

Article

# Phytoneuston and Chemical Composition of Surface Microlayer of Urban Water Bodies

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**Abstract:** The concentration of chemical and biological parameters in the ecotone of the surface microlayer (SML) occurring between the hydrosphere and the atmosphere of urban water bodies was investigated. Parallel, sub-surface water (SUB) analyses were carried out to compare the SML properties with the water column. The concentrations of trace metals, macronutrients, nutrients, chlorophyll *a*, pheophytin, abundance and biomass of phytoplankton and the number of heterotrophic bacteria in both studied layers were analyzed. Each of the studied groups of chemical parameters was characterized by specific properties of accumulation. Trace metals occurring in concentrations below 1 ppm, such as Al, Ba, Cd, Cr, Cu, Fe, Mn, Ni, Zn and metalloid As, were accumulated to a higher degree in SML than in SUB. Macroelement concentrations, with the exception of Mg, were lower in the SML compared to the SUB. Nutrients, autotrophic and heterotrophic microorganisms occurred in the SML to a higher degree than in the SUB. Bacillariophyceae dominated the analyzed water bodies, which are typical for the spring period, as well as Chrysophyceae, Chlorophyceae, Dinophyceae and Euglenophyceae. Cyanobacteria dominated in one of the ponds. The abundance of individual phytoplankton groups was significantly correlated with Ca, K, Na, P-org, SO<sub>4</sub><sup>2-</sup>, F<sup>-</sup>, Al and Sr.

**Keywords:** surface microlayer; phytoneuston; phytoplankton; metals; nutrients; urban water body

## 1. Introduction

The surface microlayer (SML) is an ecotone, which constitutes an interface between the hydrosphere and the atmosphere. It is a thin layer of maximum 1000 µm in thickness [1]. The SML is unique due to its physical, chemical and biological properties, which differ from those of subsurface water (SUB) [1,2]. The SML is capable of accumulating microorganisms and chemical substances at a rate as high as 100-fold greater than that observed in the SUB [3]. The SML is the zone of matter and energy exchange between the hydrosphere and the atmosphere, and, as such, it is affected by global climate changes [4].

The accumulation of chemical substances in the SML may vary, as it is dependent on many factors such as the chemical composition of water, salinity, the nutrient status and the presence of neustonic organisms (organisms that live upon the upper surface of waters or beneath its surface film, the SML) [5,6]. The SML may also accumulate toxic substances at greater amounts than observed in the pelagic zone [7]. At the same time, it is the zone that accumulates nutrients [5,8]. In turn, such substances as calcium, magnesium, potassium or sodium, being macroelements found at high concentrations in the pelagic zone, are usually not accumulated in the SML [9]. The SML is inhabited by neustonic autotrophic and heterotrophic microorganisms, which exhibit both enzymatic and high respiratory activity [5,10–12]. The SML structure may be disturbed as a result of physical non-equilibrium processes such as temperature fluxes, irradiance, wind and wave action that influence

its biogeochemical properties. However, it is well fit for a rapid self-reconstruction of its original structure [3]. Physical forces such as adhesion, cohesion, surface tension, vortex motion and the Langmuir circulations, associated with its unique chemical and biological structure, form the specific properties of SML, including its stability [2].

Chemical contaminants are accumulated in the SML because of physical, chemical and biological processes. These processes include, e.g., hydrosphere–atmosphere exchange, convection, upwelling of underlying waters, transport by bubbles, atmospheric deposition, simple diffusion, buoyant particles, turbulent mixing, scavenging and chelation of inorganic components by organic matter [3]. Important sources of contaminants in urban objects are connected with urban pollutants supplied with wet and dry atmospheric deposition [13,14].

The taxonomic composition of phytoplankton is dependent on the chemical composition of the aquatic environment, which it colonizes [5,15]. Consequently, communities of the phytoneuston and phytoplankton vary in the SML and the SUB in terms of their taxonomic composition and population size [16].

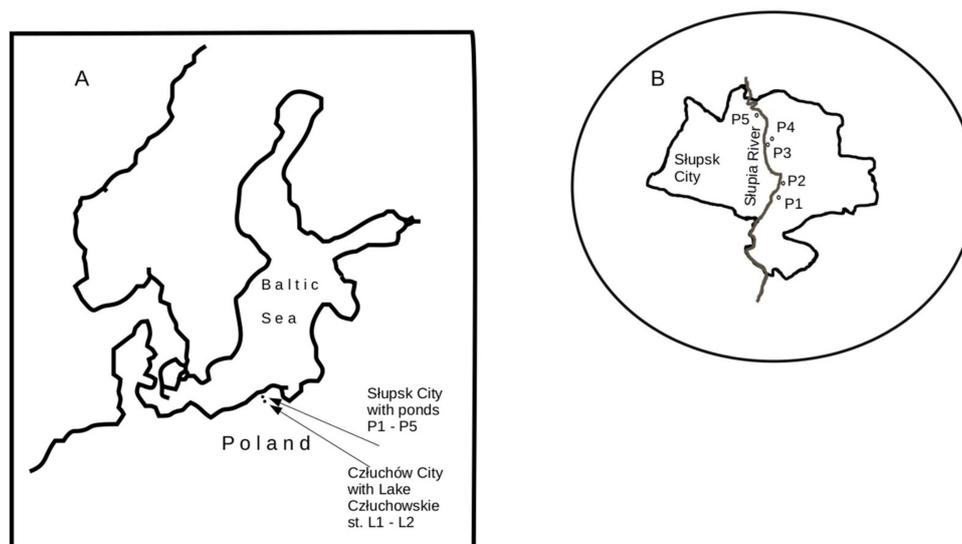
We hypothesized that, regardless of the type of analyzed urban water body, i.e., a lake vs. ponds, concentrations of nutrients and heavy metals would be higher in the SML than in the SUB. In turn, macroelement concentrations would be comparable in both layers. Therefore, the counts of microorganisms, i.e., heterotrophic bacteria and phytoneuston, were also expected to be higher in the SML than in the SUB.

The aim of this study were: to determine the taxonomic composition, abundance and biomass of phytoplankton in the SML and SUB layers of a freshwater urbanized lake and ponds; to characterize the chemical structure of two different habitats: the SML and the SUB; and to ascertain relationships between the studied chemical and biological components.

## 2. Materials and Methods

The studies were conducted in water bodies located in the Pomerania Region (northern Poland) in areas of moderate anthropogenic pressure under the influence of urban infrastructure. Pollutants generated by heavy industry did not affect the studied lake or urban ponds. Additionally, the towns in which the analyzed water bodies are situated are located near protected areas, i.e., for Słupsk it is the Dolina Słupii Landscape Park, while Człuchów lies near the Bory Tucholskie National Park. As a result, heavy metal contamination is relatively low in both areas. Water samples collected from the SML and SUB were analyzed for a wide range of chemical elements, composition and abundance of phytoneuston and phytoplankton as well as counts of heterotrophic bacteria.

The sampling stations were situated in areas representative for the studied water bodies, i.e., within five ponds (1P–5P) in the town of Słupsk and two stations in the lake in the town of Człuchów (Figure 1). The coordinates of these sampling stations are: 1P, 54°27′00.38″ N, 17°02′23.86″ E (at Arciszewskiego Street, trees at the bank); 2P, 54°27′27.03″ N, 17°02′25.85″ E (at Nad Śluzami St., station next to the trees on the island); 3P, 54°28′29.05″ N, 17°01′58.82″ E (at Orzeszkowej St., station in the north part of the pond, near the trees on the island); 4P, 54°28′32.66″ N, 17°02′16.10″ E (at Kaszubskiej St., next to the trees on the island); 5P, 54°28′47.26″ N, 17°01′21.50″ E (at Portowa St., Słupsk, Poland); and Lake Człuchowskie, 53°39′25″ N 17°21′33″ E with Stations 6 L in its northern part and 7 L in the southern part of the lake.



**Figure 1.** Locations of city ponds in Słupsk and Lake Człuchowskie on contour map of north Europe (A); and locations of city ponds in contour map of city Słupsk (B).

The water bodies are used for recreation and leisure activities. Ponds located in Słupsk are inhabited by such fish species as *Rutilus rutilus* (roach), *Carassius carassius* (crucian), *Abramis brama* (bream), *Tinca tinca* (tench) and *Esox lucius* (pike) [17]. Urban ponds in Słupsk are also habitats for waterfowl, e.g., swans and ducks [10]. The presence of these animals increases the value of leisure in urban ponds. For many years Lake Człuchowskie was the immediate receiver of municipal sewage, including that discharged by the hospital, containing high concentrations of nutrients; as a result, the lake waters did not meet water quality standards. A sewage treatment plant was commissioned [18]; sewage discharge to the lake was limited and the condition of the lake has now improved. The recorded concentrations of nutrients are lower. Nevertheless, the ecological status of the lake still needs to be improved.

Samples were collected in spring 2012. The SML samples ( $242 \pm 40 \mu\text{m}$  in thickness) were collected using a Garrett screen [19]. Samples of the SUB layer were collected from a depth of 10 cm, using a sampler with a PET bottle. Two samples from each station (the SML and the SUB) were taken for analysis ( $n = 14$ ). Collected samples were stored in clean PET containers [20]. Water samples for analyses of phytoplankton were fixed with formalin. A portion of the sample material was not fixed to conduct qualitative analyses. For microbiological analyses prior to sampling, the Garrett screen was rinsed with distilled sterile water (Hydrolab) and ethyl alcohol. The collected samples of water were transported to the laboratory in ice containers at a temperature of maximum  $7^\circ\text{C}$ .

Water samples for analyses of metals were mineralized using a microwave mineralizer (Ertec Magnum II) using Suprapur<sup>®</sup>  $\text{HNO}_3$  [21]. Metals were analyzed with a mass spectrometer (Thermo Scientific). Concentrations of dissolved  $\text{Cl}^-$ ,  $\text{F}^-$  and  $\text{SO}_4^{2-}$  ions were assayed according to APHA [22]. Metals found in water at concentrations below 1 ppm according to Duffus [23] were classified as trace metals.

For nutrients, phosphate phosphorus ( $\text{P-PO}_4$ ) was analyzed using the method with ascorbic acid, while ammonia nitrogen ( $\text{N-NH}_4$ ) with the direct nesslerization method and the nitrate nitrogen ( $\text{N-NO}_3$ ) using sulfanilic acid. Total phosphorus (TP) was assayed after mineralization. Absorption was measured using a UV-Vis spectrophotometer (Hitachi), while total Kjeldahl nitrogen (TN) was assayed with the distillation method. Organic nitrogen and phosphorus concentrations were calculated according to APHA [22].

The concentration of dissolved oxygen was determined measured (only in the SUB) using a Martini Instruments oxygen meter. Water temperature (temp., measured only in the SUB), electrolytic conductivity (EC) and pH were measured with Elmetron apparatuses. Abundance of heterotrophic bacteria (in CFU (colony forming units)) was established using the culture method. The analyses were

described in detail by Mudryk et al. [24]. Concentrations of chlorophyll *a* (chl *a*) and pheophytin (pheo) were determined after extraction in ethanol [25].

The abundance and taxonomic composition of the phytoplankton and phytoneuston were examined under a biological microscope (Olympus with led lightning, the abundance of phytoplankton was determined in counting chambers and at 40–400× magnification). Phytoplankton biomass was calculated for each species according to Wetzel and Likens [26] and Hutorowicz [27]. Taxa were considered dominant when their percentage share in total phytoplankton abundance reached at least 5% in one sample. Statistical parameters such standard deviation (SD), means, medians, coefficient of variation (CV) and Spearman correlation coefficients between the SML and the SUB were conducted using Statistica 13 software [28]. The type of distribution was determined using the Shapiro–Wilk test. To show differences in the level of a given nutrient in the SML in relation to its level in the SUB, the enrichment factors (EF) were calculated according to the following formula presented by Estep et al. [29]:  $EF = C_{SML}/C_{SUB}$ , where  $C_{SML}$  is the level of a given nutrient in SML and  $C_{SUB}$  is the level of a given nutrient in SUB. EF were calculated for each pair of results and averaged [30].

The response of the phytoplankton taxonomical groups to environmental conditions was investigated using multivariate statistical analyses. A preliminary Detrended Correspondence Analysis (DCA) was used and its results allowed choosing Canonical Correspondence Analysis (CCA), as the most appropriate technique [31–35]. Analyses were conducted jointly for the SML and SUB using the CANOCO software package, version 4.5 [32].

### 3. Results

#### 3.1. Physico-Chemical and Biological Parameters

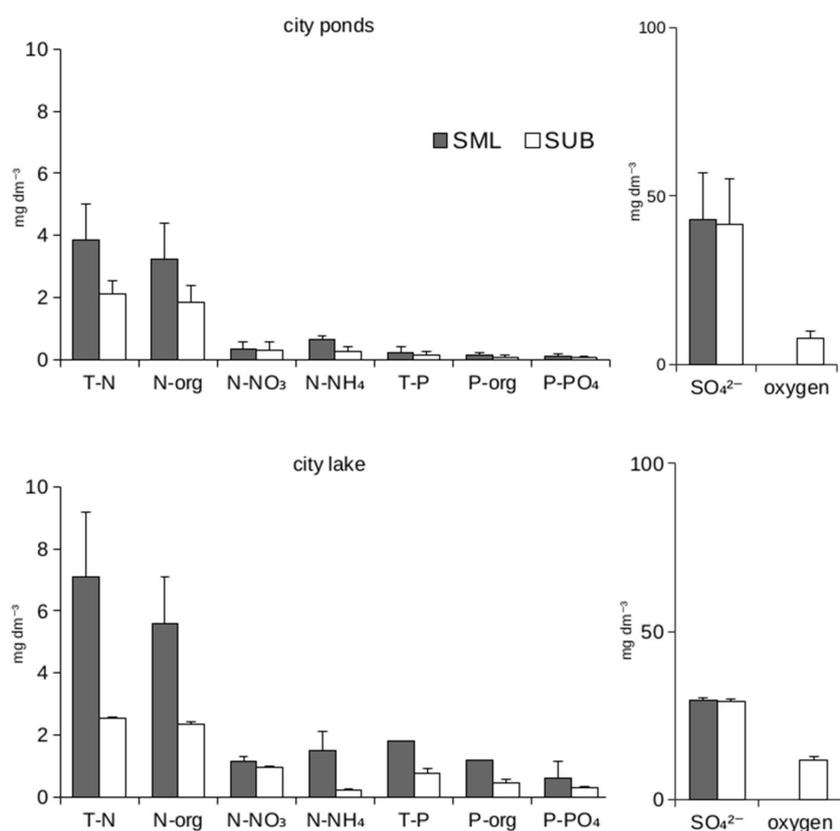
Irrespective of the sampling station, nitrogen and phosphorus compounds were accumulated at a greater amount in the SML than in the SUB (EF from 1.40 to 4.38) (Figure 2 and Table 1). Trace elements, i.e., metals Al, Ba, Cd, Cr, Fe, Mn, Ni, Sr, V and Zn; metalloid As; and non-metal Se, were accumulated in the SML. The obtained enrichment factors (EF) ranged from 1.26 to 34.52. Trace elements were accumulated in the SML to a greater extent regardless of the water sample origin (lake vs. pond) (Figure 3). In turn, parameters recorded at concentrations exceeding 1 ppm, namely Ca, K, Mg, Na and  $Cl^-$  and  $SO_4^{2-}$ , generally showed comparable concentrations in the SML and SUB, or slight enrichment in the SML (EF = 1.10–1.35). An atypical pattern was observed for the accumulation of  $F^-$ , for which mean EF was high, whereas its median indicated a lack of accumulation (Table 1). Values of EC and pH were comparable in both layers (EF = 1.05 and 0.97, respectively), while pH values in the SML were lower than in the SUB.

**Table 1.** Mean, median and variation coefficients (CV) calculated for enrichment factors (EF) obtained from the examined urban water bodies (both city ponds and city lake,  $n = 7$ ).

Parameter	Mean	Median	CV
biom	2.43	2.01	82.05
abund	1.45	1.54	40.07
chl <i>a</i>	2.00	1.77	47.91
pheo	2.22	2.24	32.95
CFU	6.49	5.30	82.37
Al	4.20	2.20	98.79
As	1.84	1.57	42.81
Ba	1.57	1.30	42.91
Ca	1.22	1.16	13.61
Cd	34.52	7.10	209.86
$Cl^-$	1.10	1.03	15.09
Cr	2.61	2.69	42.36
F	4.69	1.09	107.75

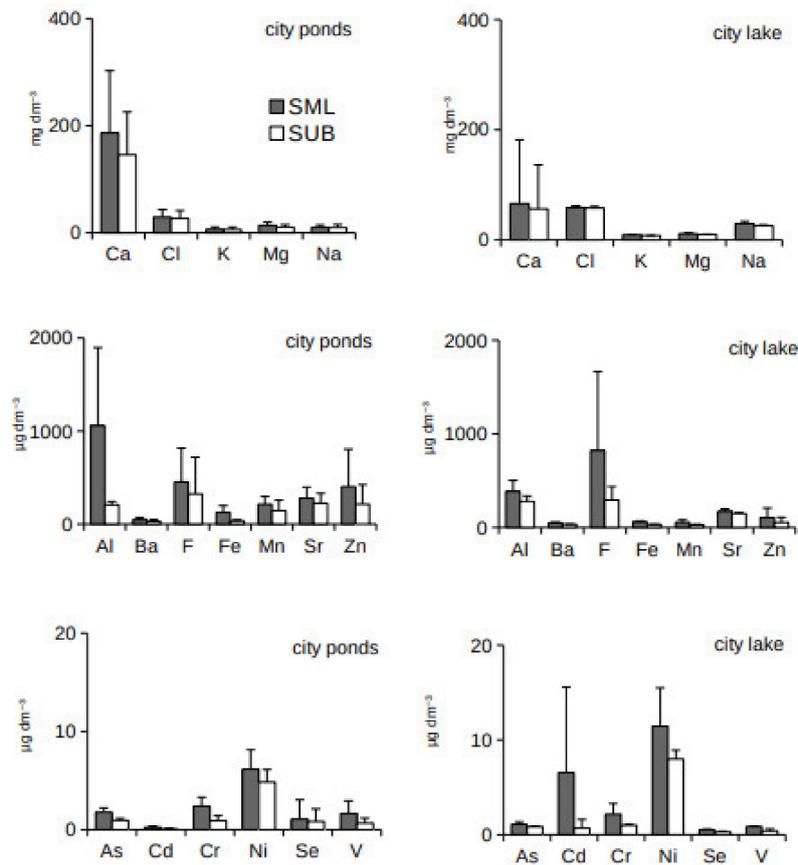
Table 1. Cont.

Parameter	Mean	Median	CV
Fe	3.27	2.85	65.69
K	1.23	1.24	18.88
Mg	1.35	1.17	37.10
Mn	2.16	2.57	65.90
Na	1.14	1.03	19.13
Ni	1.42	1.17	47.64
N-NO <sub>3</sub>	1.40	1.28	34.77
Norg	1.91	1.79	25.14
TN	2.09	1.90	29.63
N-NH <sub>4</sub>	4.38	4.69	53.26
Porg	2.09	2.11	25.95
P-PO <sub>4</sub>	1.88	1.84	13.18
TP	2.00	1.96	19.35
SO <sub>4</sub> <sup>2-</sup>	1.03	1.02	2.53
Se	2.42	1.64	104.01
Sr	1.26	1.21	22.75
V	25.60	3.01	240.77
Zn	1.77	1.93	38.46
EC	1.05	1.04	4.12
pH	0.97	0.97	4.89

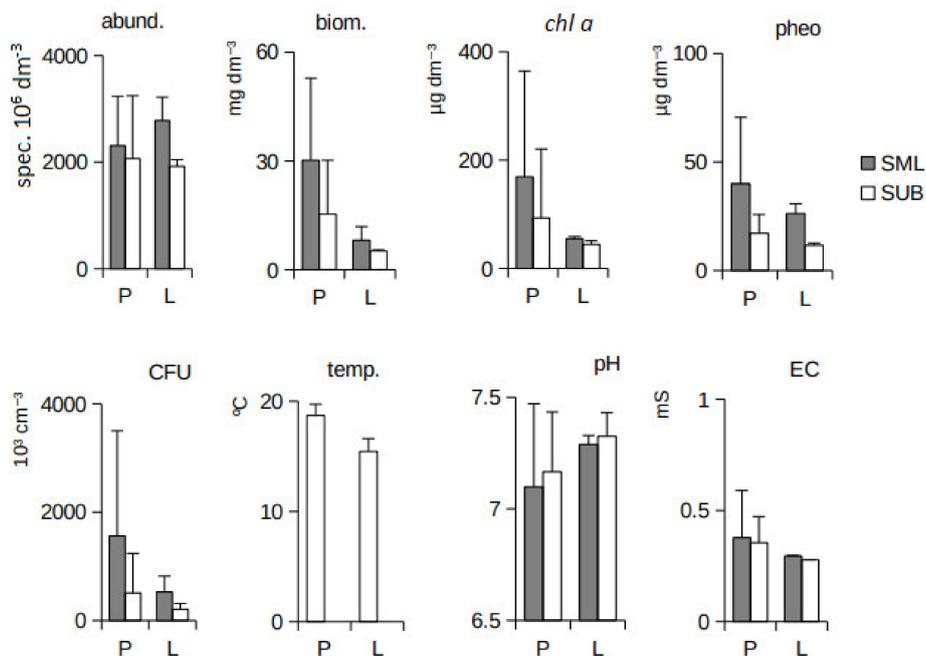


**Figure 2.** Comparison of the availability of nutrients in the SML and SUB of the studied urban water reservoirs (ponds in the city of Słupsk and Lake Człuchowski). Standard deviation (SD) values are marked.

Values of the enrichment factors for biological parameters such as biomass and counts of phytoplankton, concentrations of chlorophyll a and pheophytin as well as counts of heterotrophic bacteria (in CFU) were higher in the SML than in the SUB (EF range of 1.45–6.49) (Table 1 and Figure 4).



**Figure 3.** Comparison of the availability of macronutrients, trace metals and non-metals in the SML and SUB of the studied urban water bodies (ponds in the city of Słupsk and Lake Czluchowskie). For more information, see Figure 2.



**Figure 4.** Comparison of biomass level, phytoplankton abundance, chlorophyll a concentration, pheophytin, heterotrophic bacteria, pH, electrolytic conductivity and temperature in the SML and SUB of the studied urban water bodies (P, ponds in Słupsk; L, Lake Czluchowskie). For more information, see Figure 2.

Analyzed nitrogen and phosphorus forms were found in most cases at higher concentrations at the sampling stations in the lake than in the urban ponds. Mean concentrations of TN, N-org and N-NH<sub>4</sub> in the SUB were comparable in the lake and in the ponds, while that of N-NO<sub>3</sub> was three-fold higher in the lake compared to the ponds. Phosphorus compounds were recorded at concentrations ranging from 6.0- to 6.3-fold higher in the SUB of the lake than in the ponds. Concentrations of all the analyzed nitrogen compounds in the SML were from 1.7- to 3.4-fold higher in the lake when compared to the ponds, and those of phosphorus compounds were from 5.3- to 9.7-fold higher. Nevertheless, the urban ponds were characterized by SO<sub>4</sub><sup>2-</sup> concentrations on average 1.4-fold higher than those in the lake waters. In addition, concentrations of Ca, Mn, Sr, V, Zn and Se in the SUB were higher in ponds than in the lake waters, but Cd, Cl<sup>-</sup>, K, Na and Ni were higher in the lakes. Lake water was more oxygenated than ponds water (1.5 times), while water temperature in the ponds was by 3 °C higher than in the lake (Figure 4). Water pH in the analyzed water bodies was close to neutral (mean in SUB 7.1 in ponds and 7.3 in lake) and electrolytic conductivity was comparable at all studied stations (mean in SUB 0.38 in ponds and 0.30 in lake).

### 3.2. Phytoneuston and Phytoplankton Composition

Biomass of phytoplankton and phytoneuston and concentrations of chlorophyll a and pheophytin were higher in both analyzed layers in the urban ponds (Table 1 and Figure 4). Biomass of phytoneuston in the SML was larger by 3.7-fold in the pond waters, whereas biomass of phytoplankton in the SUB was three-fold higher. In addition, the count of heterotrophic bacteria was three-fold greater in the SML and 2.5-fold higher in the SUB in the ponds when compared to the respective levels in the lake. EF was higher for the phytoplankton biomass, chlorophyll a, pheophytin and bacterioneuston counts for the urban ponds than for the lake.

The identified phytoplankton species in all the water bodies represented seven taxonomic groups (Figure 5). Both in the case of phytoplankton abundance and biomass greater values were found in the SML. The highest abundance for phytoplankton species was recorded in Pond P3 in the SML and SUB. The greatest share in Ponds P1–P4 were reported for Bacillariophyceae, while in Pond P5 it was for Chrysophyceae both in the SML and SUB. In turn, in the urban lake Chlorophyceae accounted for the greatest share. When analyzing phytoplankton biomass in the ponds the greatest share was recorded for Dinophyceae in both layers of Pond P1. In Ponds P2 and in P4, it was for Chlorophyceae and Bacillariophyceae as well as Euglenophyceae (in Pond P2) and Chrysophyceae (in Pond P4). In, Pond P3, it was for Bacillariophyceae and Cyanobacteria, whereas in Pond P5 it was Chrysophyceae. In contrast, Chlorophyceae were dominant in the lake waters.

Bacillariophyceae were abundant in the SML and SUB at all sampling stations (except for Pond P5) ranging from 1% to 67%. In the biomass, the percentage share ranged from close to 0% up to 50%. The species found in the ponds in greatest abundance included *Asterionella formosa*, *Fragilaria capucina*, *Melosira varians*, *Ulnaria acus* and *U. ulna* (Table 2). In contrast, a high abundance of *Nitzschia palea* and *Tabellaria flocculosa* was recorded in the lake.

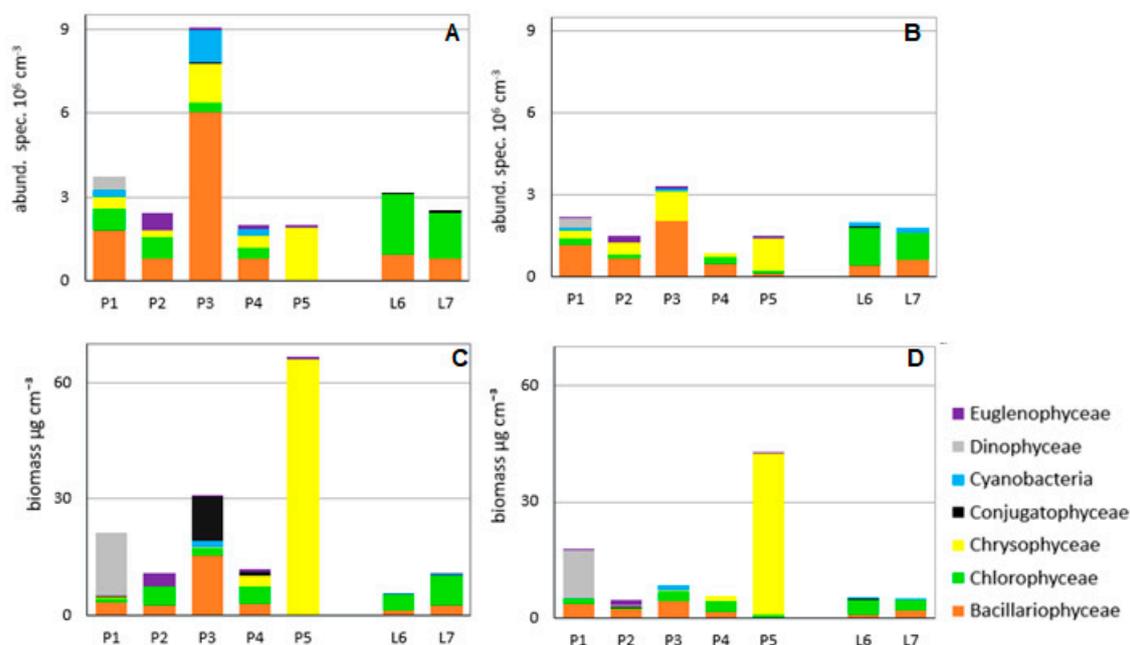
The percentage share of Chlorophyceae in the total abundance ranged from 0.6% to 70%. Its share in the biomass ranged from close to 0% to 71%. In the ponds, the greatest share was recorded for *Eudorina elegans* and *Chlorella vulgaris*, whereas in the lake waters it was for *Desmodesmus communis*, *D. magnus*, *Binuclearia lauterbornii* and *Tetrastrum glabrum*.

Representatives of Chrysophyceae ranged from 0% to 94% of the total abundance, while in the biomass from 0% to 98% at individual sampling stations. Among representatives of Chrysophyceae, the greatest share in the pond waters was recorded for *Synura uvella*, *Dinobryon divergens* and *D. sociale*.

Dinophyceae was reported at individual stations at 0–16% in terms of abundance and 0–77% in terms of biomass. *Peridinium* sp. was reported in the greatest numbers in Pond P1.

Cyanobacteria were represented in greatest abundance by *Limnothrix redekei*, while Euglenophyceae by the genus *Trachelomonas* sp.





**Figure 5.** Phytoplankton abundance (in the SML (A) and in the SUB (B)) and biomass (in the SML (C) and the SUB (D)) and taxonomic groups at individual sampling stations.

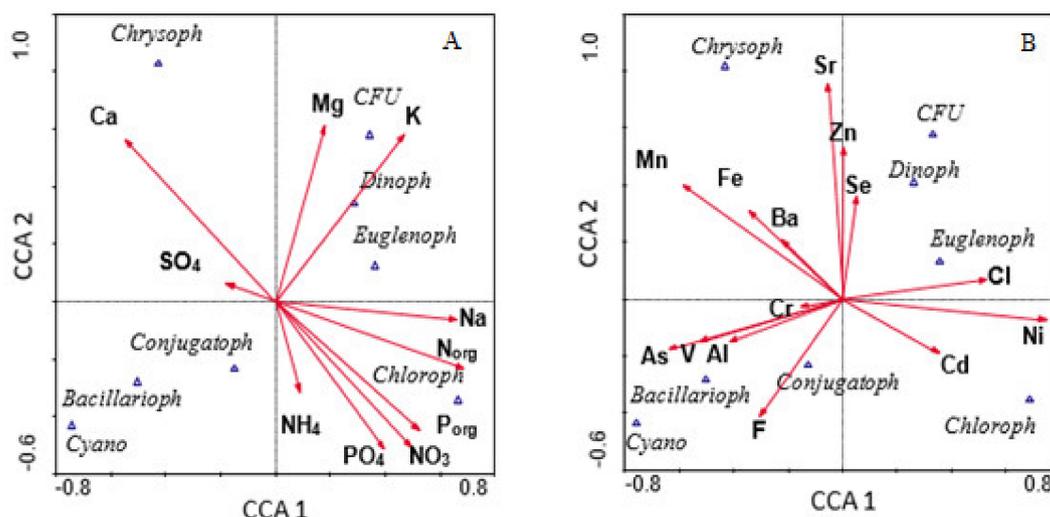
### 3.3. Phytoplankton and Bacterioplankton Versus Chemical Parameters

Phytoplankton biomass, bacterioneuston and bacterioplankton number (CFU), chl *a*, EC, Sr, Zn, Ca,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ , Na, K, N- $\text{NO}_3$ ,  $\text{N}_{\text{org}}$ , TN,  $\text{P}_{\text{org}}$ , P- $\text{PO}_4$  and TP showed a statistically significant positive correlation between the SML and SUB (Table 3). In turn, the concentration of V showed a negative correlation between the SML and SUB.

**Table 3.** Statistically significant Spearman correlation coefficients calculated between the concentrations of the tested parameters in the SML and SUB ( $n = 7$ ,  $p < 0.05$ , significant for one-sided critical area).

Parameter	r
biom	0.86
chl <i>a</i>	0.75
CFU	0.93
EC	0.89
Sr	0.93
Zn	0.86
V	-0.75
Ca	0.96
$\text{SO}_4^{2-}$	0.96
$\text{Cl}^-$	0.86
Na	0.86
K	0.96
N- $\text{NO}_3$	0.96
$\text{N}_{\text{org}}$	0.96
TN	0.82
$\text{P}_{\text{org}}$	0.93
P- $\text{PO}_4$	0.93
TP	0.93

Using CCA, a significant effect was found in the case of both macronutrients such as Ca, Na, K,  $\text{SO}_4^{2-}$  and  $\text{P}_{\text{org}}$  on the abundance of the phytoplankton taxonomic groups and heterotrophic bacteria (Figure 6A). Statistically significant correlations were also recorded between abundance of phytoplankton, CFU and trace elements such as Ni, Sr and  $\text{F}^-$  (Figure 6B).



**Figure 6.** Ordination plot of canonical correspondence analysis (CCA) for phytoplankton abundance and chemical parameters: macroelements and nutrients (A); and trace metals (B) (in both layers).

#### 4. Discussion

The investigated objects are located in an area of moderate human impact resulting from their immediate vicinity to urban infrastructure. Urban pollutants comprise a wide range of chemicals, including nutrients that cause eutrophication [18,36] of these water bodies, as well as trace metals [7]. In the SUB layer, the concentrations of N-org, TN and N-NH<sub>4</sub><sup>-</sup> were comparable both in the ponds and in the lake. Concentrations of N-NO<sub>3</sub> and phosphorus compounds were higher in the lake waters (Figure 1). When compared to the studies of this lake in the 1990s [18], the observed TN concentration was two-fold lower at a continuously high phosphorus concentration. In the 1990s, the lake water was classified as bad, which was the result of sewage inflow [18]. Moreover, high N-NO<sub>3</sub> concentrations were recorded in the lake, which may have been a consequence of N-NO<sub>3</sub> leaching from the catchment [37–40] and biological nitrification of ammonium nitrogen in the lake, particularly since good aerobic conditions were recorded there. Levels of nutrients in the studied water bodies indicate their eutrophic and hypereutrophic character, which is consistent with their levels reported in previous studies [10,18,41].

Concentrations of trace metals Mn, Sr, Zn, Se and V in the SUB (Figure 2) were higher in the ponds than in the lake; in contrast, higher concentrations of Cd, Ni and Al were recorded in the lake. The concentrations of trace metals found in the SUB layers of the investigated urban water bodies are comparable to those for other surface waters in Poland [42], while their values indicate moderate anthropogenic pollution associated with low household emissions [41].

The surface microlayers of the ponds and the urban lake accumulated the phytoneston, trace metals and nutrients in comparison to the SUB layer. Chemical substances and organisms are supplied to the SML from subsurface water and the atmosphere. Greater accumulation of trace metals in the SML compared to the SUB has also been observed in other inland waters, both lotic and lentic as well as marine [6,7,10]. In the case of trace metals, the recorded EF values for the investigated urbanized water bodies were particularly high for Cd and V. They are the elements found at slight concentrations in the SUB layer. Low concentration of metals in the SUB may have contributed to their high accumulation in the SML.

In contrast, macroelements such as Ca, Na, K, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> in waters of the analyzed urban water bodies showed comparable concentrations in the SML and SUB (EF values 1.03–1.23). Only Mg had a slightly higher enrichment factor (EF = 1.35). Macroelements are typically accumulated only periodically in the SML, e.g., in the period of spring phytoplankton and phytoneston growth, Mg may have been taken up to form chlorophyll *a* [9].

In urban water bodies, the accumulation of trace metals in the SML may largely be the result of atmospheric deposition compared to in the case of water bodies located at a distance from urban areas.

The SML is the zone of matter exchange between the hydrosphere and the atmosphere [1,5]. Chemical substances from the atmosphere reach urban water bodies in the form of wet and dry deposition. Municipal transport and urban consumption result in the production of large amounts of gaseous pollutants as well as particulate matter subsequently deposited in urban areas [43,44], therefore they may be deposited in urban water bodies. Municipal and industrial pollutants include such metals as Fe, Mn, Cd and Ni [7]. Trace metals such as Pb, Cd and Ni, as well as the metalloid As may be bound by PM<sub>2.5</sub> and PM<sub>10</sub> dusts and thus be deposited in water bodies; as such, they are common urban pollutants [13,45,46].

Statistically significant correlations between metal concentrations in the SML and SUB layers indicate the SUB as a source of the components in the SML, while in the case of a negative correlation a greater effect of the atmosphere is suggested. Substances can be delivered to the SML from both the atmosphere and the SUB. The SML supply from the water column occurs during the movement of matter from deeper layers to the surface together with gas bubbles raised from the bottom of the water body and the surface of plants and diffusion movements [3]. Moreover, neustonic organisms, usually derived from the SUB [2], have the ability to bioaccumulate metals [6] and thus can affect the enrichment and chemical composition of the SML. In view of the above, it may be assumed that Sr, Zn, Ca, Cl<sup>-</sup>, Na and K mainly originated from the pool accumulated earlier in the SUB layer, particularly since the concentrations of these elements in the atmosphere are much lower when compared with those recorded in the SUB layer [13,17]. Similarly, parameters describing aquatic microorganisms, i.e., phytoplankton biomass, chlorophyll *a* and counts of heterotrophic bacteria, were correlated between the SML and the SUB.

A negative SML–SUB correlation was observed in the investigated urban water bodies for V at a lack of statistically significant correlations for the trace metals Al, As, Ba, Cd, Cr, Fe, Mn, Ni and Se as well as the nonmetal F<sup>-</sup> (Table 3). It may be assumed in these cases that accumulation in the SML for V was determined by the load of atmospheric depositions, while for the other above-mentioned elements the share of the pollutants was more uniform between the sources from the hydrosphere and the atmosphere. The level of contaminants in urban water bodies such as ponds or lakes results from the sum of local factors as well as wet and dry deposition [17]. In this study, high accumulation of Ni and Cd was found in the SML layer in Człuchowskie Lake and Al in the ponds of the city of Słupsk. These accumulations did not correlate with concentration in the SUB. Hence it can be assumed that this accumulation could have resulted from atmospheric deposition, especially since Ni and Cd are typical urban pollution [7].

The SML is an unstable environment, on the one hand rich in nutrients and on the other hand dangerous for the neuston, as it may contain various substances, e.g., heavy metals, at toxic concentrations [7,17]. The presence of noxious substances, not exceeding toxic concentrations, may lead to the increased activity of neuston microorganisms [11,12], thus these microorganisms colonize the unstable SML environment even though it is harmful for them over a longer time perspective. Most research concerning the phytoneuston focuses on studies on primary production and analyses of photosynthetic pigments, primarily chlorophyll *a*, rather than the phytoneuston species composition or population size. The abundance of algae and cyanobacteria in the present study was higher in the SML than in the SUB, similar to other studies carried out in other places and conditions [10,29]; it was analogous to the contents of nutrients and trace metals [14,47].

Shares of taxonomic groups in individual water bodies varied in terms of their abundance and biomass. Both weather factors and catchment conditions affected this pattern [48,49]. Diatoms and chrysophytes were dominant in most water bodies [50,51]. *Asterionella formosa* was dominant among diatoms (particularly Ponds P4 and P5), which is characteristic of mixed, eutrophic small to medium water bodies [52]. Apart from this species, *Aulacoseira granulata*, *Fragilaria capucina* and *Melosira varians* were dominant in the ponds. These taxa prefer high-nutrient availability and water mixing [53,54]. The most abundant species in the lake were popular taxa reported both in small water bodies and in lakes, e.g., *Navicula tripunctata*, *Nitzschia acicularis* and *N. palea* [55].

In turn, among chrysophytes, particularly in Pond P5, the dominant species was *Synura uvella*, typical of small water bodies rich in organic compounds [40,53,56], including also astatic ones [57] and those with high trophic status [58]. Other chrysophytes such as *Dinobryon divergens* and *D. sociale* were dominant in Ponds P1–P3. Representatives of this group are typically dominant in the spring season, as they prefer lower water temperatures [59–62]. Because of chromatic adaptation, chrysophytes may develop in shaded water bodies (such as Pond P4); they can lead a heterotrophic life and can supplement nutrient uptake by the phagotrophic ingestion of bacteria [63–65]. As indicated by CCA, chrysophytes preferred water bodies characterized by lower concentrations of nitrogen and phosphorus.

Chlorophytes constituted another numerous represented group of phytoplankton. A particularly high share in the analyzed lake was recorded for the abundance of such taxa as *Desmodesmus communis*, *D. magnus*, *Binuclearia lauterbornii* and *Tetrastrum glabrum*, characteristic of eutrophic lakes [66–68]. The dominance of *Eudorina elegans* was reported in the ponds, a cosmopolitan species [69], characteristic of small eutrophic water bodies with stagnant water [55].

In Pond P2, where concentrations of nutrients were high, particularly TN, euglenids were dominant, i.e., *Euglena* sp. and *Trachelomonas* sp. (Table 2). Dominance of these genera in the water bodies indicates their strong eutrophication [50,70]. They are common in small water bodies, rich in organic matter [71,72], as well as dammed reservoirs [73].

Cyanobacteria being dominant in Pond P3 pose a particularly serious threat to the recreational use of small water bodies because of toxin production [74–76]. Some reports indicate that the cyanotoxins may inhibit algal growth, which increases the chance for Cyanobacteria development [77]. In contrast to the other groups, Cyanobacteria respond to the anthropogenic effect of the catchment, which is particularly significant in the case of small water bodies [78]. They are equipped with several specific adaptation mechanisms, making it possible for effective competition with other groups of autotrophic plankton [79]. They are also equipped with effective mechanisms, such as binding metals by proteins or polysaccharides, methylation, complexing by organic matter, development of energy-driven efflux pumps, precipitation, oxidation, vaporization and complexing with excreted metabolites, which protect them against toxic concentrations of heavy metals [80]. The dominant species were *Limnothrix redekei*, *Microcystis aeruginosa* and *Merismopedia glauca*, frequently reported in small eutrophic water bodies [81–83].

A high share of dinoflagellates from the genus *Peridinium*, recorded in Pond P1, indicated the presence of various trophic types, both those with higher trophic status such as in hypereutrophic water bodies [84], as well as those with lower trophic status, showing an improved water quality, e.g., during restoration processes [85,86]. Species from this genus may generate intensive blooms, such as those observed in urban lakes situated in northeastern Poland [87]. It needs to be mentioned here that species from the genus *Peridinium* are less numerous represented in the SML or they were reported only in the subsurface layer. They are characterized by large size, tend to sink to the bottom and are found in deeper layers of the photic zone [88,89].

Neuston bacterial counts expressed in CFU were more numerous compared to the bacterial populations in the SUB, which may be explained by the higher concentrations of organic substance recorded in the SML [90]. Analogous densities of heterotrophic bacteria have also been reported in other water bodies such as Jeziorak Mały [91] or Lake Łebsko [6]. The studied heterotrophic bacteria usually accumulated more in SML than in the SUB. It should be mentioned, that heterotrophic bacteria are only a part of total bacteria that can occur in the water environment [10,24]. Correlations (CCA) among phytoplankton, phytoneuston, heterotrophic bacteria and chemical parameters were observed (Figure 6A,B). Phosphorus is the basic component limiting growth of phytoplankton [92], thus abundance of chlorophytes was closely related with high values of organic phosphorus and phosphates [93,94]. Potassium is also an essential nutrient for phytoplankton [92].

Calcium is a macroelement, and its high concentration in the analyzed waters was correlated with the high abundance of Chrysophyceae, which in turn prefer a low phosphate content. Calcium may be found in the form of acid calcium carbonate ( $\text{Ca}(\text{HCO}_3)_2$ ), which reacts with phosphates and precipitates to the bottom sediments [95], thus the high Ca content may result in a decreased

concentration of phosphorus available for phytoplankton. Some chlorophytes and cyanobacteria utilize Ca as well as Sr and Ba to produce amorphous calcium carbonate inclusions [96]. Another macroelement, Na, showed a positive correlation with phytoplankton. Analyses were conducted in the spring period; the response of phytoplankton to Na may be connected with the leaching of this nutrient from the urban catchment in which together with the surface runoff Na, originating from salt used for the roads and urban street de-icing, may penetrate urban water bodies [9,97]. With surface runoff, sulfur compounds, while being nutrients, may penetrate water bodies, although they are harmful at excessively high concentrations. Sulfur compounds are emitted in cities during the heating season, particularly from coal-heated households.

Statistically significant correlations were also observed with elements found in trace concentrations. Al and F<sup>-</sup> are elements constituting urban pollutants, supplied via the atmosphere together with PM<sub>10</sub> and P<sub>2.5</sub> dusts [17]. This would explain the high content of Al and F<sup>-</sup> in the SML ponds of the city of Stupsk. Fluorine is commonly used in cities, e.g., in cooling liquids, in electrical components and to produce halons, herbicides and pharmaceuticals [98]. Both fluorine and aluminum are considered toxic for phytoplankton organisms, causing a decrease in their populations [99]. It needs to be remembered that there are taxa, e.g., the diatom *Nitzschia palea*, dominant in the analyzed lake, which can tolerate high F<sup>-</sup> concentrations [100]. In turn, a high Al content in water reduces the ability of algae to absorb phosphates, forming insoluble salts. At the pH ranges observed in the analyzed urban water bodies, Al was probably inactive since it forms sparsely soluble compounds [101,102]. Additionally, this element shows a high capacity to form organic complexes in solutions. It is worth noting that the molar ratio of Al to other ions is important with respect to Al toxicity and reduction of aluminum toxicity is observed when Ca ions increase [103].

## 5. Conclusions

In the investigated urban water bodies such chemical parameters as trace metals and nutrients were accumulated to a greater extent in the SML than in the SUB. Macroelements showed no such accumulation, with the exception of Mg, which was accumulated in the SML probably due to its incorporation into chlorophyll *a*. Heterotrophic bacteria and phytoplankton were found at greater abundance in the SML than in the SUB. The investigated water bodies were abundant in phosphorus compounds and macroelements. The analysis of the taxonomic structure of phytoneuston in the SML and phytoplankton in the SUB layer indicates that the SML is a separate habitat showing specific properties that determine its taxonomic composition.

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