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SEASONAL CHANGES IN THE ACCUMULATION OF NUTRIENTS IN THE HYDROSPHERE-ATMOSPHERE INTERFACE OF URBAN PONDS (SŁUPSK, NORTHERN POLAND)

Józef Piotr Antonowicz[1], Magdalena Wolska[2], Aneta Libera[3]

[1] *Department of Environmental Chemistry, Institute of Biology and Environmental Protection, Pomeranian University in Słupsk, ul. Arciszewskiego 22b, 76-200 Słupsk, Poland*
e-mail: antonowicz@apsl.edu.pl
[2] *Target S.A., Kartoszyno, ul. Przemysłowa 5, 84-110 Krokowa, Poland*
[3] *Group of Pomeranian Landscape Parks, Wdzydze Landscape Park, ul. Świętojańska 5E, 83-400 Kościerzyna, Poland*

Abstract

Seasonal changes were investigated in concentrations of biogenic substances in the surface microlayer and subsurface water in ponds in the city of Słupsk (Northern Poland). Water samples from the surface microlayer were collected using the Garrett screen. Those water samples were analysed to determine concentrations of nitrogen and phosphorus compounds. It was found that biogenic substances are accumulated in the surface microlayer to a greater extent than in the subsurface water layer. This accumulation is subjected to seasonal changes. The source of the analysed nitrogen and phosphorus compounds in the surface microlayer was connected with their concentration in subsurface water.

Key words: pond, surface microlayer, nutrients, seasonal changes

INTRODUCTION

Ponds are small water bodies, mostly freshwater ones, typically characterised by lack of profoundal and pelagial zone (Żmudziński et al. 2002). Ponds may be compared to the lake littoral zone, since light reaches the benthic zone and vegetation develops over the entire bottom area. Ponds are characterised by liable environmental conditions. Usually, winds cause mixing of water reaching down to the bottom and large temperature amplitudes are observed, particularly in the seasonal cycle (Żmudziński 1997). Ponds located within urban areas can particularly be susceptible to urban pollution. Such factors as the vicinity of urban infrastructure, traffic routes and fertilisation of urban green areas expose them to deposition of pollutants form surface run-off, the atmosphere and leachate. Sewage discharge, road and traffic-related pollutants as well as air pollution increase the rate of hypertrophy in ponds in urban areas (Kubiak and Tórz 2005). In contrast, pond self-purification processes are limited (Kostecki and Krodkiewska 2005) due to the small size of the waterbody. Urban ponds play the role of objects for recreation and leisure activities of city inhabitants, while at the same time they are refuges for terrestrial organisms (e.g. *Anatinae*, *Cygnini*). Regular monitoring and sustainable use are required (Kubiak and Tórz 2005).

Surface microlayer (SML) covers the surface of all bodies of water. It is an interface between the hydrosphere and the atmosphere. SML is a thin layer contributing to a regulated exchange of substances between the hydrosphere and the atmosphere (Kostrzewska-Szlakowska 2003, Mudryk et al. 2003, Antonowicz et al. 2015). It is a layer of water, which is first to respond to atmospheric contamination. SML constitutes a protective filter due to its absorbing capacity and occurring biochemical processes (Mudryk et al. 2003, Rumbold and Snedaker 1999). Chemical substances are contained in the surface microlayer at higher concentrations than in the limnetic zone. These substances include lipophilic carbohydrates, aromatic hydrocarbons, biogenic substances, metals and pesticides (Norkrans 1980, Trojanowski et al. 2001, Antonowicz et al. 2015). These pollutants may be detoxified by neuston organisms living in SML, which naturally leads to a reduction of water pollutants (Walczak and Donderski 2003). Also SML as a film protects water bodies against UV radiation, acid rain, heavy metals (Mudryk et al. 2001, Sieburth 1983) as well as PCB, DDT and detergents (Walczak and Donderski 2003). These substances are bound in SML and by binding they are detoxified, resulting in self-purification processes of standing water (Hillbricht-Ilkowska and Kostrzewska-Szlakowska 2004). SML is enriched in pollutants due to specific chemical biological and physical properties. Physical forces contributing to nutrient accumulation in SML include surface tension forces, physical adsorption, atmospheric transport, flotation processes, Langmuir circulation and chemical absorption. Penetration of substances to the limnetic zone is inhibited by the hydrophobic properties of the lipid membrane, being the most external section of SML (Norkrans 1980, Kostrzewska-Szlakowska 2003, Antonowicz et al. 2015) as well as interfacial tension forces (Johnson and Cooke 1980). According to Estep and Remsen (1985), SML may be compared to an environmental factory, since it is the site of production as well as transport of products to the atmosphere and hydrosphere.

The aim of this study was to determine the capacity to accumulate biogenic substances in surface microlayer of water of four ponds in the city of Słupsk and to show seasonal dynamics of their concentrations.

MATERIALS AND METHODS

Sampling

The object of the study were four ponds located in the city of Słupsk. Water samples for analyses were collected of the phenological seasons during the period from October 2008 to September 2009. The ponds are situated along the north-south axis. Pond 1 is located farthest to the north at Bałtycka street, pond 2 is located at Kaszubska street, pond 3 at Nad Śluzami street, while pond 4 is situated farthest to the south at Arciszewskiego street (Fig. 1). Ponds are located within the catchment area of the river Słupia. Main source of pollution of the ponds are diffuse pollution, mainly from traffic routes, urban settlements.

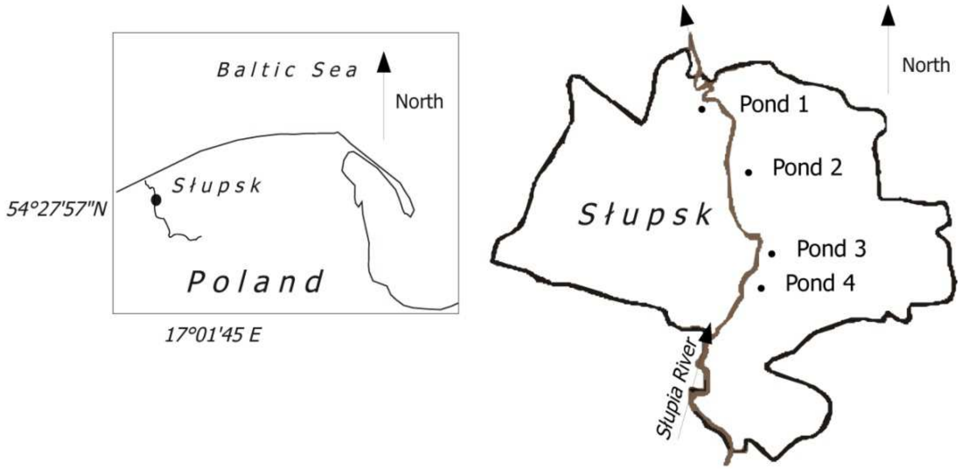

Fig. 1. Localisation studied ponds in Słupsk

Samples of the surface microlayer (SML) (thickness 242 μm ± 40) were collected with a Garrett screen (Garrett 1965), while samples of the subsurface layer (SUB) were taken at the depth of about 15 cm. The Garrett screen was sterilised with ethanol and deionised distilled water in the laboratory, and immediately before the sampling procedure with the first water samples from the pond.

Chemical analyses

Chemical analyses included determinations of concentrations of ammonium nitrogen ($N\text{-}NH_4$) by direct nesslerization and nitrate nitrogen ($N\text{-}NO_3$) using sodium salicylate. Concentrations of both nutrients were determined spectrophotometrically. Organic nitrogen (N-org) was assayed after mineralisation. Total nitrogen according to Kiejdahl (N-TK) was calculated mathematically from the sum of total nitrogen according to Kiejdahl and ammonium nitrogen (Hermanowicz et al. 1999). Phosphate phosphorus ($P\text{-}PO_4$) was determined using ascorbic acid, total phosphorus (P-T) was assayed after mineralisation, while absorbance was next determined spectrophotometrically. Spectrophotometric analyses were performed using a Shimadzu UV-VIS 1202 spectrophotometer. Organic phosphorus (P-org) was the difference between total and phosphate phosphorus. Chlorine ions were assayed by argentometry (Hermanowicz et al. 1999). Electrolytic conductivity (PE) was determined by potentiometry using a CP-315 Elmetron microcomputer conductometer, while water reaction (pH) was determined by potentiometry using a CC-315 Elmetron pH meter.

Statistical analysis

In order to compare the investigated layers, i.e. the 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).

Statistical analyses such as the Shapiro-Wilk normality test as well as the mean, median, minimum, maximum, standard deviation and Spearman's rs correlation values were calculated using the Past computer software (Hammer et al. 2001). Cluster analysis was performed using the Statistica package (Statsoft 2012).

RESULTS

In Tables 1-4 there are summarized statistical parameters for concentrations of biogenic substances, chlorides as well as pH, PE and temperature for the results obtained for subsurface water and the surface microlayer in four ponds in the city of Słupsk. In the SUB layer the mean concentration of N-NH_4 was highest in pond 4, those of N-NO_3, P-PO_4 and P-T were highest in pond 1, those of N-org and N-TK in pond 3, while that of P-org was greatest in pond 2. In SML the highest concentrations of N-NH_4 and P-org were recorded in pond 2, those of N-TK, N-org, N-NH_4 and P-PO_4 in pond 1, whereas the concentration of P-T was greatest in pond 3. Mean concentration of chloride ions in SML and SUB was highest in pond 1. The pH value was comparable in all the investigated ponds, with the mean value in SML and SUB ranging from 7.5 to 7.6, which indicates a weakly basic reaction. The highest electrolytic conductivity was recorded in pond 1 (0.69 mS). Mean temperature in pond 3 was highest, amounting to 12.5ºC, while in pond 2 mean temperature was 9.2ºC.

Investigated biogenic substances were accumulated in the surface microlayer to a greater extent than it was observed in the limnetic zone. Table 5 presents enrichment factors for each of the analysed ponds. In the case of N-NO_3 obtained enrichment factors ranged from 1.36 in pond 3 to 1.93 in pond 2, for N-org from 1.14 in pond 1 to 1.73 in pond 3; N-TK from 1.30 in pond 4 to 2.19 in pond 3, respectively. In turn, for N-NH_4 the enrichment factor recorded in ponds 1-3 was 1.36-

Table 1

Statistical parameters of concentration of nutrients and pH, PE and T
in SML and SUB of Pond 1

Layer	Parameter	Unit	Mean	Min.	Max.	SD
SML	$N\text{-}NH_4$	µg dm^{-3}	31.7	12.7	61.4	16.1
	$N\text{-}NO_3$	µg dm^{-3}	80.7	38.3	154.0	44.5
	N-org	mg dm^{-3}	1.15	0.33	1.67	0.55
	N-TK	mg dm^{-3}	1.18	0.22	4.39	1.49
	$P\text{-}PO_4$	µg dm^{-3}	36.0	3.8	65.6	23.3
	P-org	µg dm^{-3}	15.3	8.3	18.3	3.3
	P-T	µg dm^{-3}	51.3	17.5	81.8	24.7
	Cl^-	mg dm^{-3}	708.7	21.8	1435.5	569.8
	pH	degrees	7.5	7.2	8.0	0.3
	PE	mS	0.69	0.59	0.75	0.07
SUB	$N\text{-}NH_4$	µg dm^{-3}	21.0	6.5	38.2	9.9
	$N\text{-}NO_3$	µg dm^{-3}	56.9	17.3	147.4	44.1
	N-org	mg dm^{-3}	1.01	0.26	1.76	0.52
	N-TK	mg dm^{-3}	1.18	0.35	1.68	0.55
	$P\text{-}PO_4$	µg dm^{-3}	25.4	2.58	63.5	21.8
	P-org	µg dm^{-3}	12.0	7.2	15.9	2.9
	P-T	µg dm^{-3}	37.4	14.2	79.4	23.1
	Cl^-	mg dm^{-3}	606.8	13.9	1664.3	636.2
	pH	degrees	7.5	7.0	8.0	0.3
	PE	mS	0.69	0.62	0.75	0.06
	T	°C	11.4	1.0	22.5	12.0

Table 2

Statistical parameters of concentration of nutrients and pH, PE and T in SML and SUB of Pond 2

Layer	Parameter	Unit	Mean	Min.	Max.	SD
SML	$N\text{-}NH_4$	µg dm^{-3}	34.2	6.2	80.3	23.3
	$N\text{-}NO_3$	µg dm^{-3}	67.3	11.8	183.2	61.5
	N-org	mg dm^{-3}	2.33	0.99	4.85	1.44
	N-TK	mg dm^{-3}	2.37	1.00	4.89	1.45
	$P\text{-}PO_4$	µg dm^{-3}	15.4	5.6	30.4	8.9
	P-org	µg dm^{-3}	34.0	8.3	65.3	23.2
	P-T	µg dm^{-3}	44.0	13.9	77.8	24.3
	Cl^-	mg dm^{-3}	300.5	19.8	709.5	259.1
	pH	degrees	7.6	7.3	8.3	0.4
	PE	µS	0.59	0.48	0.83	0.12
SUB	$N\text{-}NH_4$	µg dm^{-3}	23.0	4.9	71.3	20.4
	$N\text{-}NO_3$	µg dm^{-3}	35.0	8.7	91.9	29.7
	N-org	mg dm^{-3}	1.56	0.76	3.22	0.88
	N-TK	mg dm^{-3}	1.58	0.77	3.23	0.88
	$P\text{-}PO_4$	µg dm^{-3}	9.5	3.3	21.1	6.4
	P-org	µg dm^{-3}	26.3	4.2	59.8	23.4
	P-T	µg dm^{-3}	32.0	7.4	72.1	24.0
	Cl^-	mg dm^{-3}	259.3	16.6	407.0	187.4
	pH	degrees	7.6	7.0	8.3	0.5
	PE	µS	0.54	0.46	0.62	0.06
	T	°C	9.2	1.0	17.0	5.4

Table 3

Statistical parameters of concentration of nutrients and pH, PE and T in SML and SUB of Pond 3

Layer	Parameter	Unit	Mean	Min.	Max.	SD
SML	$N\text{-}NH_4$	µg dm^{-3}	25.4	10.4	53.7	15.4
	$N\text{-}NO_3$	µg dm^{-3}	64.7	25.3	135.7	48.4
	N-org	mg dm^{-3}	3.45	0.93	6.92	2.06
	N-TK	mg dm^{-3}	4.57	0.86	6.98	2.09
	$P\text{-}PO_4$	µg dm^{-3}	28.2	11.7	58.9	19.8
	P-org	µg dm^{-3}	28.2	18.8	40.4	7.7
	P-T	µg dm^{-3}	57.3	36.88	99.3	24.61
	Cl^-	mg dm^{-3}	520.8	15.4	1163.2	475.5
	pH	degrees	7.6	7.2	8.5	0.4
	PE	µS	0.66	0.55	0.68	0.05
SUB	$N\text{-}NH_4$	µg dm^{-3}	18.7	3.4	34.5	11.8
	$N - NO_3$	µg dm^{-3}	47.6	21.0	125.8	40.7
	N-org	mg dm^{-3}	1.99	0.21	4.52	1.73
	N - TK	mg dm^{-3}	2.09	0.22	4.55	1.69
	$P\text{-}PO_4$	µg dm^{-3}	19.6	4.8	50.5	15.6
	P-org	µg dm^{-3}	16.1	5.9	24.9	7.8
	P-T	µg dm^{-3}	35.7	17.6	75.0	20.9
	Cl^-	mg dm^{-3}	426.6	36.6	1092.3	420.6
	pH	degree	7.5	7.1	8.9	0.5
	PE	µS	0.64	0.55	0.69	0.05
	T	°C	12.5	1.0	23.0	8.4

Table 4

Statistical parameters of concentration of nutrients and pH, PE and T
in SML and SUB of Pond 4

Layer	Parameter	Unit	Mean	Min.	Max.	SD
SML	$N\text{-}NH_4$	μg dm^{-3}	25.6	11.8	36.8	8.6
	$N\text{-}NO_3$	μg dm^{-3}	62.5	23.5	135.1	39.2
	N-org	mg dm^{-3}	2.03	0.48	4.78	1.40
	N-TK	mg dm^{-3}	2.06	0.51	4.81	1.40
	$P\text{-}PO_4$	μg dm^{-3}	18.6	4.6	44.0	13.0
	P-org	μg dm^{-3}	17.0	7.2	29.3	9.1
	P-T	μg dm^{-3}	35.5	22.2	65.2	15.1
	Cl^-	mg dm^{-3}	348.5	13.5	755.7	286.6
	pH	degrees	7.6	7.1	7.9	0.3
	PE	μS	0.62	0.32	0.8	0.15
SUB	$N\text{-}NH_4$	μg dm^{-3}	27.3	4.2	97.6	30.2
	$N - NO_3$	μg dm^{-3}	35.6	4.4	128.3	41.2
	N-org	mg dm^{-3}	1.57	0.20	5.54	1.69
	N - TK	mg dm^{-3}	1.59	0.21	5.57	1.69
	$P\text{-}PO_4$	μg dm^{-3}	13.6	2.4	39.3	11.6
	P-org	μg dm^{-3}	11.7	4.4	28.7	9.3
	P-T	μg dm^{-3}	25.3	15.3	43.7	11.2
	Cl^-	mg dm^{-3}	369.8	10.2	933.9	340.1
	pH	degrees	7.5	7.1	7.8	0.2
	PE	μS	0.65	0.56	0.85	0.09
	T	°C	11.8	1.0	22.0	7.6

Table 5

Summary enrichment factors in all studied periods

	Pond 1	Pond 2	Pond 3	Pond 4
$N\text{-}NH_4$	1.51	1.49	1.36	0.94
$N\text{-}NO_3$	1.42	1.93	1.36	1.75
N-org	1.14	1.49	1.73	1.29
N-TK	1.44	1.50	2.19	1.30
$P\text{-}PO_4$	1.42	1.62	1.44	1.36
P-org	1.27	1.29	1.75	1.45
P-T	1.37	1.37	1.61	1.40
Cl^-	1.17	1.16	1.22	0.94
pH	1.00	1.01	1.01	1.00
PE	1.00	1.09	1.03	0.95

1.51, while in pond 4 EF = 0.94. Phosphorus compounds were also accumulated in SML: $P\text{-}PO_4$ ranged from 1.36 in pond 4 to 1.62 in pond 2, P-org from 1.27 in pond 1 to 1.75 in pond 3 and P-T from 1.37 in ponds 1 and 2 to 1.61 in pond 3. Water reaction was almost identical in SML and SUB, while PE values were slightly higher in SML in ponds 2 and 3. Chloride ions were accumulated in SML to a very limited degree, within the range from 0.94 to 1.22.

Changes in concentrations of investigated parameters were analysed in terms of seasons of the year. In most cases the highest concentrations of $N\text{-}NH_4$ were recorded in the summer in SML and SUB. In most cases concentrations in SML indicated a greater accumulation of $N\text{-}NH_4$ in SML than it is observed in the SUB layer (Fig. 2). Only in the summer in pond 4 a depletion of this nutrient was observed in SML. In the other seasons in pond 4 higher concentrations were recorded in SML than in SUB. The concentration of $N\text{-}NO_3$ in SUB was greatest in the summer and autumn in ponds 3 and 4, in pond 2 it was in the spring, while in pond 1 in the winter and summer (Fig. 3). Generally in all the ponds and seasons greater concentrations were observed in SML in comparison to SUB, except for pond 3 in the autumn. The highest N-org concentration in the SML and SUB layers was recorded in ponds 1, 3 and 4 in the summer-autumn period, whereas in pond 2 it was in the spring-summer period (Fig. 4). Since N-org accounted for approx. 99% N-TK, the distribution of N-org and N-TK in the seasons was comparable.

The highest $P\text{-}PO_4$ concentration was recorded in the summer season in SML and SUB (Fig. 5), similarly as it was for P-org in ponds 2-4. Maximum P-T values were recorded in SML and SUB in the summer period in ponds 3 and 4, in pond 1 in SUB, while in pond 2 it was in the spring (Figs 6 and 7). In the case of seasonal changes in pH the highest pH values were observed in the investigated ponds in the winter period both in SML and SUB (Fig. 8).

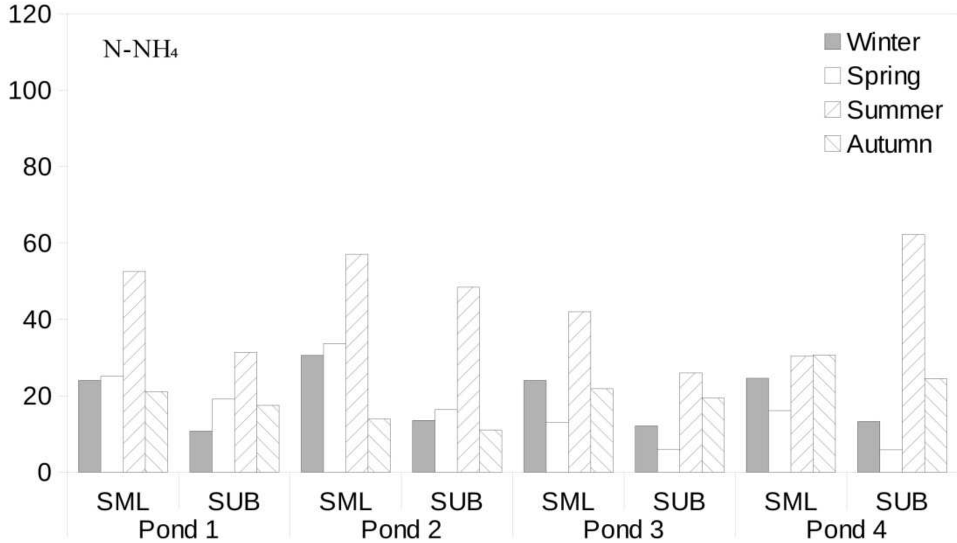

Fig. 2. Seasonal dynamic of $N-NH_4$ in SML and SUB of studied ponds

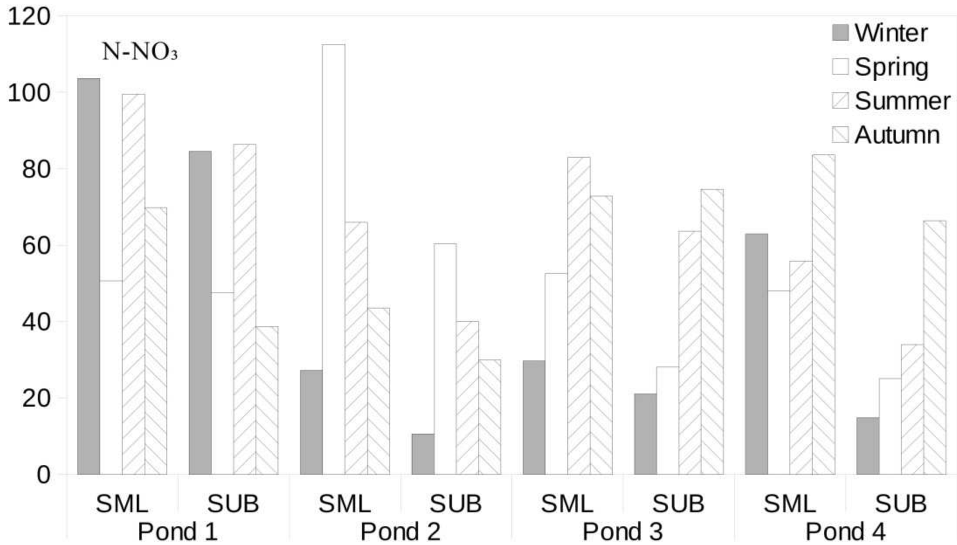

Fig. 3. Seasonal dynamic of $N-NO_3$ in SML and SUB of studied ponds

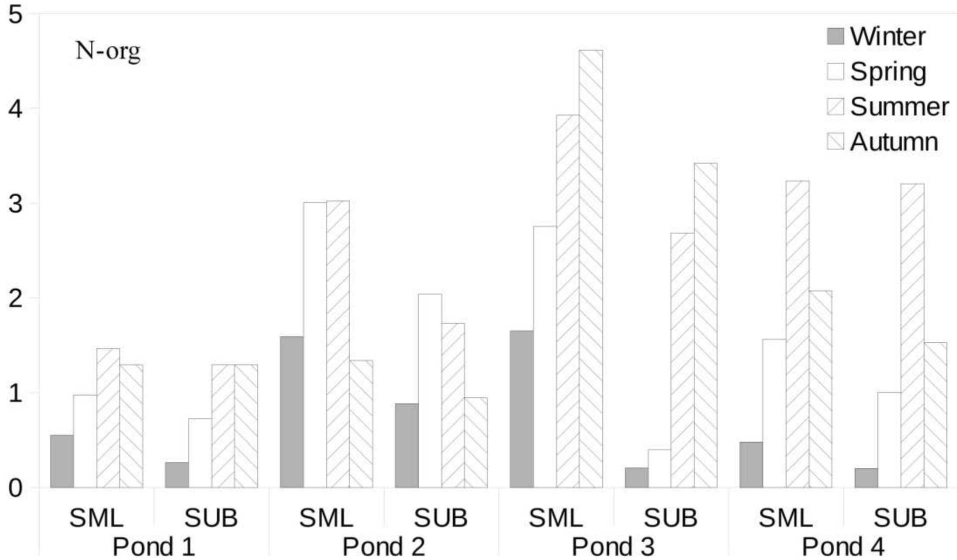

Fig. 4. Seasonal dynamic of N-org in SML and SUB of studied ponds

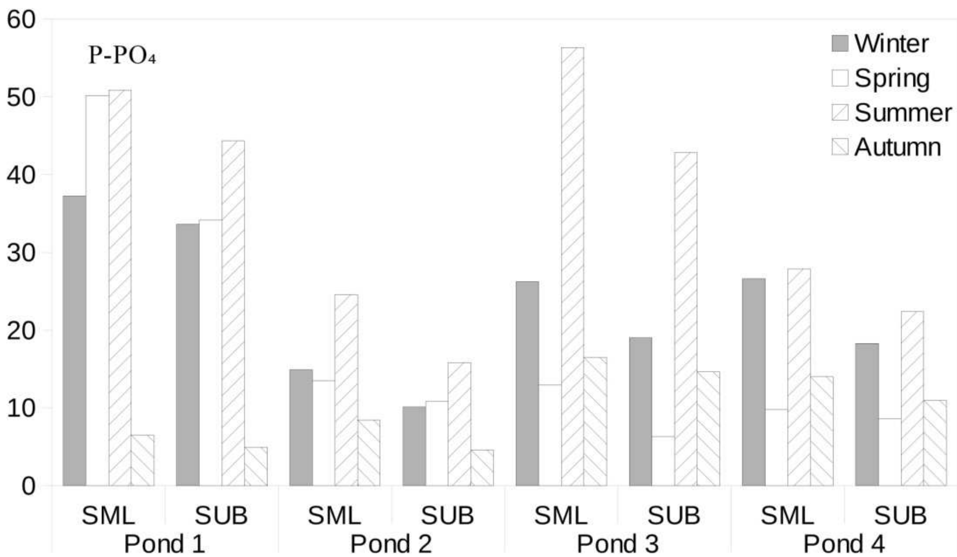

Fig. 5. Seasonal dynamic of $P\text{-}PO_4$ in SML and SUB of studied ponds

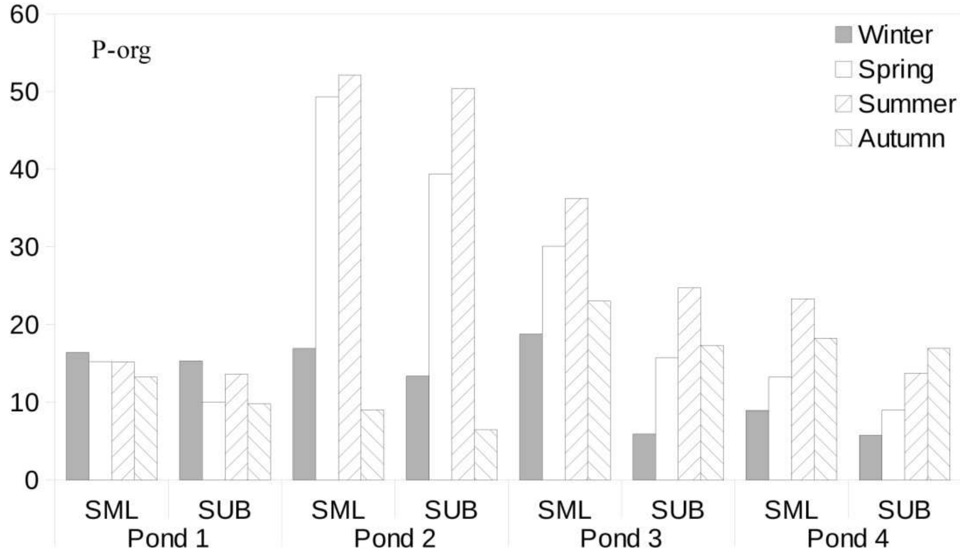

Fig. 6. Seasonal dynamic of P-org in SML and SUB of studied ponds

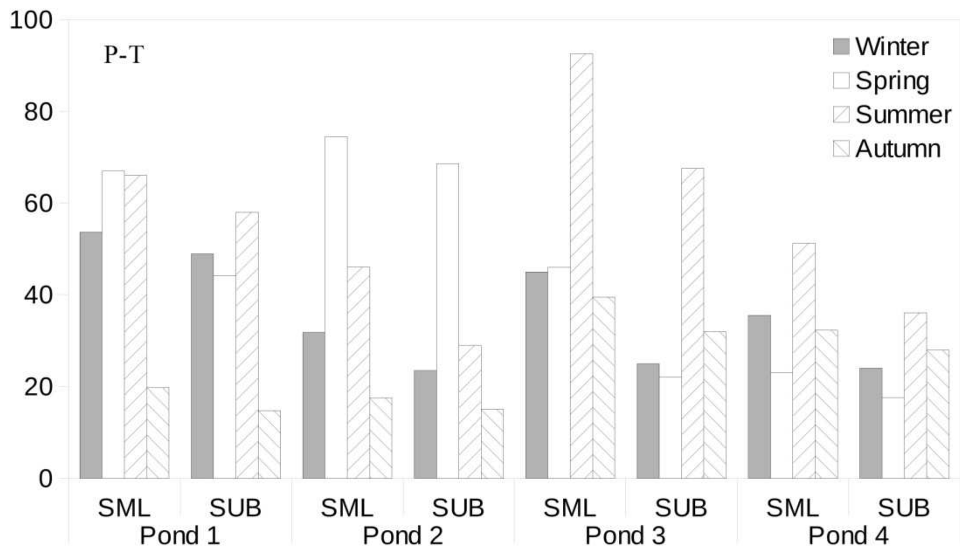

Fig. 7. Seasonal dynamic of P-T in SML and SUB of studied ponds

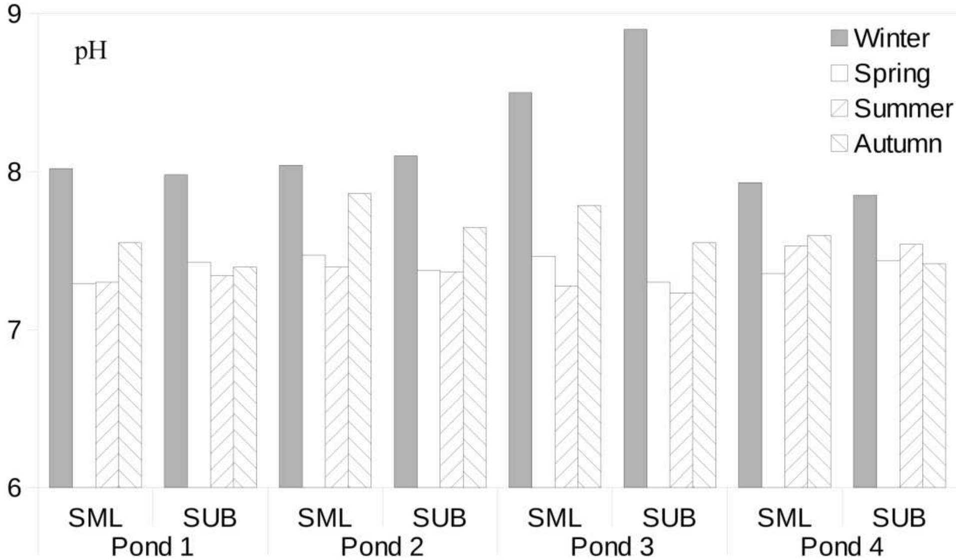

Fig. 8. Seasonal dynamic of P-T in SML and SUB of studied ponds

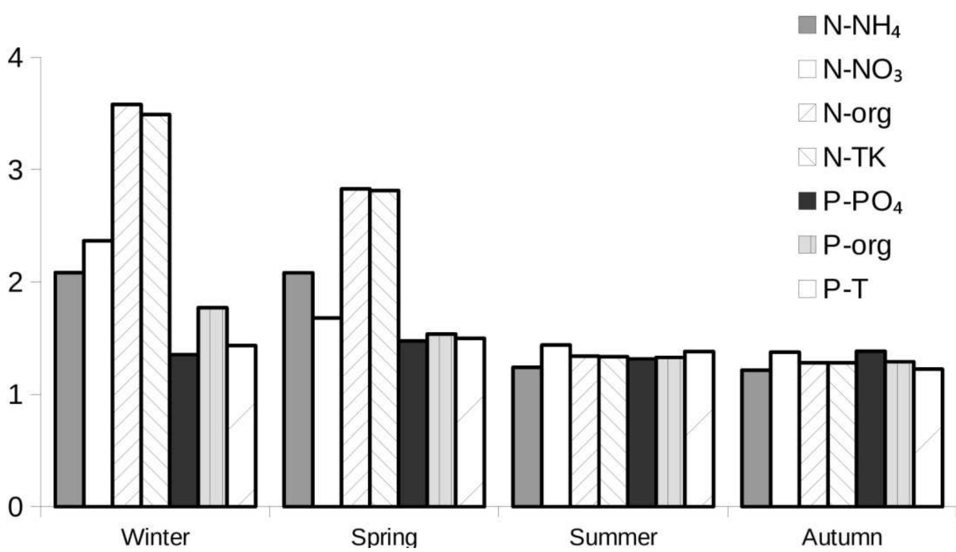

Fig. 9. Seasonal dynamic of enrichment factor in studied ponds

Figure 9 gives enrichment factors recorded for all the 4 analysed ponds for individual biogenic substances in the seasonal cycle. Analysis of the data presented in the graph shows the highest enrichment factors for N-org and N-TK in the winter period (EF = 3.6, 3.5) and the spring period (mean EF = 2.8), while in the summer and autumn periods it was on average EF = 1.3. Analogously calculated enrichment factors for mineral nitrogen forms were also higher in the winter and spring periods. For ammonium nitrogen EF = 2.08 and in the winter and spring it was by 58% greater than in the autumn and summer. In the case of N-NO_3 the highest enrichment factor EF = 2.4 was recorded in the winter, while the lowest EF values were observed in the summer and autumn (EF = 1.4). For P-PO_4, P-org and P-T the obtained seasonal enrichment factors recorded in the winter and spring seasons (total EF = 1.5) were slightly higher than in the summer and autumn periods (total EF = 1.3). The highest enrichment factor was obtained for P-org in the winter at EF = 1.8 and in the spring at EF = 1.5, while for P-PO_4 it was EF = 1.4 and P-T EF = 1.5.

Table 6
Spearman correlations of studied parameters between SML and SUB in four ponds of Słupsk

	Correlation coeficient
N-NH_4	0.83
N-NO_3	0.90
N-org	0.74
N-TK	0.73
P-PO_4	0.96
P-org	0.84
P-T	0.91
Cl^-	0.77
pH	0.63
PE	0.87

Correlation analysis was conducted (Table 6). Spearman's correlation coefficients between concentrations of the analysed parameters in SML and SUB were calculated. The obtained high correlation coefficients indicate that the primary source of analysed biogenic substances and chlorides in SML was connected with the concentration of these substances in SUB. Cluster analysis was also conducted (Fig. 10). The hierarchical diagram presents two clusters. The first cluster contains PE, Cl, P-T, P-PO_4 and N-NO_3, while the other cluster consists of pH, P-org, N-T, N-org and N-NH_4.

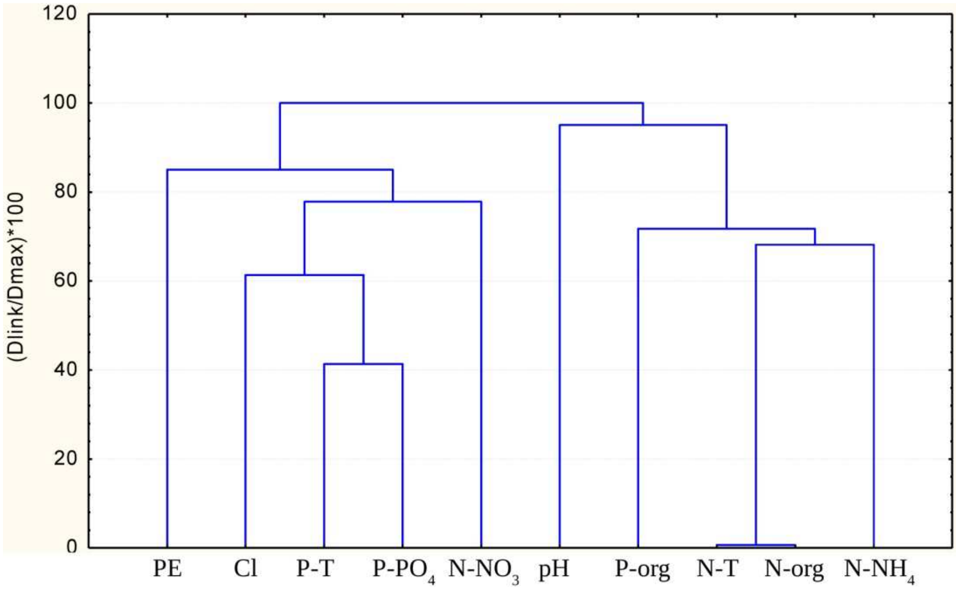

Fig. 10. Cluster analysis of particular enrichment factors performed for all analysed parameters of Słupsk ponds (parameters applied: Complete Linkage, Euclidean distances)

DISCUSSION

Accumulation of nitrogen compounds in the surface water microlayer is connected with physical, chemical and biological processes. Accumulation mechanisms were described in studies by Norkrans (1980) and Mudryk et al. (2003). A significant element influencing enrichment of the surface microlayer with nitrogen compounds is connected with the neuston accumulation in this layer (Burchard and Marshall 2003, Mudryk et al. 2003, Estep et al. 1985, Walczak and Donderski 2003). These microorganisms are involved in such processes as incorporation of mineral nitrogen and phosphorus compounds in organic structures, through their metabolism they change oxidation rate of mineral nitrogen forms, they run mineralisation processes of organic compounds and while dying they release organic compounds (Kajak 2001, Dojlido 1996, Mudryk et al. 2003, Walczak and Donderski 2003). High concentrations of dissolved nutrients in the ponds were the results of biological activity within the SML (Estep and Remsen 1985). As a result, it affects the dynamics of fluctuations in the concentrations of nitrogen and phosphorus compounds in pond water.

Studies on the accumulation of biogens in SML of ponds are scarce. Their results concerning the accumulation of nitrogen compounds in SML are consistent with our data. As a rule we observe a greater accumulation of nutrients in SML than in SUB (Danos et al. 1983, Estep and Remsen 1985). Among available studies concerning ponds in order to compare the presented results we need to mention a study by Estep and Remsen (1985), conducted in an experimental pond of the Wisconsin-

Milwaukee Field Station, USA. In that pond they obtained the following enrichment factors: $EF_{N\text{-}NO3}$ = 3.03 and $EF_{N\text{-}NH4}$ = 2.25. Comparable results were also recorded for N-TK in three lakes varying in their trophic levels, ranging from 1.6 to 2.6 for N-TK, and 1.5 to 2.3 for T-P (Hillbricht-Ilkowska and Kostrzewska-Szlakowska 2004). In sites located in the vicinity of the analysed ponds studies were conducted on the accumulation of nitrogen compounds in a small coastal lake Dołgie Wielkie providing $EF_{N\text{-}T}$ = 1.20, $EF_{N\text{-}org}$ = 1.18, $EF_{N\text{-}NH4}$ = 1.03, $EF_{N\text{-}NO2}$ = 1.21 (Antonowicz et al. 2010), while for phosphorus it was $EF_{P\text{-}T}$ = 1.74, $EF_{P\text{-}Porg}$ = 3.22 and $EF_{P\text{-}PO4}$ = 1.07 (Antonowicz 2013) in an estuarial lake Gardno: $EF_{N\text{-}NH4}$ = 2.3, $EF_{N\text{-}NO3}$ = 3.6, EF_{TKN} = 3.5, $EF_{P\text{-}PO4}$ = 3.4, EF_{Porg} = 3.9 and $EF_{T\text{-}P}$ = 3.6 (Trojanowski et al. 2001).

Seasonal dynamics of fluctuations in biogen levels within SML is also a rarely described problem. Information on this subject was given in a previously mentioned paper by Estep and Remsen (1985). It could be observed that samples collected in the period from August to September had higher $EF_{N\text{-}NO3}$ = 3.85-4.06 and $EF_{N\text{-}NH3}$ = 1.16-4.16 than in May and June with $EF_{N\text{-}NO3}$ = 0.57-2.89 and $EF_{N\text{-}NH3}$ = 1.20-2.29. In the ponds in Słupsk in the autumn period we also observed higher enrichment factors, while in the summer and spring they were comparable. Successive phenological seasons stimulate growth and metabolism of plankton in periods of the greatest insolation (spring, summer), followed by their reduction particularly in the winter season. An inevitable effect of fluctuations in the population size of plankton is connected with changes in nutrient concentrations as a result of their metabolisation by plankton as well as its degradation (Pliński 1992). In urban ponds municipal pollutants constitute another significant factor affecting the dynamics of biogens (Kubiak and Tórz 2005). The analysed ponds are located at a distance of maximum several hundred metres from the Słupia River. This river carries pollutants, including biogens (Jarosiewicz and Dalszewska 2008). It is likely that to a certain extent surface runoff, capillary ascension and narrow channels may influence chemistry of these ponds, particularly in the soil pores at a high water stage in the Słupia. Based on the dendrogram provided by cluster analysis it may be assumed that large amounts of pollutants penetrate to the analysed ponds with contamination generated most probably by surface runoff, e.g. chlorine ions, constituting a primary component of salt mixtures used in deicing of city streets (Czarna 2013), with such nutrients as P-T, $P\text{-}PO_4$ and $N\text{-}NO_3$ being found together with chlorine ions in the first cluster. The other cluster comprises organic nitrogen and phosphorus forms, being important components of organic matter, ammonium nitrogen being the final product of denitrification, and pH, which reacts to chemical changes in the ponds. The N-T value includes a very high share of N-org.

Recorded nutrients concentrations indicate high trophic levels in waters of the analysed ponds and they are typically higher or comparable to those recorded in the neighbouring Pomeranian lakes such as e.g. lake Gardno (0.61 mg dm^{-3} N-TK, 18.4 µg dm^{-3} $N\text{-}NH_4$, 24.9 µg dm^{-3} $N\text{-}NO_3$, $P\text{-}PO_4$ 11.7µg dm^{-3}, P-org 11.6 µg dm^{-3} and P-T 23.2 µg dm^{-3}) (Trojanowski et al. 2001). In lake Dobra the N-T concentration was 1.27 mg dm^{-3}, $N\text{-}NO_3$ – 0.11 µg dm^{-3} and $N\text{-}NH_4$ 0.13 µg dm^{-3} (Jarosiewicz and Hetmański 2009).

Seasonal fluctuations in biogenic substances within SML are most likely connected with the fluctuations of their concentrations in SUB. Correlation analysis confirms this assumption. In the investigated ponds we obtained high Spearman's correlation coefficients, calculated from data obtained from nutrients concentrations in SML and SUB. High values of correlation coefficients suggest that most investigated parameters are supplied to SML from SUB. Hillbricht-Ilkowska and Kostrzewska-Szlakowska (2004) also obtained high correlation coefficients between SML and SUB for biogenic substances. Those researchers also observed that trophic levels in lakes have a significant effect on the capacity to accumulate nutrients in SML and on the obtained correlation coefficients between the concentration of nutrients in SML and SUB.

CONCLUSIONS

Nitrogen and phosphorus compounds were accumulated in the studied ponds in the surface microlayer in higher amounts than in the subsurface water layer.
Seasonal dynamics of concentration of studied biogenic substances were observed in both layers: surface microlayer of water and subsurface water. Seasonal dynamics of concentration of studied biogenic substances in the SML usually were correlated to their concentration in the SUB.

REFERENCES

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(5), 817-826.

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

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.

Burchard L., Marshall H.G., 2003. Algal composition and abundance in the neuston surface microlayer from a lake and pond in Virginia (U.S.A.). *J. Limnol.*, 62(2), 139-142.

Czarna M., 2013. Przegląd środków chemicznych stosowanych w zimowym utrzymaniu dróg w Polsce (Overwiew of chemicals applied to winter road maintenance in Poland). *Zesz. Nauk. Inż. Środ. Uniwersytet Zielonogórski*, 151, 18-25, (in Polish).

Danos S.C., Maki J.S., Remsen C.C., 1983. Stratification of microorganisms and nutrients in surface microlayer of small freshwater ponds. *Hydrobiol.*, 98, 193-202.

Dojlido J., 1996. Chemia wód powierzchniowych. (Chemistry of surface waters), Wydawnictwo Ekonomia i Środowisko, Białystok, (in Polish).

Estep K.W., Remsen C.C., 1985. Influence of the surface microlayer on nutrients, chlorophyll and algal diversity of a small eutrophic bog pond. *Hydrobiol.*, 121, 203-213.

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.

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

Hammer Ø., Harper D.A.T., Ryan P.D., 2001. Past: paleontological statistics software package for education and data analysis. *Palaeontol. electron.*, 4(1), 9.
Hermanowicz W., Dojlido J., Dożańska W., Koziorowski B., Zerbe J., 1999. Fizyczno-chemiczne badanie wody i ścieków. (Physico-chemical analyses of water and sewage). Arkady, Warszawa, (in Polish).
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.
Jarosiewicz A., Hetmański T., 2009. Sezonowa zmienność stężenia substancji biogenicznych w wodach jeziora Dobra (Pojezierze Pomorskie). (Seasonal changes in nutrients concentration in lake Dobra (Pomeranian Lake District); trophic state of lake). Słupskie Pr. Biol., 6, 71-79, (in Polish).
Jarosiewicz A., Dalszewska K., 2008. Dynamika składników biogenicznych w rzece Słupi – ocena zdolności samoczyszczenia rzeki. (Biogens dynamics in the Słupia River – self-purification ability of the river). *Słupskie Pr. Biol.*, 5, 63-73, (in Polish).
Johnson B.D., Cooke R.C, 1980. Organic particle and aggregate formation resulting from the dissolution of bubbles in seawater. *Limnol. and Oceanogr.*, 25, (4), 653-661.
Kostrzewska-Szlakowska I., 2003. Mikrowarstwa powierzchniowa wód. Charakterystyka i metody badań. (Surface microlayer of waters. Characteristics and research methods). *Wiad. ekol.*, XLIX, 3, 183-203, (in Polish).
Kostecki M., Krodkiewska M., 2005. Zbiornik Paprocany. Limnologia – Hydrobiologia. (The Paprocany water reservoir. Limnology – Hydrobiology). Polska Akademia Nauk, Zabrze, (in Polish).
Kajak Z., 2001. Hydrobiologia – Limnologia. Ekosystemy wód śródlądowych. (Hydrobiology – Limnology. Inland water ecosystems). Wydawnictwo Naukowe PWN, Warszawa, (in Polish).
Kubiak J., Tórz A., 2005. Eutrofizacja. Podstawowe problemy ochrony wód jeziornych na Pomorzu Zachodnim. (Eutrophication. Primary problems in protection of lake waters in Western Pomerania). *Słupskie Pr. Biol.*, 2, 17-36, (in Polish).
Mudryk Z., Donderski W., Skórczewski P., Walczak M., 2001. Liczebność i biomasa heterotroficznych bakterii neustonowych i planktonowych w estuariowym jeziorze Gardno. (Population size and biomass of heterotrophic neuston and plankton bacteria in the estuarian Lake Gardno). *Słupskie Pr. Przyr.*, 1, 95-104, (in Polish).
Mudryk Z., Trojanowski J., Skórczewski P., Antonowicz J., 2003. Chemical and bacteriological studies of surface and subsurface water layers in estuarine Lake Gardno. *Pol. J. Environ. Stud.*, 12, 199-206.
Norkrans B., 1980. Surface microlayer in aquatic environments. *Adv. Microb. Ecol.*, 4, 51-85.
Pliński M., 1992. Hydrobiologia ogólna. (General hydrobiology). Wydawnictwo Uniwersytetu Gdańskiego, Gdańsk, (in Polish).
Rumbold D., Snedaker S., 1999. Sea-surface microlayer toxicity off the Florida Keys. *Mar. Environ. Res.*, 47, 457-472.
Sieburth J.N., 1983. Microbiological and organic-chemical processes in the surface and mixed layers. Air-sea exchange of gases and particles. *Math. Phys. Sci.*, 108, 121-172.
StatSoft, Inc., 2012. STATISTICA (data analysis software system), version 12, www.statsoft.com.
Trojanowski J., Trojanowska C., Antonowicz J., 2001. Nitrogen and phosphorus in surface microlayers of an estuarine, shallow lake (north Poland). *Ecohydrol. & Hydrobiol.*, 1, 457-463.
Walczak M., Donderski W., 2003. Decomposition of anionic surface active substances by bacteria from the surface microlayer of Lake Jeziorak Mały. *Pol. J. Environ. Stud.*, 13 (3), 325-331.
Żmudziński L., 1997. Hydrobiologia: Życie wód słodkich i morskich. (Hydrobiology: Life in fresh water and seawater). Wydawnictwo Wyższej Szkoły Pedagogicznej w Słupsku, Słupsk, (in Polish).

Żmudziński L., Kornijów R., Bolałek J., Górniak A., Olańczuk-Neyman K., Pęczalska A., Korzeniewski K., 2002. Słownik hydrobiologiczny. (Hydrobiological dictionary). Państwowe Wydawnictwo Naukowe, Warszawa, (in Polish).

SEZONOWE ZMIANY AKUMULACJI SUBSTANCJI BIOGENICZNYCH W INTERFAZIE HYDROSFERA-ATMOSFERA STAWÓW MIEJSKICH (SŁUPSK, PÓŁNOCNA POLSKA)

Streszczenie

Badano sezonowe zmiany stężeń substancji biogenicznych w mikrowarstwie powierzchniowej i wodzie podpowierzchniowej w stawach w Słupsku (północna Polska). Próbki wody z mikrowarstwy powierzchniowej pobierano za pomocą siatki Garretta. W pozyskanych próbkach wody badano stężenie związków azotu i fosforu. Stwierdzono, że substancje biogeniczne akumulują się w mikrowarstwie powierzchniowej w wyższym stopniu niż w wodzie podpowierzchniowej. Akumulacja ta podlega sezonowym zmianom. Źródłem badanych związków azotu i fosforu w mikrowarstwie powierzchniowej jest ich koncentracja w wodzie podpowierzchniowej.