Macroelements in the surface microlayer of water of urban ponds

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Abstract: Analyses were conducted concerning the accumulation of four metals representing the group of macroelements, i.e. sodium, potassium, calcium and magnesium in two ponds located in the city of Słupsk. Water samples for chemical analyses were collected from the surface microlayer using a Garrett net. At the same time subsurface water samples were collected. Concentrations of metals were determined using a mass spectrometer. Generally, amounts of sodium, potassium, calcium and magnesium were similar in surface microlayer and subsurface water. Only in the case of potassium and calcium was low enrichment observed in the surface microlayer in one pond, while the greatest extent for magnesium enrichment was observed in the spring period.

Key words: pond, surface microlayer, macroelements

Introduction

The air-water interface is the surface microlayer (*SML*) found at the interface of two environments: the hydrosphere and the atmosphere (Norkrans 1980; Cunliffe and Murrell 2009). The *SML* covers the surface of all water bodies, which accounts for 71% Earth's surface area. The *SML* is the physical boundary between the hydrosphere and the atmosphere. Roughly considered to be the uppermost 1 mm of the hydrosphere, the *SML* is physically and chemically distinct when compared with the subsurface water (Liss and Duce 2005). The *SML* is a zone of matter and energy exchange between the hydrosphere and the atmosphere. It is a habitat for neustonic organisms. It exhibits specific physical, chemical and biological properties (Hillbricht-Ilkowska and Kozłowska-Szlakowska 2004; Cunliffe and Murrell 2009; Antonowicz et al. 2015). The presence of the surface film and surface tension properties means that the sea-surface microlayer is a unique habitat that is often referred to as the neuston (Liss and Duce 2005). The *SML* is characteristically enriched with organic compounds, such as lipids, proteins and polysaccharides (Liss and Duce 2005), herbicides and heavy metals (Wurl and Obbard 2004). However, not all chemical substances exhibit this accumulation ability. Such substances as Ca

and Mg are typically accumulated to a limited extent or only periodically. According to Antonowicz (2015), periodical Mg enrichment in *SML* from Lake Dołgie Wielkie was probably connected with accumulation in the phytoneuston chloroplasts.

The aim of this study was to investigate the capacity of the surface microlayer of urban ponds to accumulate Na, K, Ca and Mg to determine their concentrations in *SML* and *SUB* (subsurface layer) by mass spectrometry; and to investigate seasonal variation in the concentrations of these macroelements in *SML* and *SUB* in the analysed ponds.

Materials and methods

The analyses were conducted on two ponds located in the city of Słupsk in urban green areas in the vicinity of busy roads. One pond is located in the vicinity of Arciszewskiego Street, while the other pond is situated at Kaszubska Street (Fig. 1). The ponds differ greatly in terms of water surface area (pond 1 has an area of approx. 2.8 ha, while pond 2 has an area of approx. 0.15 ha). Samples from the ponds were collected from October 2007 to September 2008. The ponds are located in the vicinity of the River Słupia, which flows through the city. Samples of the surface microlayer (*SML*) (thick-

Fig. 1. Location of analysed ponds

ness $242 \mu\text{m} \pm 40$) were collected with a Garrett net (Garrett 1965), while samples of the subsurface layer (*SUB*) were taken at a depth of about 10–15 cm. For chemical analyses samples were collected in PET containers, which were pickled in HNO_3 and rinsed with demineralized water.

Chemical and statistical analyses

The concentrations of metals, i.e. Ca, Mg, K and Na, were determined using a Perkin Elmer Elan DRC-e mass spectrometer. Water samples were mineralized in *trace pure* nitric acid V (Merck, Darmstadt, Germany). Correction formulas were applied to introduce adjustments for the presence of compounds forming unstable bonds with a molecular mass equivalent to those of assayed elements (Perkin Elmer Sciex 2005). These results were then compared sequentially for each metal separately with the reference standard samples (Perkin Elmer) with the instrument controlled by the ELAN Perkin Elmer SCIEX Instrument Control software. As a blank sample, the sample obtained from the water deionizer (Hydrolab company) was used. The recovery rate of the standard added to samples was determined, ranging from 91.2 to 114.3%. In order to verify the accuracy of the method, a reference material, ES-L-1 (Ground Water, EnviroMAT) was used.

Statistical analysis

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

$$EF = C_{SML} / C_{SUB}$$

where: C_{SML} and C_{SUB} are concentrations of analysed metals (Estep et al. 1985) calculated partly from each measurement from SML_i and SUB_i .

Statistical analyses such as the Shapiro-Wilk normality test, mean, median, minimum, maximum, standard deviation and Spearman or Pearson correlations were calculated (Statsoft 2012; Luszczewicz and Słaby 2008).

Results

Tables 1 and 2 present data on the concentrations of Na, K, Ca and Mg and statistical parameters describing them for the *SML* and *SUB* collected from the two ponds located in the city of Słupsk. The analysis of data given in the tables shows that in pond No. 1 concentrations of Na, K and Ca in the *SUB* layer were greater than in pond No.2, whereas the situation was opposite in the case of Mg. Mean concentrations in *SUB* in ponds No. 1 and No. 2 were as follows: Na – 19.1 mg dm^{-3} and 11.3 mg dm^{-3} , K – 2.8 mg dm^{-3} and 1.3 mg dm^{-3} , Mg – 6.6 mg dm^{-3} and 7.6 mg dm^{-3} , Ca – 60.6 mg dm^{-3} and 52.1 mg dm^{-3} . In *SML* greater concentrations were recorded in pond No.1 for Na, K and Mg, while for Ca the concentration was greater in pond No.2. Mean concentrations of the analysed elements in *SML* and *SUB* were ordered according to the increasing concentrations as follows: $\text{K} < \text{Mg} < \text{Na} < \text{Ca}$.

The capacity to enrich the surface microlayer varied in both these ponds. Obtained enrichment factors were low. In pond No. 1 concentrations of Ca, Mg, K and Na were comparable in *SML* and *SUB*, with the obtained enrichment factors (*EF*) falling within the range of 0.99 for K to 1.11 for Na. In pond No. 2 the recorded concentrations for Mg and Na were comparable with

Table 1. Statistical parameters of studied metals in the surface microlayer and subsurface water of Pond No. 1 (near Arciszewskiego St.)

		Na	K	Mg	Ca
<i>SML</i>	Mean	20.3	3.0	7.7	61.0
	Maximum	77.4	8.2	29.8	141.9
	Minimum	7.7	0.7	2.0	13.2
	Median	15.8	1.1	4.8	50.1
	SD	20.4	3.3	8.3	44.9
<i>SUB</i>	Mean	19.1	2.8	6.6	60.6
	Maximum	75.2	6.7	18.5	166.2
	Minimum	8.4	0.7	2.6	16.7
	Median	13.9	1.6	4.6	42.5
	SD	19.9	2.3	4.9	48.0
<i>EF</i>	<i>EF</i>	1.11	0.99	1.06	1.02

Table 2. Statistical parameters of studied metals in the surface microlayer and subsurface water of Pond No. 2 (near Kaszubska St.)

		Na	K	Mg	Ca
SML	Mean	13.5	1.7	10.1	67.2
	Maximum	17.9	5.1	38.7	179.2
	Minimum	7.7	0.7	2.6	32.7
	Median	14.0	1.3	6.2	46.5
	SD	3.5	1.3	10.7	51.0
SUB	Mean	11.3	1.3	7.6	52.1
	Maximum	16.1	3.4	24.0	154.7
	Minimum	2.4	0.6	1.9	29.3
	Median	11.9	0.8	5.2	40.4
	SD	4.0	0.9	6.2	35.7
EF	EF	1.15	1.34	1.06	1.24

those in *SML* and amounted to $EF = 1.06$ – 1.15 , while for Ca and K enrichment was found at $EF = 1.24$ – 1.34 .

Seasonal variation was observed for the analysed chemicals. Figure 2 presents the seasonal dynamics for Na and K concentrations in the *SML* and *SUB* of these ponds. In the spring in pond No. 1 sodium concentration was almost 3-fold greater in *SML* and than in *SUB* the other seasons. In turn, in pond No. 2 the greatest concentration was observed in *SML* and *SUB* in the winter, while it was lowest in the autumn. In the case

Table 3. Correlations of concentrations of analysed metals between their concentrations in *SML* and *SUB* (Spearman, *Pearson correlations). Correlations given in bold are statistically significant at $p < 0.05$

Metal	Pond No. 1	Pond No. 2
Na	0.69	0.94*
K	0.49	0.77
Ca	0.90	0.43
Mg	0.83	0.81

of K the greatest concentration of this element in both ponds was recorded in the autumn. In the same period a slight K enrichment was found in *SML* ($EF = 1.23$). Calcium concentration was highest in both analysed ponds in the autumn (Fig. 3). In both ponds the concentration of calcium was almost 3 times greater than in the other seasons. Magnesium concentrations in both ponds showed maximum value in the spring and autumn. In the spring Mg enrichment was recorded in *SML* (mean $EF = 1.44$) in relation to *SUB*.

Table 3 presents analyses of correlation depending on the type of data distribution: the Spearman and Pearson distributions describing correlations between concentrations of the analysed macroelements in *SML* and *SUB*. Recorded correlation coefficients were significant ($p < 0.05$) between *SML* and *SUB* for Na and Mg

Fig. 2. Seasonal changes in Na and K concentrations in *SML* (white bars) and *SUB* (grey bars) of studied ponds (pond No. 1 on the left, pond No. 2 on the right)

Fig. 3. Seasonal changes in Ca and Mg concentrations in *SML* (white bars) and *SUB* (grey bars) of studied ponds (pond No. 1 on the left, pond No. 2 on the right)

in both ponds, while for K they were significant in pond No. 2 and for Ca in pond No. 1.

Discussion

Results from world literature show that most chemicals and microorganisms are accumulated in the surface microlayer water at higher concentrations than are observed in the subsurface layer – this refers to heavy metals (Wurl and Obbard 2004; Antonowicz et al. 2015), biogenic substances (Trojanowski et al. 2001; Mudryk et al. 2003), organic substances (Cincinelli et al. 2001) as well as chlorophyll (Knulst et al. 1997; Antonowicz 2014), bacteria (Estep et al. 1985; Walczak 1998) or viruses (Aller et al. 2005).

In the case of heavy metals concentrations in *SML* were found to be even as much as several dozen times greater than in the bulk of the water column. For example, EF for Pb in Puget Sound in Washington ranged from 26 to 65 (Hardy et al. 1985). The enrichment of heavy metals in *SML* depends on many factors, including pH, salinity, binding affinities and organic matter composition of the *SML* (Wurl and Obbard 2004). However, not all metals are capable of accumulating in *SML* at much greater concentrations than those observed in *SUB*. However, based on the re-

sults it may be observed that Ca and Mg are typically accumulated in *SML* in slight amounts in comparison to *SUB* and if accumulation in *SML* takes place, it is frequently a seasonal phenomenon. For example, this may be reflected by studies on the accumulation of calcium and magnesium in Lake Dołgie Wielkie, located at a distance of only approx. 25 km from the investigated ponds, which showed $EF_{Mg} = 1.08$ and $EF_{Ca} = 0.98$ (Antonowicz 2015). The surface microlayer with a thickness ranging from 15.7 to 75 μm collected from Lake Skjervatjern showed values of enrichment factors $EF_{Ca} = 0.9$ –2.1 and $EF_{Mg} = 1.1$ –1.3. Similarly, enrichment factors obtained for Ca during studies conducted seasonally in eutrophic lakes Gardno, Dołgie Wielkie and Jasień were as follows: $EF = 1.10$ –1.11, $EF = 1.10$ –1.11 and $EF = 1.07$ –1.08 (Antonowicz 2008). In those lakes analyses were also conducted in *SML* collected from the thinner layer of 100 μm . It was found that the obtained factors for *SML* with a lesser thickness were slightly greater (Antonowicz 2008, 2015).

No data concerning Na and K were found in studied literature, which would confirm the capacity for enrichment for these macroelements in *SML* collected with the Garrett net. The only study on the subject is presented in the investigations undertaken by Knulst et al. (1997). The method applied in this study was differ-

ent, as a teflon cylinder was used which made it possible to collect a thinner *SML* closer to the water surface. In view of considerations on the laminar structure of *SML*, we may observe that thinner *SMLs* accumulate greater concentrations of heavy metals (Estep et al. 1985; Trojanowski and Antonowicz, 2011). According to data presented by Knulst et al. (1997) recorded for Lake Skjervatjern factors for sodium for *SML* ranged from 1.0 to 1.1, while for potassium they were found to range from 2.1 to 23. Only in pond No. 2 was a low enrichment factor for potassium recorded at $EF = 1.34$.

One of the causes for the accumulation of metals may be connected with the capacity to bind these macroelements by physical forces such as surface tension, forces of adhesion, cohesion, retention of chemicals in *SML* and bioaccumulation in microorganisms (Norkrans 1980; Wurl and Obbard 2004). However, to a lesser extent it is probably connected with deposition from the atmosphere. This is confirmed by statistically significant correlation coefficients between *SML* and *SUB* ($r = 0.69\text{--}0.94$) as well as low concentrations of these elements in the precipitation recorded at the Hel peninsula: $1.27 \text{ mg Na dm}^{-3}$, $0.38 \text{ mg K dm}^{-3}$, $2.3 \text{ mg Ca dm}^{-3}$, $0.28 \text{ mg Mg dm}^{-3}$ (Szefer and Szefer, 1986) as well as in data reported by Sapek and Sapek (2011) at $8.24 \text{ mg Ca dm}^{-3}$ and $1.58 \text{ mg Mg dm}^{-3}$.

Analyses of seasonal changes indicate the effect of urban pollutants on transport of substances to *SML* and *SUB* waters in the analysed ponds. It is likely that a significant factor affecting the increase in Na and K concentrations in the spring in pond No. 1 included surface run-off (Lis and Pasieczna 1995). Sources of these elements may be salt mixtures applied in the winter for road deicing, which in the spring flow to lower areas, in this case ponds. Mixtures used in the removal of snow and ice most frequently contain NaCl with such additives as potassium ferrocyanide (Czarna 2013). In the spring we may observe Mg enrichment in both ponds (mean $EF = 1.44$), which may be connected with the accumulation of magnesium by the developing phytoplankton and phytoneuston. These microorganisms contain chlorophyll molecules containing magnesium in their cells. In turn, in the autumn the increase in the concentrations of potassium, calcium and magnesium in *SML* and *SUB* may be explained by the decomposition of dying organisms and the release of these macroelements to waters.

Recorded concentrations of calcium, magnesium, sodium and potassium in *SUB* are comparable to those given in literature sources. Calcium content in surface waters of Poland typically falls within the range of $50\text{--}150 \text{ mg dm}^{-3}$, while in small water bodies it is $4\text{--}66 \text{ mg dm}^{-3}$ (Lis and Pasieczna 1995). According to data given by Weihsa et al. (2013) collected from 26

lakes mean concentrations ranged from $8.4\text{--}62.8 \text{ mg Ca dm}^{-3}$ and $2.6\text{--}25.6 \text{ mg Mg dm}^{-3}$. According to Lis and Pasieczna (1995) concentration of magnesium in surface waters of Poland was at a minimum of 0.6 mg dm^{-3} , a mean of 11.5 mg dm^{-3} and in small reservoirs it was 11.8 mg dm^{-3} . Small water bodies contained potassium at $< 1 \text{ mg dm}^{-3}$ (mean 9 mg dm^{-3}). Orlik and Oboślak (2005) reported mean K concentration in ponds from 2.0 to 2.1 mg dm^{-3} . Average Na concentration in inland surface waters of Poland is within the range of $0\text{--}50 \text{ mg dm}^{-3}$, small water bodies contain a minimum of <1 and a mean of 20 mg Na dm^{-3} (Lis and Pasieczna 1995).

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