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ORIGINAL PAPER

THE SURFACE MICROLAYER OF A LOBELIA LAKE: DAILY DYNAMICS OF THE METAL CONTENT AND PHYTONEUSTON/ PHYTOPLANKTON TAXONOMIC COMPOSITION*

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Abstract

The study presents differences in the elemental composition between the surface microlayer (SML) and the subsurface (SUB) water sampled from a low trophy lobelian lake in the course of 48-hour monitoring supplemented with chlorophyll *a* and microalgae analyses. In this study, we examined daily dynamics of such elements as Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Na, Ni, Mg, Mn, Pb, Se, Sr, Zn and chlorophyll *a* content in the SML and SUB as well as the capacity for enrichment of these elements in the SML. Our analysis of metals by mass spectrometry showed that concentrations of the mentioned elements, including heavy metals, in the SML were statistically significantly higher than in the SUB. The amplitude of changes in the metal concentration dynamics observed in the SML for most of the investigated elements and chlorophyll *a* was greater than in the case of the SUB. A circadian dynamics, frequently cyclical in character, was found in both analysed layers. Based on cluster analysis, groups of chemical elements were selected, showing a similar circadian course of changes in the concentrations during the monitoring. Moreover, observations of the taxonomic composition of the phytoneuston and phytoplankton showed the occurrence of algal species characteristic of water bodies with low trophy levels. The results provide insight into the functioning of interrelationships between physical parameters such as salinity, temperature and biological chlorophyll and possible mechanisms causing the accumulation of such chemical components as metals, metaloids, in the SML of a lobelia lake.

Keywords: elemental analyses; surface waters, surface microlayer, lobelia lake, chloropyll *a*, microalgae.

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INTRODUCTION

The surface microlayer (SML) of water is a thin layer (max. 1-1000 μm) found at the interface of two environments, the hydrosphere and the atmosphere (Wurl, Obbard 2004). It is a significant element of the aquatic environment, as it covers 71% of the Earth's surface. Because of its vast area, it is an important zone for the exchange of matter and heat energy between the hydrosphere and atmosphere (Trojanowski et al. 2001, Kostrzewska-Szlakowska 2003, Kozarec et al. 2003). Chemical substances are transported from the SML surface to the atmosphere in bubbles of liquid formin in this layer and then lifted by wind into the air, where they form aerosols (Grammatika, Zimmerman 2001). Autochthonous and allochthonous matter is deposited in the opposite direction, i.e. from the atmosphere to the surface of this ecotone, and thus matter, including chemical substances, is transferred to bulk water (Kostrzewska-Szlakowska 2003). The SML is largely enriched with chemical substances from subsurface water (SUB) (Kostrzewska-Szlakowska 2003). Wurl, Obbard (2004) reported that boundary layers between different environmental compartments represent critical interfaces for biological, chemical and physical processes (Kostrzewska-Szlakowska 2003). A distinguishing characteristic of the SML ecotone is the accumulation of heavy metals, biogenic and organic compounds, and microbial populations, which are frequently much more numerous than those observed in the SUB (Donderski et al. 1999, Mudryk et al. 2003, Antonowicz et al. 2015). The capacity to accumulate chemical substances, microalgae and bacteria in the SML ecotone results from many processes occurring simultaneously. Retention of matter in the SML is promoted mainly by physical forces such as surface tension, adhesion, cohesion, rotational movements within SML, Langmuir circulation (Kostrzewska-Szlakowska 2003, Antonowicz et al. 2015), capacity of organic substances to chelate inorganic substances and bioaccumulation of metals in the neuston. A considerable role in the capacity of SML for enrichment with chemical substances is played by neuston microorganisms (Mudryk et al. 2003, Antonowicz et al. 2015). Enrichment of the SML with matter and organisms is not identical in all water bodies. The chemical composition of water, including salinity, may affect the capacity to enrich SML (Trojanowski, Antonowicz 2011). Additionally, a study conducted by Hillbricht-Ilkowska, Kostrzewska-Szlakowska (2004) showed variation in the SML enrichment capacity in the analysed lakes differing in their trophic levels. Lobelia lakes exhibit low trophic levels and they are highly sensitive to anthropogenic factors (Kraska et al. 2013). Lake Gubisz (Poland), selected for this study, is a closed lake located remotely from considerable sources of urban/industrial pollution. According to Kraska et al. (1996), it is a lobelia lake in the state of equilibrium. The lake has no major tributaries carrying pollution loads from the adjacent land. As a result, the lake water contains low concentrations of trace elements.

The aim of this study was to investigate the interdependencies between circadian variation in heavy metal concentrations in the SML and SUB, and the level of chl *a* in the phytoneuston and phytoplankton of a lobelia lake called Lake Gubisz in Poland. At the same time, these layers were analysed in terms of their content of metals (macro- and micronutrients), playing a significant structural function and participating in the metabolism of organisms, e.g. algae that inhabit layers of this lake. It was crucial to show the capacity to accumulate metals in the SML and the species composition of algae found in the SML and SUB, while the affected physicochemical parameters of lake water were monitored.

MATERIAL AND METHODS

Studied site and sampling

The investigated lobelia Lake Gubisz is situated in the north of Poland at 54°09.0′ and 17°35.2′. Morphometric parameters according to Jańczak (1997) are presented in Table 1. Lake Gubisz contains boreal Atlantic relicts such as the evergreen herbaceous perennial water *Lobelia dortmanna* L. Other species such as *Isoëtes lacustris* L., *Littorella uniflora (*L.*) Asch.* and *Myriophyllum alterniflorum DC.* were also noted in this lake (Kraska et al. 1996). Jarosiewicz, Fryda (2011) classified Lake Gubisz as a mesotrophic lake based on the multimetric Trophic State Index (TSI); however, these values

Table 1

Morphometric characteristics of Lake Gubisz according to Jańczak (1997)

Parameter	Value
Latitude	54°09.0′
Longitude	17°35.2′
Altitude a.s.l. (m)	187.2
Area surface of water level (ha)	14.3
Maximum depth (m)	17.6
Average depth (m)	7.3
Maximum length (m)	500
Maximum width (m)	460
Average capacity (10^3 m^3)	1043.9
Length of shore line	1570
Expansion of shore line	1.17
Indicator unveiling	2.0

are close to ones reported for oligotrophic lakes and some indices (PSItot) even indicate the oligotrophic character. Samples of water from Lake Gubisz were collected over a period of 48 hours in August 2007; they were drawn from the littoral zone at 4-hour intervals (Figure 1). Water samples from the

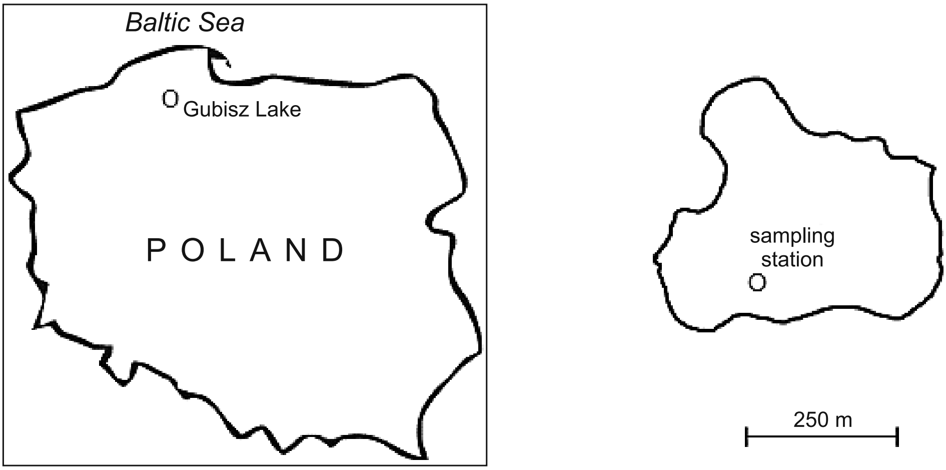

Fig. 1. Location and map of the lobelia Lake Gubisz

surface microlayer (SML) were collected with a Garrett net, which is used to collect samples from an SML with a thickness of 242 μm ± 40 (Garrett 1965). Subsurface water (SUB) was collected by immersing a container to a depth of about 15 cm from the water surface.

Chemical and biological analysis

Water samples from Lake Gubisz were mineralised in *Tracepur*® HNO_3 (v/v 1/20) (Merck, Germany). The concentrations of Ag, Al, As, Ba, Cd, Co, Cr, Cu, Fe, Li, Na, Ni, Mn, Pb, Se, Sr were measured using a Perkin Elmer Elan DRC-e mass spectrometer (USA). Analyses were conducted applying multielement standards by Perkin Elmer. In the case of such elements as Ca, K, Mg and Zn, a Perkin Elmer Analyst 300 atomic absorption spectrophotometer (USA) was used. The accuracy of the method was verified using TM-24.3 Certified Reference Water for Trace Elements, Environment Canada (elements: Al, As, Ba, Cd, Cr, Co, Cu, Fe, Pb, Li, Mn, Ni, Se, Sr, Zn) (recovery 94 - 106%) and the recovery of medium standards digested in the same procedure was recorded for that sample.

Electric conductivity (EC), pH and temperature were recorded with an Elmetron apparatus (Poland), chloride ions were assayed with a Methrom ion chromatograph (Switzerland), while dissolved oxygen was determined according to the Winkler method (APHA, 2005). Illumination intensity was measured using a CM3 pyranometer by Kipp & Zonen (USA).

Concentration of chlorophyll *a* was determined using the method proposed by JEFFREY, HUMPHREY (1975). Water samples were filtered through Whatman (UK) filter paper with pore diameter of 0.45 μm using a Merck Millipore (Germany) filtration set for water samples equipped with an Aga Labor vacuum pump (Poland), and next the filters were extracted. Absorption was measured using a UV-VIS Shimadzu spectrophotometer (Japan).

Taxonomic composition of the analysed phytoneuston and phytoplankton was examined under an inverted microscope manufactured by Nikon (Japan).

Statistical analysis

In order to compare both investigated media, i.e. water from the SML and SUB, enrichment factors (EF) according to ANTONOWICZ et al. (2010) were applied:

$$EF = \frac{\sum\left(\frac{C_{SML1}}{C_{SUB1}} + \frac{C_{SML2}}{C_{SUB2}} + \cdots + \frac{C_{SML1}}{C_{SUB1}}\right)}{i},$$

where: successive unit indices calculated according to individual partial values, e.g. C_{SML1} – concentrations in the first hour of monitoring in the SML, C_{SUB1} – concentrations of a component at the same hour and at the same sampling station in the SUB and by analogy the 2nd result up to the i-th result.

The statistical analyses such as the Shapiro-Wilk normality test, *t*-test (which confirmed the normal distribution), the Mann-Whitney *U* test (no normal distribution found) were performed using a Statistica package. In order to group the analysed parameters according to their specific properties, cluster analysis (Ward method, Euclidean distance) was applied.

RESULTS AND DISCUSSION

Mean concentrations of the analysed metals, except for Ca, Mg, K, and Na, in the SML of Lake Gubisz ranged from 0.04 μg dm^{-3} for Ag to 436.99 μg dm^{-3} for Al (Table 2). Mean concentrations of chemical elements found in the SML of Lake Gubisz are presented in the decreasing order: Ca>Na>K>Mg>Al>Fe>Mn>Zn>Sr>Ba>Pb>Ni>Cu>Co>Cr>As>Li>Cd>Se>Ag. In turn, in the SUB of the investigated water body the lowest concentration was recorded for Ag (0.03 μg dm^{-3}), while the highest was found for Al (239.58 μg dm^{-3}). The greatest differences in concentrations of the analysed heavy metals between the SML and SUB were observed for Co and Mn, as indicated by the greatest values of their enrichment factors (EF = 6.52 and 5.98). The lowest EF values were found for Sr, Pb, Ni, Fe and Cr (at 1.32, 1.42, 1.50, 1.58 and 1.60, respectively). Also, the respective enrichment factors for macronutrients such as Ca, Mg, K and Na were low and ranged from 1.03 to 1.41. Values of EF representing the capacity to enrich the SML with

Table 2

Mean concentrations, medians, standard deviations, enrichment factors and statistical test (*t*-Student or $^{\#}$ *U* Mann-Whitney) differentiating concentrations of analysed parameters in SML and SUB

Parameter	Unit	SML		SUB		EF	*P*
		mean & SD	median	mean & SD	median		
Ag	(μg dm^{-3})	0.04 ± 0.03	0.04	0.03 ± 0.02	0.02	2.04 ± 2.74	ns$^{\#}$
Al		436.99 ± 240.97	386.47	239.58 ± 156.19	268.57	2.84 ± 2.75	*
As		0.92 ± 0.34	0.82	0.64 ± 0.61	0.49	1.84 ± 0.75	***$^{\#}$
Ba		32.03 ± 13.48	33.29	15.66 ± 9.26	12.16	2.38 ± 1.22	***
Cd		0.82 ± 0.53	0.64	0.44 ± 0.18	0.51	3.42 ± 5.07	ns$^{\#}$
Co		4.99 ± 4.45	4.23	2.46 ± 1.61	2.34	6.52 ± 11.07	ns
Cr		1.98 ± 1.42	1.63	1.23 ± 0.33	1.26	1.60 ± 0.98	*$^{\#}$
Cu		3.67 ± 1.83	1.82	2.50 ± 1.25	1.99	1.91 ± 1.66	**$^{\#}$
Fe		269.29 ± 120.58	232.97	193.83 ± 104.39	165.38	1.58 ± 0.75	ns$^{\#}$
Li		1.85 ± 0.94	1.54	0.64 ± 0.32	0.57	3.44 1.83	***$^{\#}$
Mn		130.30 ± 109.14	82.99	29.83 ± 26.59	15.10	5.98 ± 4.26	**$^{\#}$
Ni		4.41 ± 1.96	4.19	3.23 ± 1.32	2.91	1.50 ± 0.89	ns
Pb		8.39 ± 2.18	8.59	6.88 ± 2.35	7.45	1.42 ± 0.84	ns
Se		0.23 ± 0.09	0.20	0.13 ± 0.06	0.11	2.08 ± 1.56	**$^{\#}$
Sr		24.19 ± 4.48	24.58	18.39 ± 1.35	18.21	1.32 ± 0.23	***
Zn		50.55 ± 33.15	41.73	19.83 ± 8.72	18.44	3.01 ± 2.62	**
Ca	(mg dm^{-3})	2.64 ± 0.70	2.49	1.94 ± 0.41	1.85	1.41 ± 0.45	***$^{\#}$
K		1.68 ± 0.47	1.51	1.47 ± 0.43	1.46	1.16 ± 0.18	ns
Mg		1.11 ± 0.15	1.06	0.91 ± 0.08	0.89	1.22 ± 0.14	***$^{\#}$
Na		2.55 ± 0.31	2.44	2.62 ± 0.74	2.24	1.03 ± 0.27	ns$^{\#}$
Chl *a*	(μg dm^{-3})	225.1 ±232.8	232.8	10.2 ± 2.3	9.6	20.0 ± 18.5	***$^{\#}$

Level of significance: $p < 0.05$ *, $p < 0.01$ **, $p < 0.001$ ***, ns – non significant the studied components appeared in the following order: Co>Mn>Li>Cd>Zn>>Al>Ba>Se>Ag>Cu>As>Cr>Fe>Ni>Pb>Ca>Sr>Mg>K>Na. Analyses of the biological and chemical parameters revealed that concentrations of the analyzed elements in the SML were statistically significantly higher than in the SUB for Chl *a*, Li, Cr, Mn, Cu, As, Se, Sr, Ba, Zn, Mg, Al and Ca (Table 2).

Similarly to our observations, Hardy et al. (1985) recorded the accumulation of such heavy metals as Pb, Zn, Cu, Cd and Fe in the sea-surface microlayer (SML) and subsurface water from an urban and rural bay. In turn, Zhang et al. (2003) also stated greater accumulation of Cu, Zn, Cd and Pb in the SML rather than in the SUB in Daya Bay. Additionally, the accumulation of heavy metals, i.e. Pb, Cd and Mn, was determined in the SML of eutrophic lakes such as an inland Lake Jasień in northern Poland (Antonowicz, Trojanowski 2010), while Mn, Zn, Pb, Cu, Ni, Cr, Co, Cd and Ag were found to accumulate in a lagoon Lake Dołgie Wielkie (Antonowicz et al. 2015), and Cu, Pb and Zn were determined to accumulate in the estuary of Lake Gardno (Trojanowski, Antonowicz 2011). The SML enrichment with heavy metals has been confirmed in many studies (Rumbold, Snedaker 1999, Wurl, Obbard 2004, Coung et al. 2008), while few results concern the lake's SML (Antonowicz, Trojanowski 2010, Antonowicz et al. 2015). It was documented that the presence of heavy metals in the SML may be toxic to neustonic organisms (Wurl, Obbard 2004). To a certain degree, toxicity of free metals, including heavy metals, may be reduced by phytoplankton, which releases into the environment organic ligands capable of complexing metals (González-Dávila 1995).

In Lake Gubisz, the concentrations of the analysed metals fluctuated dynamically both in the SML and SUB. Values of enrichment factors were also changing. Generally for most metals such as Ag, Cd, Co, Cu, Li, Ni, Pb and Zn, elevated EF levels were frequently observed during the night (most typically in the period from 12 a.m. to 4 a.m.), while well as in the afternoon (primarily between 12 p.m. and 8 p.m.) elevated EF levels were frequently reported for such elements as Al, As, Ba, Cd, Co, Cr, Cu, Fe, Mg, Na, Ni, Se, Sr and Zn (Figures 2, 3*a*,*b*). During the same period the lowest chlorophyll concentrations were also recorded (Figure 4) in SML, but it was only until 4 a.m. Subsequently chlorophyll concentration increased rapidly. At 12 p.m., when the highest solar radiation was observed, the chl *a* concentration in SML decreased and the phytoplankton was observed to escape from the high radiation zone to lower water layers at a simultaneous increase in the amount of oxygen (Figure 5) in SUB, which was probably connected with an increase in the photosynthetic activity.

Circadian changes in concentrations of the analysed metals in the SML showed a much greater dynamics than in the SUB (Figure 2, 3*a*,*b*). This was evident for such metals as Mn, Zn, Co, Cd, Ba and Cr. The mean amplitude of fluctuations in Sr concentrations in the SUB is approximately 3 μg dm^{-3}, while in the SML it is 3-fold greater. An even greater difference was observed in the case of Cr and Mn. This is probably associated with the dyna-

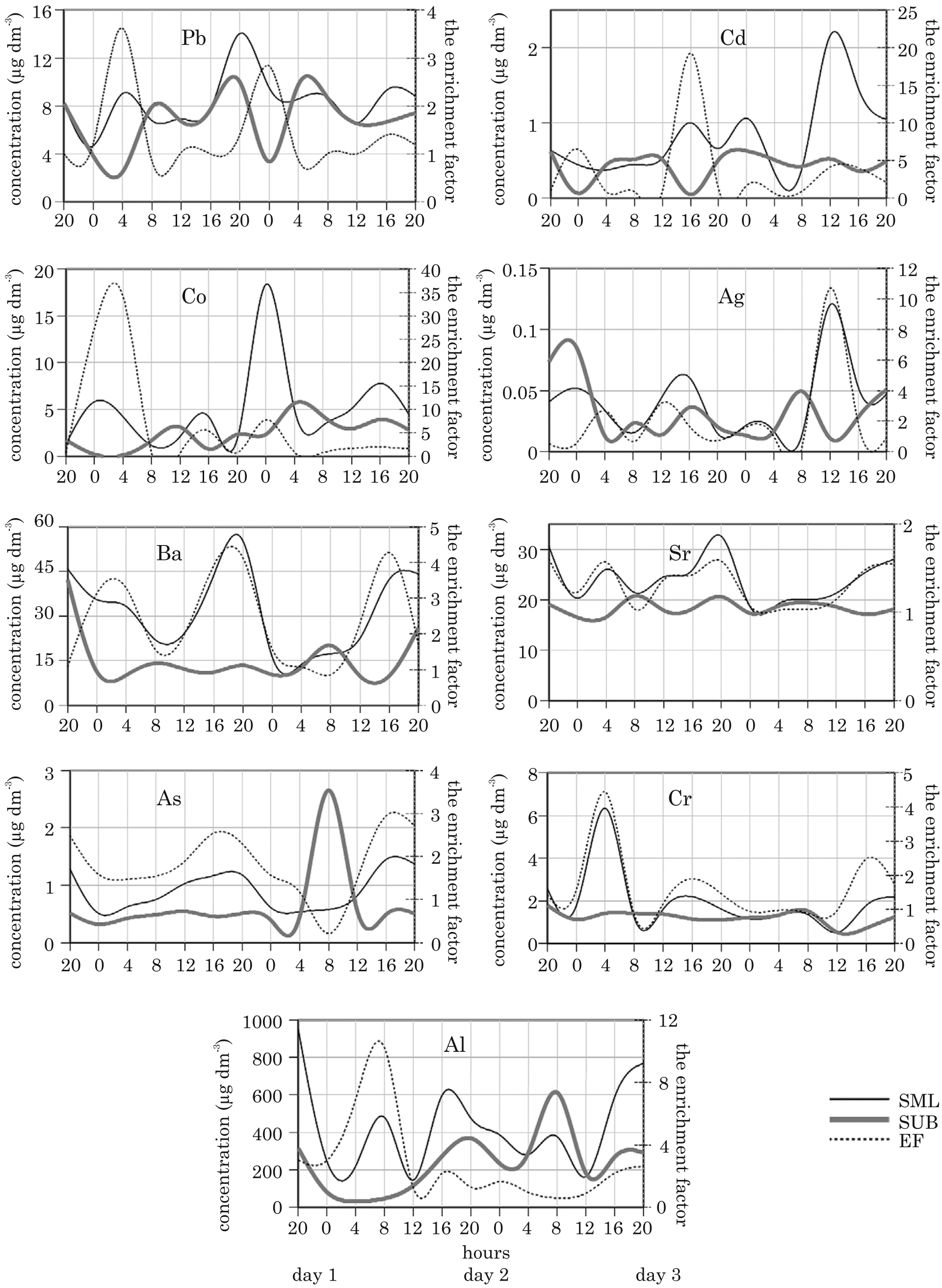

Fig. 2. Circadian dynamics of concentrations of metals exhibiting toxic properties towards microalgae (Pb, Cd, Co, Cr, Ag, and Al) alkaline earth metals (Sr, Ba) and metalloid As in the SML and SUB

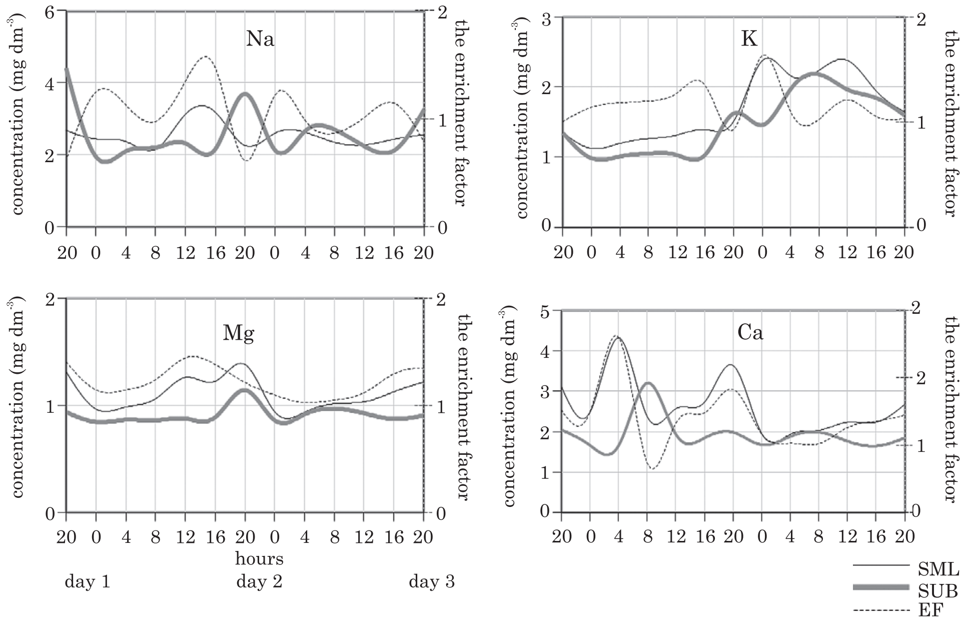

Fig. 3*a*. Circadian dynamics of metal concentrations of macronutrients of a potential metabolic importance for organisms and other and enrichment factors (EF)

mics of changes in chlorophyll concentrations (Figure 4) in both analysed water layers of Lake Gubisz.

Chl *a* detected in waters originates from phytoplankton. Parallel to the higher content of chl *a* in the SML in waters of lobelia Lake Gubisz (Figure 4), Mg, a chemical element being a component of chl *a*, was also more abundant in this water layer than in the SUB (Figure 3*a*). For instance, at 8 p.m. on day 2 of the monitoring it was observed that the Mg level was 21% higher in the SML than in SUB water. Macro- and micronutrients are elements significant for phytoneuston. Elements such as C, H, O, N, P, S, K, Mg, Ca, Na, Fe, Mn, Cu, Zn, Mo, V, B, Cl, Co and Si are required for phytoplankton growth (Rahaman et al. 2014). Among the analysed microelements, changes in the level of Mn in the SML layer are worth noting. The concentration of this chemical element was over 4-fold greater in the SML than in the SUB, which is confirmed by the EF value of 5.98. The enrichment capacity was shown by regular maxima and minima resembling a sinusoid variation, with the highest EF (14.02) observed at 8 a.m. on day 2. This micronutrient participates in the water degradation reactions and release of oxygen in the process of photosynthesis. Moreover, Mn activates many enzymes involved in metabolism. Moreover, other microelements such as Cu and Fe also participate in many redox reactions and they may also play a significant role in the process of photosynthesis (Hossain et al. 2012, Ravet, Pilon 2013). Lis et al. (2015) demonstrated that cyanobacteria take up iron. Moreover, Xue et al. (1988) reported that the surfaces of algal cells have a high affinity to Cu^{+}

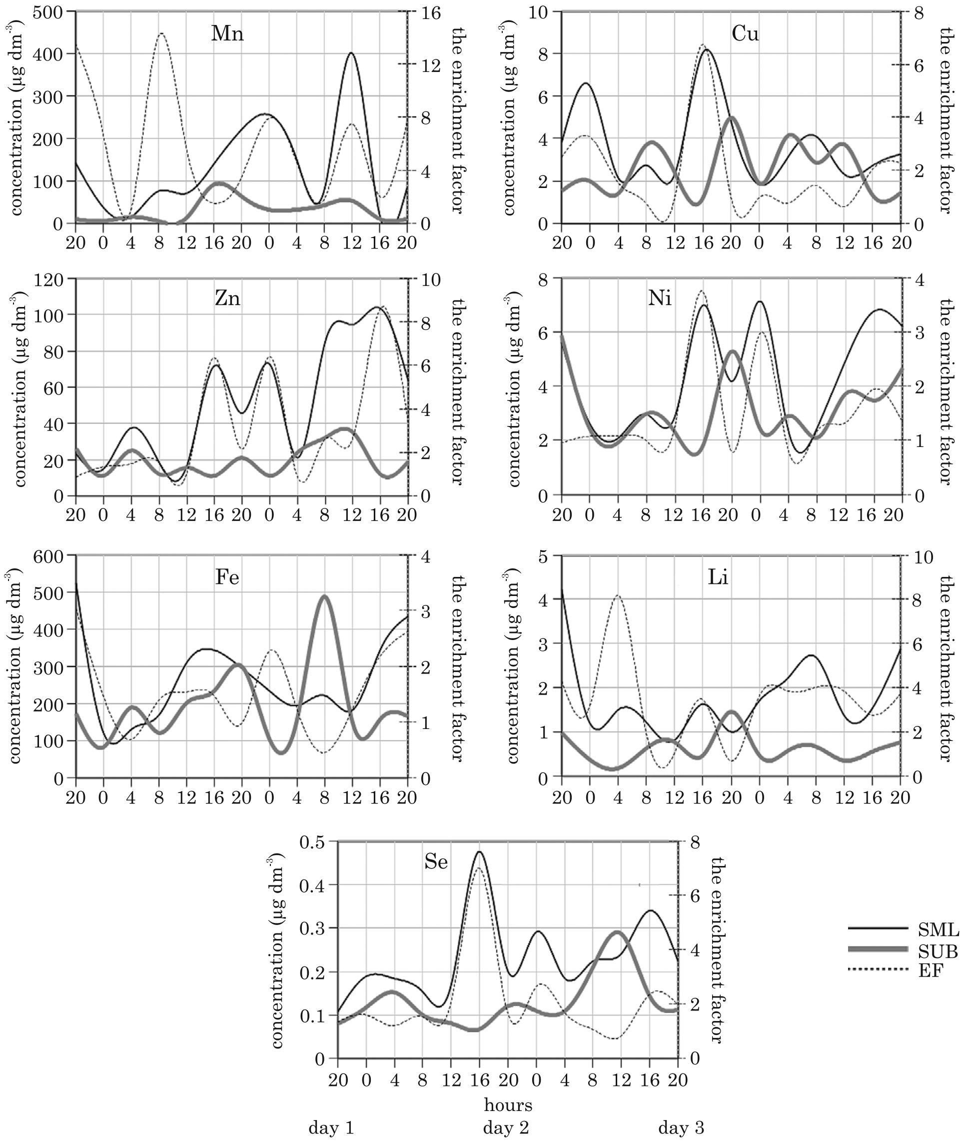

Fig. 3*b*. Circadian dynamics of metal concentrations, micronutrients of a potential metabolic importance for organisms and enrichment factors (EF)

and Cd; their functional group ligands can compete with soluble complex formers typically present in natural waters.

It was observed that changes in the levels of such metals as Cd, Co, Ag, Mn, Zn and Ni in the SML are similar at certain time periods in the circadian cycle. These changes were characterised by higher concentrations of these metals around 12 a.m. and 4 p.m. of day 2 and around 12 a.m. and

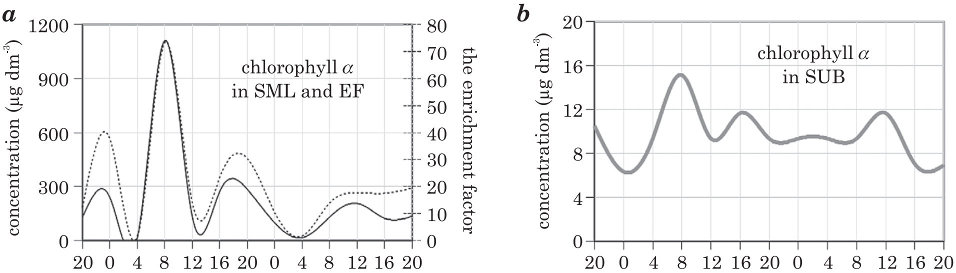

Fig. 4. Daily dynamics of chl *a* concentration in the SML (*a*) and SUB (*b*). The dotted line in the left figure presents dynamics of EF (Antonowicz 2014, modified)

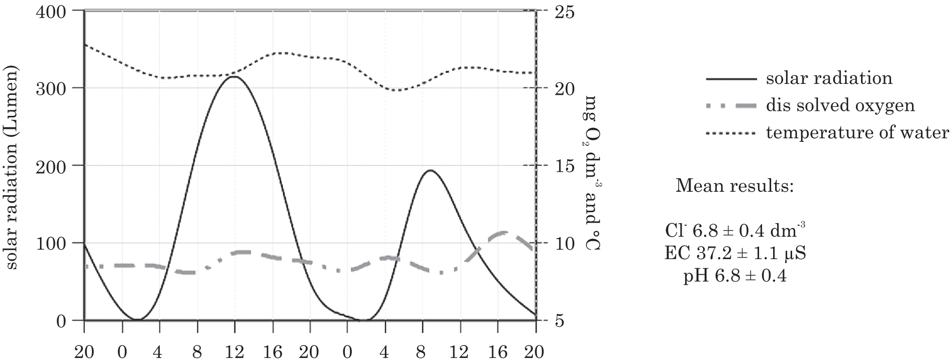

Fig. 5. Physicochemical parameters: solar radiation, temperature, pH, electric conductivity and dissolved oxygen, chloride ions in Lake Gubisz

12 p.m. of day 3. Figures 2, 3*a*,*b* clearly show the maxima at these time points. In turn, the dynamics of changes in concentrations of these metals in the SUB varied and no similarities were observed between the metals. This means that other regularities are probably found in both analysed layers, which may result from the fact that the SML is influenced by the atmosphere and subsurface water as well as the bioaccumulation of microorganisms migrating between the SML and SUB. Metals in the SML are bound by particles (Wurl, Obbard 2004), which, together with the bound metals, may settle down to deeper water layers, to the bottom deposits, where they can be accumulated. In closed water bodies such as Lake Gubisz, more of the metals accumulated in the lower water layers and in the sediments probably originate from the atmosphere than in water bodies fed with inflowing waters.

Most analysed metals (Al, Ba, Ca, Co, Cr, Cu, Fe, Mg, Na, Ni, Se, Sr, Zn and metalloid As) in the SML showed repeated fluctuations in the circadian cycle (Figures. 2, 3*a*,*b*), i.e. an increase in their concentrations in the period from 12 p.m. to 8 a.m. Typically, in this time period, concentrations of these metals decreased in the SUB, with the exception of Al and Fe. This shows a close relationship between these layers. The above observations suggest that both animate and inanimate matter containing the analysed metals migrate from the SUB to SML at those time points.

Apart from monitoring the level of heavy metals in both layers (SML and SUB) in lobelia Lake Gubisz, we also observed circadian changes in metals belonging to the groups of macro- and micronutrients (including such heavy metals as Cu, Zn, Fe, Ni) with potential structural and physiological roles for organisms found in the two layers (Figures 3*a*,*b*). Values of the EF calculated for macronutrients, i.e. Ca, Mg, K and Na (Figure 3*a*), were much lower than for heavy metals. Similar EF values for these macronutrients were also reported in Lake Skjervatjern in Norway, e.g. Ca 0.9 - 2.1, Mg 0.8 - 1.7 and Na 1.0 - 1.5 (Knulst et al. 1997).

When analysing changes in Cu levels in the SML of Lake Gubisz, we observed accumulation of this chemical element at approximately 16-hour intervals. The mean EF value for Cu was 1.91 with the peak of 6.75. In turn, repeated accumulation of Fe was observed in the period of 4 p.m. - 8 p.m. hours during the monitoring of the SML layer. From 4 a.m. to 4 p.m. hours on day 2 and from 8 a.m. to 8 p.m. hours on day 3, we observed Fe transport from the SUB layer to SML. The Fe content was higher in the SUB than SML only at 8 a.m. on day 3. Moreover, we need to focus also on three peaks in the concentration of another micronutrient, i.e. Ni, in the SML during days 2 and 3 of monitoring. It is known that Ni may influence the uptake of Fe by plants (Chen et al. 2009).

The results of the analysis shown as a hierarchical dendrogram for metal concentrations revealed two clusters in the SML and three clusters in the SUB (Figures 6). These clusters group chemical elements according to the comparable dynamics of their concentrations in the course of the 3-day monitoring in the surface microlayer and the subsurface layer:

SML: A (Ag, Cd, Co, K, Ni, Mn, Se, Zn), B (Al, As, Ba, Ca, Cr, Cu, Fe, Li, Mg, Na, Pb, Sr);

SUB: A (Ag, Ba, Na, Ni, Pb), B: (Ca, Cd, Co, Cr, Cu, K, Mg, Mn, Se, Sr, Zn), C (Al, As, Fe, Li).

Within each cluster, the dynamics of concentrations exhibit certain similarities. The formation of two clusters grouping metals in the SML and three clusters in the SUB may be due to the capacity of the SML to accumulate these chemical elements.

Analyses of phytoneuston and phytoplankton in the SML and SUB waters of Lake Gubisz showed the occurrence of algal species characteristic of water bodies with a low trophic state according to Brettum, Andersen (2005). Thus, the taxonomic composition included such taxa of algae as *Merismopedia* sp., *Cosmarium* sp., *Dinobryon* sp., *Peridinium bipes* (Table 3), typical of ultraoligotrophic/oligotrophic/mesotrophic water bodies. According to Jarosiewicz, Fryda (2011), Lake Gubisz may be classified as a mesotrophic lake based on chemical parameters (TSI). The sequence according to the abundance of phytoneuston taxa in (the SML) waters was as follows: Conju-

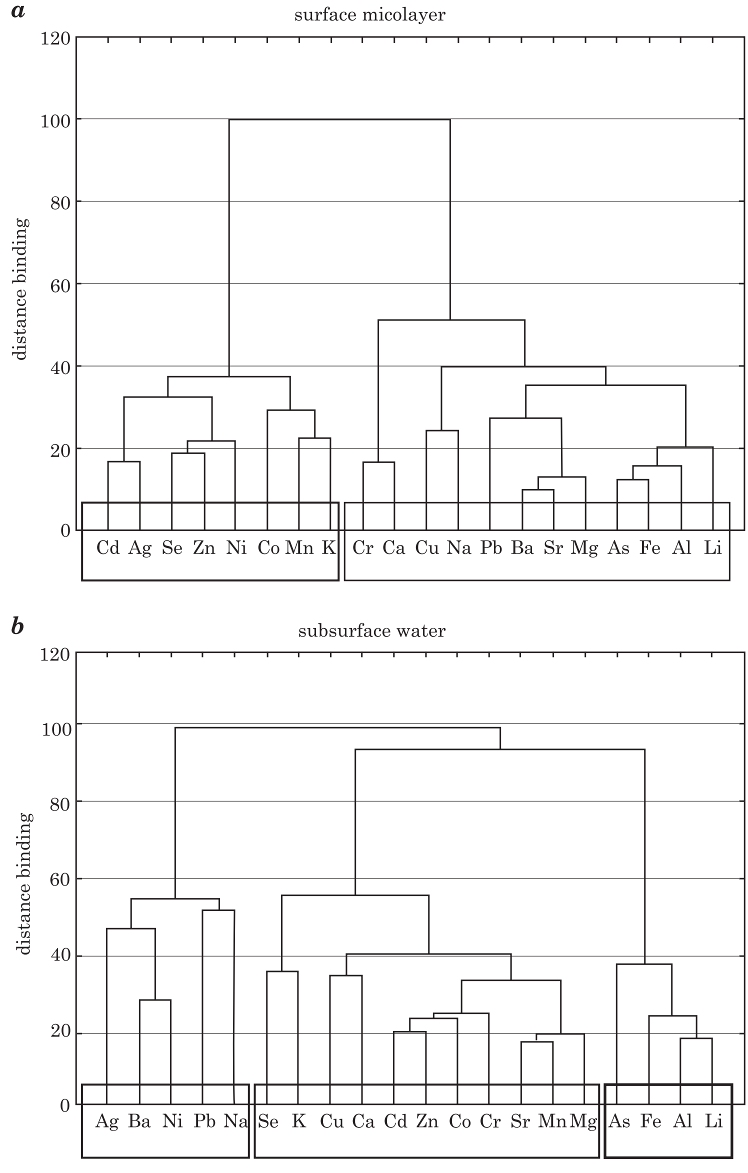

Fig. 6. The hierarchical dendrogram for classification of chemical variables for the SML (*a*) and SUB (*b*)

gatophyceae (70.4%), Bacillariophyceae (14.1%), Cyanophyceae (8.3%), Chrysophyceae (3.5%), Chlorophyceae (3.2%) and Dinophyceae (0.4%). The most numerous (>10%) algal species were *Zygnema stellinum, Spirogyra* sp. The total count of algae in the SML waters was 2.71-fold higher than in the SUB, while the biomass was 4.82-fold greater. An analysis of the taxonomic compo-

Table 3

Species abundance and biomass of phytoneuston in SML and phytoplankton in SUB (data from 2012)

Taxa	Phytoneuston		Phytoplankton	
	abundance	biomass	abundance	biomass
	n 10^3 dm^{-3}	(mg dm^{-3})	n 10^3 dm^{-3}	(mg dm^{-3})
Bacillariophyceae				
Asterionella formosa	176.6	0.132	198.7	0.149
Diatoma elongata	287.0	0.230	176.6	0.141
Gomphonema parvulum			16.6	0.033
Navicula cryptocephala			11.0	0.014
Pinnularia nobilis	110.4	0.144	5.5	0.072
Rhoicosphenia abbreviata	772.8	0.363		
Stauroneis anceps			5.5	0.020
Ulnaria ulna			11.0	0.132
Chlorophyceae				
Botryococcus braunii	110.4	0.11		
Chlorella vulgaris			55.2	0.033
Dictyosphaerium pulchellum	331.2	0.116	22.1	0.077
Elakatothrix genevensis	828.0	0.012	99.40	0.015
Tetraedron minimum			27.6	0.005
Chrysophyceae				
Dinobryon sp.	138.0	0.028	88.3	0.018
Conjugatophyceae				
Closterium sp.	110.4	0.088	16.6	0.132
Cosmarium sp.			11.0	0.166
Euastrum didelta	110.4	0.199	552.0	0.099
Pleurotaenium ehrenbergii	165.6	2.650		
Spirogyra sp.	568.6	31.271	287.0	15.787
Zygnema stellinum	2152.8	86.112	160.1	6.403
Cyanophyceae				
Merismopedia sp.	138.0	0.039		
Planktothrix agardhii	176.6	0.353	138.0	0.276
Snowella sp.	11.0	0.028	16.6	0.041
Dinophyceae				
Ceratium hirundinella	165.6	0.861		
Peridinium bipes			22.1	1.325
Euglenophyceae				
Trachelomonas sp.			71.8	0.538
Total	3919.2	122.735	1446.2	25.478
EF	2.71	4.82		

sition indicates marked quantitative and qualitative differences in the phytoneuston in the SML and in phytoplankton in the SUB, which may promote accumulation of heavy metals in both layers.

Analyses of the taxonomic composition and abundance of phytoplankton (the SUB) showed the following sequence of taxa in the decreasing order: Conjugatophyceae (33.2%), Bacillariophyceae (29.4%), Chlorophyceae (14.1%), Cyanophyceae (10.7%) Chrysophyceae (6.1%), Euglenophyceae (5.0%) and Dinophyceae (1.5%). The most numerous algal species found in the SUB waters were *Spirogyra* sp., *Asterionella formosa, Diatoma elongata* and *Zygnema stellinum*. Algal species which were recorded only in the SML waters included *Botryococcus braunii, Ceratium hirundinella, Merismopedia* sp., *Pleurotaenium ehrenbergii, Rhoicosphenia abbreviata* and these species were not detected in SUB.

Both phytoneuston biomass and chl *a* concentration were significantly higher in the SML than in SUB. Moreover, high values of the EF and chl *a* concentration in the SML may be connected with the low trophic level in that lake. This study showed considerable accumulation of chl *a* in the SML in a lobelia lake in comparison to eutrophic lakes located in the same region (Antonowicz 2008, Antonowicz et al. 2015). Thus, a possible reason for the accumulation of chl *a* in the SML could be the search by phytoplankton for macro- and micronutrients analysed in our study. Vertical migration of phytoplankton is possible in some formations of algae (Harvey, Menden-Deuer 2012).

CONCLUSIONS

In summary, the recorded results provide insight into the functioning of interrelationships concerning the accumulation of metals, including heavy metals, and chl *a* in the SML of a lobelia lake. A circadian dynamic of metals, frequently cyclical in character, was found in the SML and SUB. Based on cluster analysis, similarities were found in the circadian course of changes in these concentrations. In our investigation concerning mutual relations between concentrations of metals in waters of the given lake, the level of chl *a* and the taxonomic composition of algae, their counts and biomass, it was essential to consider the effect of physicochemical parameters of this water body. The microalgal taxonomic composition showed the occurrence of species characteristic of water bodies with low trophic levels.

REFERENCES

Antonowicz J. 2008. *Daily changes in concentrations of selected heavy metals in relation to chlorophyll content in surface water microlayer of lake Gardno.* Ecol. Chem. Engineer. S, 15: 7-15.

Antonowicz J.P. 2014. *Daily fluctuations of nutrients and chlorophyll occurrence in the ecotone hydrosphere - atmosphere of a lobelia lake* (in Polish). Pr. ECOPole, 8(2): 465-470. DOI: 10.2429/proc.2014.8(2)053

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*. Hydrobiologia, 762: 65-80. DOI: 10.1007/s10750-015-2337-7

Antonowicz J., Trojanowski. J. 2010. *Surface microlayer in eutrophic lake: variability in heavy metals contents*. Pol. J. Ecol., 58(4): 617-626.

Antonowicz J., Trojanowski J., Trojanowska Cz. 2010. *24-hour cycle of variability contents of nitrogen forms in surface microlayer of Baltic Sea lagoon lake (North Poland)*. Part I. Baltic Coastal Zone, 14: 37-47.

APHA, 2005. *Standard methods for the examination of water and wastewater*. American Public Health Association, Washington.

Brettum P., Andersen T. 2005. *The use of phytoplankton as indicators of water quality*. Norwegian Institute for Water Research SNO Report 4818-2004: 1-33.

Chen C., Huang D., Liu J. 2009. *Functions and Toxicity of Nickel in Plants: Recent Advances and Future Prospects*. CLEAN-Soil Air Water, 37(4-5): 304-313. DOI: 10.1002/clen.200800199

Cuong D.T., Karuppiah S., Obbard S.P. 2008. *Distribution of heavy metals in the dissolved and suspended phase of the sea-surface microlayer, seawater column and in sediments of Singapore's coastal environment*. Environ. Monit. Assess., 138, 255-272.

Donderski W., Walczak M., Mudryk Z. , Skórczewski P. 1999. *The influence of heavy metals ions on neustonic bacteria*. Baltic Coastal Zone, 2: 53-64.

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

González-Dávila M. 1995. *The role of phytoplankton cells on the control of heavy metal concentration in seawater*. Mar. Chem., 48: 215-236.

Grammatika M., Zimmerman W.B. 2001. *Microhydrodynamics of flotation processes in the sea surface layer*. Dynam. Atmos. Oceans, 34(2-4): 327-348. https://doi.org/10.1016/S0377-0265(01)00073-2

Hardy J., Apts C., Crecelius E., Bloom N. 1985. *Seasurface microlayer metals enrichments in an urban and rural bay*. Estuar. Coast. Shelf S., 20(3): 299-312. https://doi.org/10.1016/0272-7714(85)90044-7

Harvey E.L., Menden-Deuer S. 2012. *Predator-induced fleeing behaviors in phytoplankton: A new mechanism for harmful algal bloom formation?* PLoS ONE, 7(9): 1-8. DOI: 10.1371/journal.pone.0046438

Hillbricht-Ilkowska A., Kostrzewska-Szlakowska I. 2004. *Surface microlayer in lakes of different trophic status: nutrients concentration and accumulation*. Pol. J. Ecol., 52: 461-478.

Hossain M.A., Piyatida P., Teixeira da Silva J.A., Fujita M. 2012. *Molecular mechanism of heavy metal toxicity and tolerance in plants: central role of glutathione in detoxification of reactive oxygen species and methylglyoxal and in heavy metal chelation*. J. Bot., article ID 872875: 37. http://dx.doi.org/10.1155/2012/872875

Jańczak J. 1997. *Atlas of Polish Lakes*. Poznań, Bogucki Scientific Publishers. (in Polish)

Jarosiewicz A., Fryda E. 2011. *Trophic diversity of chosen lakes of the Słupia river catchment area*. Słupskie Prace Biologiczne, 8: 51-65. (in Polish)

Jeffrey S.W., Humphrey G.F. 1975. *New spectrophotometric equations for determining chlorophyll a, b, c1 and c2 in higher plants, algae and natural phytoplankton*. Bioch. Physiol. Pflanzen, 167: 191-194.

Knulst J., Backlund P., Hessen D., Riise G., Södergren A. 1997. *Response of surface microlayers to artificial acid precipitation in a mesohumic lake in Norway*. Wat. Res., 31(9): 2177- 2186.

Kostrzewska-Szlakowska I. 2003. *A surface microlayer of water: Characteristics and research methods*. Wiad. Ekol., 69(3): 183-203. (in Polish)

Kozarec Z., Ćosović B., Frika S., Möbious D., Hacke S. 2003. *Complex methodological approach to the studies of natural microlayer at the air/water interface*. Colloid. Surface. A, 219: 173-186. DOI: 10.1016/S0927-7757(03)00032-3

Kraska M., Klimaszyk P., Piotrowicz R. 2013. *Anthropogenic changes in properties of the water and spatial structure of the vegetation of the lobelia lake Lake Modre in the Bytów Lakeland.* Oceanol. Hydrobiol. Stud., 42(3): 302–313.

Kraska M., Piotrowicz R., Klimaszek P. 1996. *Lobelian lakes in Poland.* Chrońmy Przyrodę Ojczystą, 52 (3): 5-25. (in Polish)

Lis H., Kranzler C., Keren N., Shaked Y. 2015. A *comparative study of iron uptake rates and mechanisms amongst marine and fresh water cyanobacteria: prevalence of reductive iron uptake*. Life, 5(1): 841-860. DOI: 10.3390/life5010841.5

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

Rahaman S.M.B., Biswas S.K., Rahaman M.S., Ghosh A.K., Sarder L., Siraj S.M.S, Sheikh I.S. 2014. *Seasonal nutrient distribution in the Rupsha-Passur tidal river system of the Sundarbans mangrove forest, Bangladesh.* Ecol. Process., **3**(18): 1-11. http://www.ecologicalprocesses.com/content/3/1/18

Ravet K., Pilon M. 2013. *Copper and iron homeostasis in plants: the challenges of oxidative stress.* Antioxid. Redox Sign., 19(9): 919-932. DOI: 10.1089/ars.2012.5084

Rumbolt D., Snedaker S. 1999. *Sea-surface microlayer toxicity off the Florida Keys.* Mar. Environ. Res., 47: 457-472.

Trojanowski J., Trojanowska Cz., Antonowicz J. 2001. *Nitrogen and phosphorus in surface microlayers of the lake Gardno.* Ecohydrol. Hydrobiol., 1: 457-453.

Trojanowski J., Antonowicz J. 2011. *Heavy metals in surface microlayer in water of lake Gardno.* Arch. Environ. Prot., 37: 75-88.

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. DOI: 10.1016/j.marpolbul.2004.03.016

Xue H., Strumm W., Sigg L. 1988. *The binding of heavy metals to algal surfaces.* Water Res., 22: 917-926. DOI: 10.1016/0043-1354(88)90029-2

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 Interf. Sci., 264(1): 148-59. https://doi.org/10.1016/S0021-9797(03)00390-4