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CAPACITY TO ACCUMULATE BARIUM, STRONTIUM, CALCIUM AND MAGNESIUM IN THE WATER-AIR INTERFACE OF A COASTAL LAKE AT THE BALTIC SEA

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Abstract

Studies were conducted to determine the capacity to accumulate four metals – barium, strontium, calcium and magnesium in a coastal lake, Dołgie Wielkie. The lake is situated in World Biosphere Reserve – the Slovinski National Park. Water samples were collected from the surface microlayer (SML) using the Garrett mesh screen and at the same time samples were also collected from the subsurface water layer. Metal concentrations were analysed using a mass spectrometer. The enrichment factors were determined for metals in the surface microlayer. The greatest accumulation capacity was observed for barium. A lesser accumulation capacity was found for magnesium. Concentrations of calcium and strontium were comparable in both investigated layers. Seasonal variation was observed for all analyzed metals.

Key words: coastal lake, surface microlayer, metals

INTRODUCTION

The ecotone of the surface microlayer (SML) constitutes a thin layer at the hydrosphere and atmosphere interface, being operationally defined as the uppermost millimeter of the water column (Bigg et al. 2004, Agogué et al. 2005, Santos et al. 2011). It is defined as a complex and unique ecosystem with a total thickness of 1-1000 μm, depending on many factors such as the amount of organic matter, wind speed, etc. (Cincinelli et al. 2001).

The surface water microlayer is an important boundary as an area of exchange of matter and energy between the hydrosphere and the atmosphere (Kozarec et al. 2003), which both affects and is affected by global changes (Gašparović et al. 2007).

According to Hardy (1982), SML has a laminar structure. In the opinion of Wurl et al. (2009) and Engel and Galgani (2015), the surface microlayer has a gel-like proteinaceous composition.

The surface microlayer is a specific and very dynamic ecotone at the water interface. It is affected by a number of environmental factors, such as precipitation (e.g. rain) and wind, which disintegrate its structure and consequently this biotope undergoes dynamics changes both in time and space (Romano and Marquet 1991). Its structure is also disintegrated by photochemical reactions, water circulation and biological activity (Galgani and Engel 2015). Still, the surface microlayer is well fit for fast self-reconstruction of its original structure (Hale and Mitchell 1997). According to Green and Houk (1979), the average time of relaxation of the surface microlayer since the time of the onset of a disturbing factor is 0.2 s, while its full reconstruction of the original structure lasts about 30 minutes.

Physical forces observed in SML, such as surface tension, adhesion or cohesion forces, stabilize it and provide relative stability (Norkrans 1980, Maki and Hermansson 1994). SML is capable of accumulating many chemicals and microorganisms at much greater concentrations than those observed in the subsurface water (SUB). The accumulation capacity is connected with physical forces, as well as chemical and biological factors. In this respect we need to mention simple diffusion, turbulent mixing, scavenging, convection, upwelling of underlying waters, atmospheric deposition, transport by bubbles, buoyant particles contributing to the concentration of numerous organic and inorganic compounds as well as microorganisms at the SML (The Sea Surface... 1997, Gašparović et al. 2007, Santos et al. 2011, 2013). A high capacity to accumulate in SML was found particularly for heavy metals (Wurl and Obbard 2004, Antonowicz et al. 2015), phosphorus and nitrogen compounds (Trojanowski et al. 2001, Mudryk et al. 2003), organic carbon (Freeman and Lock 1995), fatty acids, esters and alcohols (Kozarec et al. 2003) as well as microorganisms (Estep et al. 1985, Mudryk et al. 2003). However, not all chemical substances have accumulate in the surface microlayer in greater concentrations than those found in subsurface water. For example, it was stated that chloride ions (Trojanowski et al. 2001) and calcium (Antonowicz 2008a, b) are typically found in comparable concentrations in SML and SUB.

The aim of this study was to investigate the accumulation capacity in the surface water microlayer of a coastal lake, Dołgie Wielkie, for metals of group 2 of the periodical table, such as Ba, Sr, Ca and Mg, as well as show seasonal dynamics of these metals in the surface microlayer and in the subsurface water.

MATERIALS AND METHODS

The object of the study was the Dołgie Wielkie Lake. Geographic coordinates of this lake are 54°41'29.25" – 54°42'11.10"N, 17°10'13.10" – 17°12'34.18"E (Fig. 1). The lake is located in the World Biosphere Reserve – the Slovinski National Park (Poland) in the Gardno-Łebsko Lowland between two large estuarine lakes, Gardno and Łebsko. At present the lake is not directly connected with the Baltic. Morphometric data of the lake are given in Table 1. It is a shallow lake of 156.4 ha in area, the mean depth of 1.4 m and maximum depth of 2.9 m. The shoreline of the lake basin is 6,675 m in length and it is relatively undeveloped (Atlas jezior Polski... 1997).

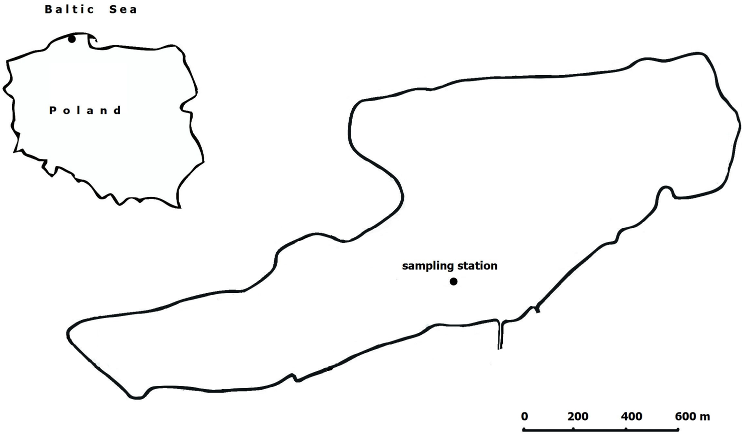


Fig. 1. The sampling station on the Dołgie Wielkie Lake (a contour map of Poland on the left)

Table 1

Morphometric parameters of the Dołgie Wielkie Lake (Atlas jezior Polski... 1997)

Parametr	Value
Area surface of water level [ha]	156.4
Average depth [m]	1.4
Maximum depth [m]	2.9
Average capacity [10^3 m^3]	2151.8
Maximum length [m]	2650.0
Maximum width [m]	930.0
Length of shore line [m]	6675.0
Expansion of shore line [m]	1.51
Height above sea level [m]	1.50

The lake is not subjected to thermal stratification or variation in dissolved oxygen levels, it is polymictic, similarly as most coastal lakes. Winds cause water mixing reaching the bottom (Trojanowski et al. 1990, Antonowicz 2013). The catchment area is covered with forests for a 87%, with the predominance of coniferous trees, particularly the scots pine (*Pinus sylvestris* L.). (Klimaszyk et al. 2015). Forests and tree plantings reduce the force of winds over the lake surface.

The nutrient concentrations presented in Table 2 indicate that it is a eutrophic lake of low salinity (Antonowicz 2013). High concentrations of biogenic substances and the eutrophic character of the lake result in natural, slow shallowing and overgrowing of the studied water body (Antonowicz et al. 2015). Heavy metal contents are low (Antonowicz et al. 2015). Generally, the lake does not have any tributaries and it is being supplied primarily with rainwater and, to a lesser extent, groundwater (Klimaszyk et al. 2015). There are not settlements, resorts or industrial facilities in the immediate vicinity of the lake. From the south lake Dołgie Wielkie is connected with a watercourse, which drains the lake and which joins it with the Gardno–Łebsko canal (Komunikat o stanie... 1995).

Table 2

Chemical and microbiological parameters of the Dołgie Wielkie Lake according to Antonowicz et al. (2010, 2015) and Antonowicz (2013)

Parameter in water	Unit of measure	Mean (SD)	Parameter in water	Unit of measure	Mean (SD)
N-T	mg dm^{-3}	0.77 (0.09)	Cr	μg dm^{-3}	2.92 (1.36)
N-org	mg dm^{-3}	0.69 (0.09)	Mn	μg dm^{-3}	86.85 (46.67)
$N\text{-}NH_4$	μg dm^{-3}	78.75 (11.85)	Co	μg dm^{-3}	0.30 (0.13)
$N\text{-}NO_2$	μg dm^{-3}	2.05 (0.79)	Ni	μg dm^{-3}	7.50 (4.10)
P-T	μg dm^{-3}	123.3 (36.53)	Cu	μg dm^{-3}	4.93 (3.26)
P-org	μg dm^{-3}	47.08 (30.53)	Zn	μg dm^{-3}	22.79 (18.86)
$P\text{-}PO_4$	μg dm^{-3}	76.21 (11.48)	Ag	μg dm^{-3}	0.02 (0.01)
Electrical conductivity	mS	0.089 (0.002)	Cd	μg dm^{-3}	0.18 (0.14)
Chlorophyll *a*	μg dm^{-3}	30.37 (32.22)	Pb	μg dm^{-3}	5.84 (6.00)
Total bacteria	10^6 cells cm^{-3}	1.99 (0.83)	Cl	mg dm^{-3}	15.86 (0.51)
Heterotrophic bacteria	10^3 cells cm^{-3}	23.63(29.29)	O_2	mg dm^{-3}	9.22 (1.99)

According to Antonowicz et al. (2015), the dominant bacterial genera recorded in the subsurface of Lake Dołgie Wielkie were *Agrobacterium (*13.3%), *Flexibacter* (12.2%) and *Cytophaga* (10.0%). The dominant phytoplankton groups were *Chlorophyta* (34.0%), *Cyanoprokaryota* (33.6%) and *Bacillariophyceae* (25.9%). The taxonomic composition of the phytoplankton confirms the eutrophic character of the lake (Brettum and Andersen 2005, Antonowicz et al. 2015).

Lake shores are covered by abundant vegetation showing a strong tendency to overgrow this water body. Rush vegetation covers 13.8% lake area and overgrows 37.1% shore line (Komunikat o stanie... 1995). In the lake we may find rich macroflora comprising 31 species of macrophytes, with *Littorella uniflora*, *Polygonum amphibium*, *Nuphar lutea*, *Potamogeton natans* and *Eleocharis palustri* as dominant species (Klimaszyk et al. 2015).

According to the ichthyologic typology the Dołgie Wielkie Lake is a tench-pike lake (Komunikat o stanie... 1995). Species reported in this lake include e.g. *Abramis brama*, *Scardinius erythrophthalmus*, *Esox lucius*, *Rutilus rutilus* and *Tinca tinca* (Ciepielewski et al. 2003). Fishing and angling are prohibited in the lake (Komunikat o stanie... 1995).

SAMPLING

Samples were seasonally collected from one sampling station located in the southern part of Lake Dołgie Wielkie (Fig. 1) during two years from October 2005 to September 2007, except for the time when the lake was covered with ice.

Samples of the surface microlayer (SML) (thickness 242 μm ± 40) were collected with a Garrett net (Garrett 1965), while samples of the subsurface layer (SUB) were taken at the depth of about 10-15 cm. The Garrett net was sterilised with ethanol and deionised distilled water in the laboratory, and just before the sampling procedure with the first water samples from the lake. According to Ahlers et al. (1990) contamination-free procedure etching with nitric acid V and then rinsing with demineralized water was used to remove chemical contamination from glass containers and PET.

CHEMICAL ANALYSES

The water samples were mineralized according to the USEPA (1998) standard in the nitric acid V *trace pure* (Merck, Darmstadt, Germany). The concentrations of heavy metals, i.e.: Ba, Sr, Ca and Mg were measured by Perkin Elmer Elan DRC-e mass spectrometer. Then these results were compared sequentially for each metal separately with the reference standard samples (produced by Perkin Elmer company) by the instrument controlled by the ELAN Perkin Elmer SCIEX Instrument Control software. As a blank sample, the sample obtained from the water deionizer (Hydrolab company) was used. In order to check the accuracy of the method, a reference material TM-24.3 (water from Lake Ontario, Environment Canada) and ES-L-1 (Ground Water, EnviroMAT) was used. By application of recovery standards, the following loss and gains were reported: Mg 105 ± 16%, Ca 112 ± 17%, Sr 105 ± 8%, Ba 102 ± 5%.

STATISTICAL ANALYSIS

In order to compare the investigated layers, i.e., surface microlayer and subsurface water, we applied average enrichment factors

$$EF = \frac{C_{SML}}{C_{SUB}}$$

where C_{SML} and C_{SUB} are concentrations of analysed metals (Estep et al. 1985).

The statistical analyses such as the Shapiro–Wilk normality test, mean, mediana, minimum, maximum, standard deviation and Spearman rs correlation was calculated according to Luszniewicz and Słaby (2008).

RESULTS

Concentrations of analyzed group 2 metals in SML formed the following series: Sr < Ba < Mg < Ca, while in the SUB layer it was Ba < Sr < Mg < Ca (Tables 3 and 4).

Mean concentrations of these metals in the surface microlayer were as follows: strontium 65.05 µg dm^{-3}, barium 77.94 µg dm^{-3}, magnesium 1.85 mg dm^{-3} and calcium 8.86 mg dm^{-3} (Table 3). Standard deviations were: Sr – 18.56 µg dm^{-3}, Ba – 119.11 µg dm^{-3}, Mg – 0.85 mg dm^{-3} and Ca – 2.86 mg dm^{-3}. In the subsurface water layer mean concentrations were as follows: strontium 56.17 µg dm^{-3}, barium 18.94 µg dm^{-3}, magnesium 1.40 mg dm^{-3} and calcium 8.04 mg dm^{-3} (Table 4). In turn, standard deviations in the SUB layer were: Sr – 8.79 µg dm^{-3}, Ba – 4.09 µg dm^{-3}, Mg – 0.38 mg dm^{-3} and Ca – 1.97 mg dm^{-3}.

Table 3

Statistical parameters of studied metals in the surface microlayer of water
of the Dołgie Wielkie Lake

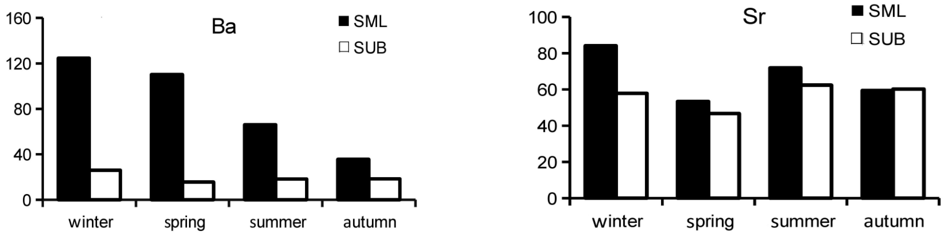
Parameters	Mean	Median	SD	Min.	Max.	EF$_{Mean}$	EF$_{Median}$
Mg [mg dm^{-3}]	1.85	1.43	0.85	0.90	3.46	1.33	1.08
Ca [mg dm^{-3}]	8.86	7.49	2.86	5.28	15.75	1.10	0.98
Sr [µg dm^{-3}]	65.05	58.43	18.56	43.31	108.22	1.16	1.05
Ba [µg dm^{-3}]	77.94	32.39	119.11	14.69	518.52	4.12	1.71

Table 4

Statistical parameters of studied metals in the subsurface water
of the Dołgie Wielkie Lake

Parameters	Mean	Median	SD	Min.	Max.
Mg [mg dm^{-3}]	1.40	1.32	0.38	0.68	2.19
Ca [mg dm^{-3}]	8.04	7.67	1.97	5.48	14.32
Sr [µg dm^{-3}]	56.17	55.84	8.79	43.32	75.98
Ba [µg dm^{-3}]	18.94	18.97	4.09	11.64	29.46

Presented enrichment factors were highest for barium at EF_{Ba} = 4.12 and lowest for calcium at EF_{Ca} = 1.10, forming a series of Ba > Mg > Sr > Ca (Table 3).
Analyzed metals showed seasonal variation in both investigated layers (Fig. 2). Barium concentrations in the surface microlayer were highest in winter. These concen-



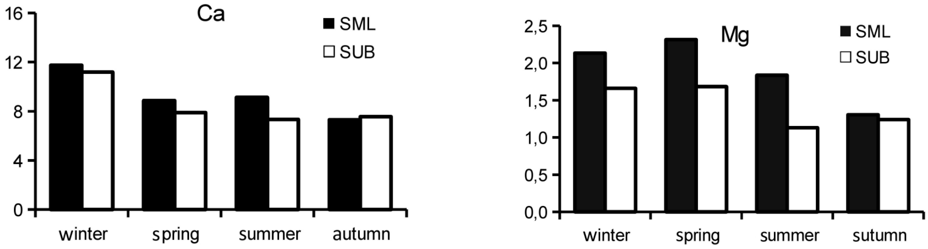


Fig. 2. Seasonal variation in the concentration of barium, strontium (μg dm^{-3}), calcium and magnesium (mg dm^{-3}) in the surface microlayer and subsurface water layer of lake Dołgie Wielkie (data show seasonal average from 2 years)

trations decreased 3.5-fold from winter to autumn. In the subsurface water layer the highest concentrations were observed in winter, being 1.7-fold greater than in spring. The highest enrichment factor was recorded in spring and it was as high as 7.04 (Fig. 3).

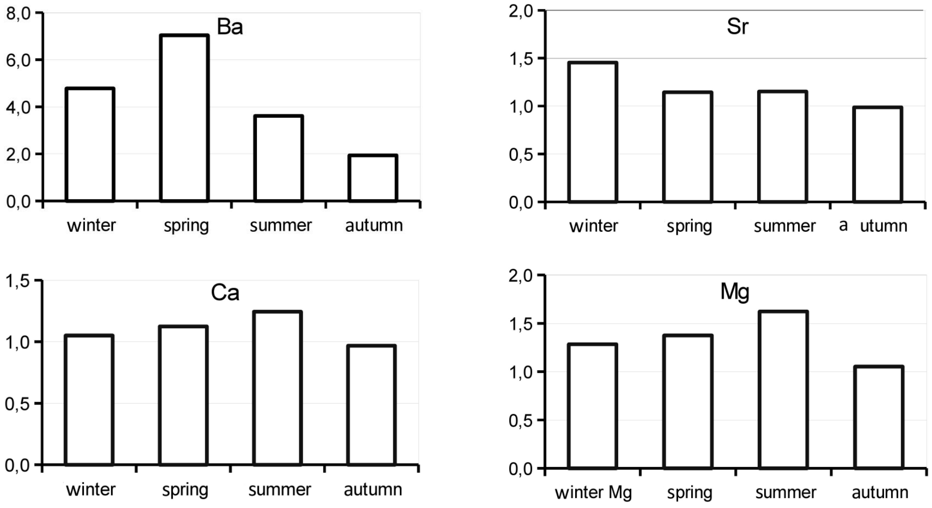


Fig. 3. Seasonal variation in the enrichment factor of barium, strontium, calcium and magnesium in the surface microlayer of lake Dołgie Wielkie (data show seasonal average from 2 years)

Strontium concentrations in the surface microlayer were highest in winter and summer, and they were by 38% higher than in spring and autumn. In the subsurface water layer the lowest concentrations were observed in spring, while the highest (by 33% greater) concentrations of strontium were recorded in summer (Fig. 2). Maximum mean EF_{Sr} of 1.45 was reported in winter, while the minimum enrichment factor of 1.04 was observed in autumn (Fig. 3).

Magnesium was found at highest concentrations in SML in spring, while in autumn concentrations of this element were almost two-fold lower. In the SUB layer the highest concentrations were recorded in spring, while they were lowest in summer (Fig. 2). Enrichment factors for magnesium ranged from 1.02 in autumn to 1.62 in spring (Fig. 3).

Seasonal dynamics of calcium in SML and SUB indicate the highest concentrations of this element in winter and the lowest in autumn (Fig. 2). Recorded enrichment factors for calcium were close to 1 and ranged from 0.96 in autumn to 1.24 in summer (Fig. 3).

Table 5 presents Spearman's rank correlation matrix for data from SML and SUB. Statistically significant correlations were observed between concentrations of calcium and magnesium (r = 0.75), barium and magnesium (r = 0.31), strontium and barium (r = 0.50), as well as calcium and barium (r = 0.43).

Table 5

Correlation of analysed parameters (all data SML and SUB layer, Spearman method, $p < 0.05$)

	Mg	Ca	Sr	Ba
Mg				
Ca	0,75			
Sr	-	-		
Ba	0,31	0,43	0,50	

DISCUSSION

The surface water microlayer in most cases showed a capacity to accumulate higher concentrations of heavy metals than those observed in SUB (Wurl and Obbard 2004, Antonowicz et al. 2015). However, not all metals have the capacity to accumulate in the surface microlayer in greater amounts than those found in SUB. Among the four analyzed metals strontium had a high EF. Both calcium and strontium had low enrichment factors (EF = 1.10-1.16). It can be assumed that EF are practically aproximated to EF = 1. For magnesium EF = 1.33, while for strontium this factor was the highest at EF = 4.12. Values of enrichment factors calculated based on the median were much lower for barium $EF_{MED\ Ba}$ = 1.71. Such a high difference between EF calculated from the median and mean values results from the fact that barium was periodically greatly enriched in SML, with the greatest EF values for barium observed in spring and winter.

Both the results of this study and literature data indicate that the capacity to accumulate calcium in the surface microlayer is low. In 24-h analyses conducted on the Gardno Lake the enrichment factor was as low as EF_{Ca} = 0.89 (Antonowicz 2008a). Results recorded in the presented study on lake Dołgie Wielkie are comparable with data obtained using the same sampling technique (Garrett screening) on an estuarine lake Gardno with EF_{Ca} = 1.10-1.11, a lagoon lake Dołgie Wielkie EF_{Ca} = 1.10-1.11 and an inland lake Jasień EF_{Ca} = 1.07-1.08 (Antonowicz 2008b). In a study by Antonowicz (2008b) a thinner SML of 100 μm in thickness was also sampled. We may observe here that the recorded EF values were slightly higher for the thinner SML, ranging from 1.09 to 1.22. Analyses of the surface microlayers of 15.7 up to 75 μm in thickness, sampled from lake Skjervatjern, showed a higher range of EF values, i.e. EF_{Ca} = 0.9-2.1 (Knulst et al. 1997). For this reason it is assumed that more calcium is accumulated closer to the surface of SML than in its lower layers, which is probably connected with physical forces such as surface tension, adhesion, cohesion, circulation within SML and bioaccumulation in microorganisms (Norkrans 1980, Maki and Hermansson 1994, Wurl and Obbard 2004), while it is probably to a limited extent connected with deposition from the atmosphere. The relatively small enrichment of the surface microlayer with calcium in comparison to most heavy metals is associated with its low content in the rain water (Antonowicz 2008b). For example, rainwater tested in the Pomerania region contains only 2.3 mg dm^{-3} of calcium (Szefer and Szefer 1986).

The capacity of magnesium enrichment in lake Dołgie Wielkie was mean EF = 1.33 and it was comparable with the result recorded in lake Skjervatjern at EF_{Mg} = 0.8-1.7 (Knulst et al. 1997). Higher magnesium concentrations in SML than in SUB are probably connected with binding of magnesium by chlorophyll found in the phytoneuston. Magnesium is a significant component of chlorophyll, being central to the porphyrin chlorophyll system, found in chloroplasts of phytoplankton and phytoneuston. It was shown that chlorophyll is accumulated in the surface microlayer in much higher amounts than it is in the subsurface water layer. In a simultaneous analysis the EF value for chlorophyll was EF_{Cha} = 3.15 (Antonowicz et al. 2015), similarly as it was reported in studies by Estep et al. (1985) and Knulst et al. (1997). This assumption would explain the greatest concentrations of magnesium in SML in spring and summer, when the conditions for algal growth are the best. Studies concerning surface microlayers in terms of the surface microlayer enrichment with strontium and barium are a novel direction of research. It seems evident that the seasonal enrichment of SML with barium observed in lake Dołgie Wielkie may be connected with the accumulation of this metal in neuston microorganisms. Dojlido (1995) reported that barium may be accumulated by aquatic organisms, e.g. as much as 800 mg/kg were detected in ash of zooplankton.

Calcium and magnesium concentrations recorded in SUB correspond to the literature data for water bodies in Poland (Lis and Pasieczna 1995, Weihs et al. 2013) but was relatively low. Concentrations of calcium and magnesium were closest to the data reported for lake Głębokie (Weihs et al. 2013). Relatively low contents of calcium and magnesium in Lake Dołgie Wielkie are probably inflow to low alkalinity of lake waters. In lake Dołgie Wielkie water alkalinity was (0.81 mval dm^{-3}), while in the neighboring lakes Gardno and Jasień it was 2.55 mval dm^{-3} and 2.28 mval dm^{-3}, respectively (Antonowicz 2008b). Lake Dołgie Wielkie is situated in a forested area (Klimaszyk et al. 2015) and soils in the vicinity of the lake contain low concentrations of calcium and magnesium and low water reaction (pH) (Lis and Pasieczna 1995, Parzych 2015), which may have affected low concentrations of calcium and magnesium in lake water.

Strontium concentrations in Lake Dołgie Wielkie need to be considered low. In Poland waters of the Pomeranian and Mazury Lake Districts are the poorest in this element (Lis and Pasieczna 1995). Strontium typically penetrates to water bodies leached from rocks containing strontium compounds and less frequently – from industrial pollution (Dojlido 1995). However, the Dołgie Wielkie Lake is situated away from major sources of anthropogenic pollutants. Strontium concentrations in surface waters in Poland range from hundredth parts of mg dm^{-3} to 1 mg dm^{-3} (Dojlido 1995, Hermanowicz et al. 1999). Strontium may sometimes be found at concentrations of several mg dm^{-3} (Dojlido 1995). On average surface waters in Poland contain 263 µg dm^{-3}. According to data collected by Lis and Pasieczna (1995), Polish lakes contain mean 164 µg dm^{-3}, small water bodies 249 µg dm^{-3}, while fishing ponds – 210 µg dm^{-3}, respectively.

Barium concentrations in lake Dołgie Wielkie are also low. The cartographic picture of the background for barium content in surface waters of Poland is not very varied (<50-100 µg dm^{-3}). Barium concentrations are determined by natural factors (Małecki 1991, Lis and Pasieczna 1995). Surface waters in Poland contain mean 55 µg dm^{-3}, including lakes with 37 µg dm^{-3}, small nameless water bodies with 56 µg dm^{-3} and fishing ponds with 63 µg dm^{-3}, respectively (Lis and Pasieczna 1995). Barium is a common component of surface waters, but its concentration is low. This results from low solubility of most barium salts and high absorbability by soils and bottom sediments (Dojlido 1995). Since Dołgie Wielkie is a lake mixed to the bottom and its mean depth is small (1.4 m) (Trojanowski et al. 1990, Antonowicz 2013), these characteristics of the lake may promote raising sparsely soluble barium accumulated in bottom sediment particles.

CONCLUDING REMARKS

Concentrations of barium, magnesium, strontium and calcium recorded in lake Dołgie Wielkie are relative low. The accumulation capacity expressed in enrichment factors EF for the surface microlayer formed a series Ba > Mg > Sr > Ca. Barium was seasonally accumulated in the surface microlayer. Recorded Sr and Ca concentrations were comparable to those reported for the subsurface water layer and the surface microlayer.

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REFERENCES

Agogué H., Casamayor E.O., Bourrain M., Obernosterer I., Joux F., Herndl G.J., Lebaron P., 2005. A survey on bacteria inhabiting the sea surface microlayer of coastal ecosystems. *FEMS Microbial Ecology*, 54, 269-280.

Ahlers W.W., Reid M.R., Kim J.P., Hunter K.A., 1990. Contamination-free sample collection and handling protocols for trace elements in natural fresh waters. *Austr. J. Mar. and Freshwat. Res.*, 41, 713-720.

Antonowicz J., 2008a. Daily changes in concentrations of selected heavy metals in relation to chlorophyll content in surface water microlayer of lake Gardno. *Ecol. Chem. and Engin.* S, 15, 473-481.

Antonowicz J., 2008b. Quantity of selected physical and chemical parameters in surface microlayers and subsurface water on the example of three lakes. *Balt. Coast. Zone*, 12, 5-19.

Antonowicz J., Trojanowski J., Trojanowska C., 2010. 24-hour cycle of variability contents of nitrogen forms in surface microlayer of Baltic Sea lagune lake (North Poland) – part I, *Baltic. Coast. Zone*, 14, 37-47.

Antonowicz J.P., 2013. Daily cycle of variability contents of phosphorus forms in surface microlayer of a light salinity Baltic Sea Lagoon lake (North Poland) – part II. *Cent. Eur. J. of Chem.*, 11, 817-826.

Antonowicz J.P., Mudryk Z., Zdanowicz M., 2015. A relationship between accumulation of heavy metals and microbiological parameters in the surface microlayer and subsurface water of a coastal Baltic lake. *Hydrobiol.*, 762, 65-80.

Atlas jezior Polski. (Atlas of Polish lakes). 1997. (Ed.) J. Jańczak, Bogucki Wydawnictwo Naukowe, Poznań, (in Polish).

Bigg E.K., Leck C., Tranvik L., 2004. Particulates of the surface microlayer of open water in the Central Arctic Ocean in the summer. *Mar. Chem.*, 91, 131-141.

Brettum P., Andersen T., 2005. Report of Norwegian Institute for Water Research. The use of phytoplankton as indicators of water quality. NIVA, Norway, 1-33.

Ciepielewski W., Sobocki M., Szczerbowski J., Korzeń J., 2003. Operat ochrony ichtiofauny. Tom XIII. W: Projekt Plan Ochrony Słowińskiego Parku Narodowego. Operaty Ochrony Przyrody Ożywionej. (Operat of the ichtiofauna protection. Volume XIII. In: Project of Protection Plan of Slovinski National Park. Living Nature Conservation Operats). 1-26, (in Polish).

Cincinelli L.A., Stortini A., Perugini M., Checchini L., Lepsi L., 2001. Organic polutants in sea-surface microlayer and aerosol in the coastal environment of Leghorn – (Tyrrhenian Sea). *Mar. Chem.*, 76, 77-98.

Dojlido J.R., 1995. Chemia wód powierzchniowych. (Chemistry of surface waters). Białystok, Wydawnictwo Ekonomia i Środowisko, (in Polish).

Engel A., Galgani L., 2015. The organic sea surface microlayer in the upwelling region off Peru and implications for air–sea exchange processes. *Biogeosc. Disc.*, 12, 10579-10619.

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. *Freshwat. Biol.*, 15, 15-19.

Freeman C., Lock M. A., 1995. The biofilm polysaccharide matrix: A buffer against changing organic substrate supply? *Limnol. and Oceanogr.*, 40, 273-278.

Galgani L., Engel A., 2015. Changes in optical characteristics of surface microlayers hint to photochemically and microbially-mediated DOM turnover in the upwelling region off Peru. *Biogeosci. Disc.*, 12, 19373-19421.

Garrett W., 1965. Collection of slick forming materials from the sea surface. *Limnol. and Oceanogr.*, 10, 602-605.

Gašparović B., Plavšić M., Ćosović B., Saliot A., 2007. Organic matter characterization in the sea surface microlayers in the subarctic Norwegian fjords region. *Mar. Chem.*, 105, 1-14.

Green T., Houk D.F., 1979. The removal of organic surface films by rain. *Limnol. Oceanogr.*, 24, 966-970.

Hale M., Mitchell J.G., 1997. Sea surface microlayer and bacterioneuston spreading dynamics. *Mar. Ecol. Prog. Ser.*, 147, 269-276.

Hardy J., 1982. The surface microlayer: Biology, chemistry and anthropogenic enrichment. *Prog. Oceanogr.*, 11, 307-328.

Hermanowicz W., Dojlido J., Dożańska W., Koziorowski B., Zerbe J., 1999. Fizykochemiczne badanie wody i ścieków. (Physicochemical studies of water and waste water). Arkady, Warszawa, (in Polish).

Klimaszyk P., Piotrowicz R., Rzymski P., 2015. Changes in the ecosystem of shallow soft-water lake induced by the Great Cormorant roosting colony. *J. Limnol.*, 74, 114-121.

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.

Komunikat o stanie czystości jeziora Dołgie Wielkie na podstawie badań przeprowadzonych w 1995 roku. (Communicate on state of cleanliness and the Great Lake Dołgie based on research carried out in 1995). 1995. (Ed.) R. Zaręba. WIOŚ, Słupsk, (in Polish).

Kozarac Z.B., Ćosović S., Frka D.M., Mobiüs 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.

Lis J., Pasieczna A., 1995. Geochemical atlas of Poland. Warszawa, Państwowy Instytut Geologiczny, (in Polish).

Luszniewicz A., Słaby T., 2008. Statystyka z pakietem komputerowym STATISTIKA PL. Teoria i zastosowania. (Statistics with the computer package STATISTICA PL. Theory and application). Wydawnictwo C.H. Beck, (in Polish).

Maki J.S., Hermansson M., 1994. The dynamics of surface microlayers in aquatic environments. In: The Biology of Particles in Aquatic Systems. (Ed.) R.S. Wotton, Ann Arbour-London-Tokyo, Lewis Publisher Boca Raton, 161-182.

Małecki J., 1991. Rola mikroorganizmów w ocenie antropogenicznych przekształceń chemizmu wód podziemnych. W: Współczesne problemy hydrogeologii. (The role of microorganisms in the assessment of anthropogenic transformations of groundwater chemistry. In: Current problems of hydrogeology). Oficyna Wydawnicza Sudety, Wrocław, 4.

Mudryk Z., Trojanowski J., Skórczewski P., Antonowicz J., 2003. Chemical and bacteriological studies of surface and subsurface water layers in estuarine Lake Gradno. *Pol. J. Environ. Stud.*, 12, 199-206.

Norkrans B., 1980. Surface microlayer in aquatic enviroments. *Adv. Microb. Ecol.*, 4, 51-85.

Parzych A., 2015. Accumulation of macro- and microelements in mosses in the Słowiński National Park. *Sylwan*., 159, 345-352.

Romano J., Marquet R., 1991. Occurrence frequencies of sea-surface slicks at long and short-time scales relation to wind speed. *Estuar. Coast. Self Sci.*, 33, 445-498.

Santos L., Santos A.L., Coelho F.J.R.C., Gomes N.C.M., Dias J.M., Cunha A., Almeida A., 2011. Relation between bacterial activity in the surface microlayer and estuarine hydrodynamics. *FEMS Microbiol. Ecol.*, 77, 636-646.

Santos L., Santos A.L., Coelho F.J.R.C., Gomes N.C.M., Dias J.M., Cunha A., Almeida A., 2013. Heterotrophic activities of neustonic and planktonic bacterial communities in an estuarine environment (Ria de Aveiro). *J. Plankton Res.*, 36, 230-242.

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.

The Sea Surface and Global Change, 1997. (Eds) P.S. Liss, R.A. Duce, Cambridge (UK), Cambridge Univ. Press.

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., Trojanowska C., Korzeniewski K., 1990. Warunki hydrochemiczne w jeziorach przymorskich. (Hydrochemical conditions in the coastal lakes). *Słupskie Pr. Mat.-Przyr.*, 8b, 123-160, (in Polish).

USEPA, 1998. Method 3015A. Microwave assisted acid digestion of aqueous samples and extracts. In: SW-846 Manual. Methods for Evaluating Solid Waste, Physical/Chemical Methods. Environmental Protection Agency, US.

Weihs S., Pełechaty M., Pukacz A., 2013. Charophyte occurrence in phytocoenoses of *Typhetum angustifoliae* association in lakes of Ziemia Lubuska (Mid-Western Poland). *Stud. Limnol. et Telmatol.*, 7, 3-12.

Wurl O., Miller L., Röttgers R., Vagle S., 2009. The distribution and fate of surface-active substances in the sea-surface microlayer and water column. *Marine. Chem.*, 115, 1-9.

Wurl O., Obbard J.P., 2004. A review of pollutants in the sea-surface microlayer (SML): a unique habitat for marine organisms. *Mar. Poll. Bull.*, 48, 1016-1030.

ZDOLNOŚĆ DO AKUMULACJI STRONTU, BARU, WAPNIA I MAGNEZU W INTERFAZIE WODA – POWIETRZE PRZYMORSKIEGO JEZIORA MORZA BAŁTYCKIEGO

Streszczenie

Przeprowadzono badania zdolności do akumulacji czterech metali – strontu, baru, wapnia i magnezu w przymorskim jeziorze Dołgie Wielkie. Jezioro usytuowane jest na terenie Słowińskiego Parku Narodowego. Próbki wody pobierano z mikrowarstwy powierzchniowej za pomocą siatki Garretta oraz równolegle z warstwy wody podpowierzchniowej. Analizy stężenia metali wykonano z użyciem spektrometru masowego. Badano zdolność do wzbogacania metali w mikrowarstwie powierzchniowej. Najwyższą zdolność do akumulacji wykazywał bar. W mniejszym stopniu akumulował się magnez. Stężenie wapnia i strontu było porównywalne w obu badanych warstwach. Stwierdzono sezonową zmienność wszystkich badanych metali.