, 1016-1030.
- Zhang Z., Liu L., Liu C., Cai W., 2003. Studies of the surface microlayer II. The layer of sudden change of physical and chemical properties. *J. Colloid Interface Sc.*, 264, 148-159.

WIELKOŚĆ WYBRANYCH PARAMETRÓW FIZYKOCHEMICZNYCH
W MIKROWARSTWIE POWIERZCHNIOWEJ
I W WODZIE PODPOWIERZCHNIOWEJ NA PRZYKŁADZIE TRZECH JEZIOR

Streszczenie

Przeanalizowano zdolność wzbogacania wybranych parametrów hydrochemicznych w mikrowarstwach powierzchniowych wybranych trzech jezior. Ustalono, że zasadowość ogólna, konduktacja, odczyn wody oraz stężenie wapnia nieznacznie odbiegają od tego, jakie uzyskuje się w wodzie podpowierzchniowej. Wynik taki świadczy, że mikrowarstwa powierzchniowa wody jeziornej w określonych przypadkach ma zdolność do kumulowania substancji chemicznych w ilościach wielokrotnie wyższych niż woda podpowierzchniowa, jednakże w przypadku parametrów omawianych w prezentowanej pracy zjawisko to występuje w znacznie mniejszym stopniu. Niemniej potwierdzono testem ANOVA, że uzyskane współczynniki EF_{SM} w przypadku konduktancji, wzbogacania w wapń i odczynu wody oraz EF_{GM} w przypadku konduktancji różniły się statystycznie w badanych trzech jeziorach. Analiza statystyczna dowodzi, że zjawisko wzbogacania lub zubożania mikrowarstwy powierzchniowej istnieje w przypadku analizowanych w prezentowanej pracy parametrów i jest zależne prawdopodobnie od składu hydrochemicznego wody w poszczególnych jeziorach.