SURFACE MICROLAYER IN EUTROPHIC LAKE: VARIABILITY IN HEAVY METALS CONTENTS

ABSTRACT: The surface microlayer is a thin layer found at the contact zone of two environments forming an ecotone at the atmosphere–hydrosphere interface. It is the boundary layer of extreme importance for both environments. In the years 2000–2004 surface water microlayer of an eutrophic, deep lake (577 ha, max. depth 32.2 m, Lake Jasień in Northern Poland) was analyzed (in four seasons each year) in terms of their capacity to accumulate lead, cadmium and manganese. The following surface water layers were collected using the different devices (plate method, net method) and compared: a microlayer of approx. 100 μm in thickness (SM), a microlayer of approx. 240 μm in thickness (PM) and subsurface water (about 20 cm below surface) (SSW). The highest concentrations of analyzed metals were observed in the microlayer of 100 μm, characterized by enrichment factor (EF-ratio of surface to subsurface values) of 2.61 for cadmium, 2.55 for manganese and 1.57 for lead, respectively. Enrichment factors for these metals are much higher than in respective microlayers of brackish lake situated close and studied before. Seasonal changes in concentrations of analyzed elements were correlated with changes in their concentrations in subsurface water. Statistical analysis of results showed that during a year variation in Cd and Mn accumulation in analyzed layers was significant. In contrast, variation in Pb accumulation was statistically non-significant. It means that in the surface microlayer of lake water a seasonal cycle is observed for changes in heavy metal concentrations and this variability in concentrations of analyzed substances is not accidental, but definitely periodical in character. The accumulation of analyzed heavy metals in the surface microlayers of the studied deep eutrophic lake seems to be a regular phenomenon.

KEY WORDS: surface microlayer, heavy metals, seasonal changes, lake

1. INTRODUCTION

The surface microlayer is a thin layer with thickness up to several hundred micrometers, found at the contact zone between water and the atmosphere (Estep et al. 1985, Falkowska 1996, Hillbricht-Ilkowska et al. 1997, Trojanowski et al. 2001, Kostrzewska-Szlakowska 2006). This layer represents a thin (between 10 and several hundred mm) (Hilbricht-Ilkowska et al. 1997) part of the aquatic environment, forming an ecotone at the atmosphere-hydrosphere interface (MacIntyre 1974, Norkrans 1980, Hillbricht-Ilkowska and Kostrzewska-Szlakowska 2004, Kostrzewska-Szlakowska 2006, Walczak 2008). It is formed at the surface of all aquatic ecosystems. This surface microlayer of water bodies is a unique chemical and
physical environment, different from subsurface water. Among other factors, adhesion forces, formed as a result of molecular attraction at the boundary of the two media, i.e., hydrosphere and atmosphere, together with their surface tension forces, are responsible for the physical stability of the surface microlayer. This surface water layer is the boundary layer of extreme importance for both environments (Falkowska 1996, Hilbricht-Iłkowska et al. 1997). Exchange processes of gases and matter, variable in time and space, occur through this layer (Falkowska 1996, Hilbricht-Iłkowska et al. 1997, Trojanowski et al. 2001). The exchange of substances and energy is a crucial process in the biogeochemical cycle of chemical elements, as it is the case in the aquatic environment. The surface microlayer affects gas exchange (Quinn and Otto 1971, Liss 1977) and transport mechanisms from the column of water to the atmosphere and vice versa (Norkrans 1980). Dissolved substances, particles and microorganisms are transported to this zone by simple diffusion, convection by gas bubbles, convection movements from bottom deposits and subsurface water, as well as with migration organisms; moreover, the surface microlayer is fed by dusts and aerosols in precipitation (Norkrans 1980, Falkowska 1996, Kostrzewska-Szalakowska 2003). All these above mentioned processes lead to the accumulation of chemical substances and microorganisms. In addition, heavy metals found in the surface microlayer react with the accumulating organic matter forming complexes, or are absorbed on organic particles (Lion and Leckie 1981).


The aim of the study was to investigate the accumulation capacity of surface microlayers of fresh water in a lake in relation to selected heavy metals and variation in concentrations of these metals throughout the year, and to compare them with the accumulation capacity of the surface layer of sea water.

2. STUDY LAKE

A deep and eutrophic Lake Jasień (Fig. 1) consists of two basins: Jasień Północny and Jasień Południowy (54°20.5’ and 18°31.6’) connected with a wide isthmus. The area of both basins in the lake is 577.2 ha, while the
maximum depth is 32.2 m (Jańczak 1997). The lake is located in the Pomorskie province in the "Dolina Słupi” Landscape Park (north Poland) (Korzeniewski et al. 1992). Lake Jasień – a lake with eutrophic properties in the analyzed period was characterized by the following concentrations of nutrient compounds in the subsurface water layer: TON (total Kjeldahl nitrogen) amounting to 0.99 mg dm⁻³, ON (organic nitrogen) – 0.96 mg dm⁻³, N-NH₄ (ammonium) – 42.2 μg dm⁻³, TP (total phosphorus) – 123.1 μg dm⁻³, OP (organic phosphorus) 78 μg dm⁻³, and P-PO₄ (phosphates) 45 μg dm⁻³, while mean chlorophyll concentration was 26.1 mg dm⁻³ (authors results). In terms of chemical properties of water, both basins are similar in character. Their waters are of purity class II. It is a dimictic lake, with marked stratification in the summer season (Korzeniewski et al. 1992, Trojanowski et al. 1999). Lake Jasien has several islands, overgrown with woody vegetation and being refuges for waterfowl.

3. METHODS

3.1. Sampling

Samples of the surface water microlayer from the lake were collected for 4 years in the years 2000–2004. Three sampling stations were established on the lake (Fig. 1). Stations no. 1 and 3 were situated at a distance of approx. 100 m from the isthmus linking both basins as it is marked on Fig. 1. The central station (No. 2) was established on a shallow isthmus connecting both water bodies. The selected sampling stations are shielded by trees growing at the lake shore, which reduces the effect of winds on the water surface at the sampling stations, and thus enhances the stability of the surface microlayer.

Samples of surface water were collected by three methods:

1. The plate method (PM) – (Harvey and Burzell 1972) was applied to sample the surface water microlayer of 80–115 mm in thickness. For this purpose a glass plate of 30 × 30 cm and a thickness of 3 mm was used. A plate was immersed in water at an angle of 45° and after then taken out at a rate of 5 to 20 cm s⁻¹. The water sample was removed from both sides of the plate to a container using a rubber wiper.

2. The Garrett method (SM) – (Garrett 1965) was used to collect the surface microlayer with a thickness of 250–300 mm. A polyethylene net of 75 × 75 cm and mesh size of 0.14 mm was mounted on a frame. The net was immersed in water in a similar manner as it was the case with the glass plate and next a wiper was used to collect water to a container (Garrett 1965, Piotrowicz et al. 1972). In order to avoid the dilution of the surface microlayer by the expansion of the material to the layer of subsurface water the boat used during sampling was allowed to float in the sampling area (Estep and Remsen 1985).

3. Subsurface water (SSW) was collected at a depth of 20 cm from the water surface by immersing the container (Hermanowicz et al. 1999).

3.2. Determination of heavy metals

Samples of water were mineralized using H-NO₃. Mineralization was performed in a Maxidigest MX 350 Prolabo microwave mineralizer coupled with a microcomputer used to program the power and time of mineralization (Prolabo Microwave Systems 1996, USEPA 1998). Mineralized samples were stored at 4°C until analyzed (Obenauf et al. 1991, Hermanowicz et al. 1999). The manganese content was determined using a Carl-Zeiss Jena AAS3 flame atomic absorption spectrophotometer. Analyses were carried out at a wave length of 279.5 nm for manganese (Atomic absorption spectrophotometer AAS3 1984, PN-ISO 8288 2002). The blank test was prepared from deionized water subjected to an identical treatment (evaporation and mineralization) as ordinary samples. After determination and automatic reading of the concentration from the calibration curve it was converted into mg dm⁻³. Next the result was reduced by deducting the value obtained for the blank test.

Determinations of lead and cadmium were performed with a Carl-Zeiss Jena AAS3 atomic absorption spectrophotometer with an attached EA3 electromagnetic atomizer and an automatic sample injector. Analyses were carried out at a wave length of 217.0 nm for lead and 228.8 nm for cadmium (Atomic absorption spectrophotometer AAS3 1984, Electromagnetic atomizer ETA 1984).
Respective standard series were prepared and a correction for the blank test was taken into consideration. In case when concentrations in samples were higher than the highest standard the sample was diluted accordingly. Results were converted into mg dm$^{-3}$.

3.3. Statistical analysis

Results were analyzed statistically using STATISTICA software (Strzałko and Rożnowski 1992, Stanisz 1998). The type of distribution for a variable was determined using the Kolmogorov-Smirnov test, which made it possible to select an appropriate test (parametric or its non-parametric equivalent) for further statistical analysis of the collected material (Stanisz 1998).

One-way analysis of variance (ANOVA) was applied along with t-Tukey's test or Kruskal-Wallis non-parametric equivalent of ANOVA, when mean values revealed a distribution other than normal (Stanisz 1998).

When analyzing correlations of two variables the coefficient of Pearson's linear correlation – $r$ was calculated and next its significance was verified. If at least one distribution was significantly different from the normal distribution, the Spearman rank test – $r$ was applied. In order to determine the power of the relationship of correlated variables a scale presented by Stanisz (1998) was used.

In order to compare both investigated media: water from the surface microlayer and subsurface water, enrichment factors (EF) were applied, which were calculated from the following formula:

$$\text{EF} = \frac{C_{SM}}{C_{SSW}}$$

where: $C_{SM}$ – concentration of the analyzed component in a respective surface microlayer;

$C_{SSW}$ – concentration of the same component in subsurface water (Estep et al. 1985, Guitart et al. 2004).

4. RESULTS

Subsurface waters of the investigated lake contained from 0.01 to 0.96 mg dm$^{-3}$ cadmium (Table 1) and were characterized by its mean concentration of 0.44 mg dm$^{-3}$ (Table 2). In this lake no statistically significant differences were found between stations in terms of the subsurface layer (ANOVA, df = 45, $F = 0.41$, $P > 0.05$). The mean enrichment factor (EF – formula 1) calculated for the thinner water microlayer (SM) of Lake Jasień was 2.61, while for the thicker microlayer (SM) it was 1.95 (Table 2). Its highest value was recorded at station No. 1 (EF = 3.48 and EF = 2.31), while the lowest at station 3 (EF = 1.90 and EF = 1.60) (Table 1). In Lake Jasień in all analyzed water layers and at all sampling stations cadmium concentration changed in a similar manner during the year. Maximum concentrations were observed in the autumn, while minimum values – in the winter. Only in the SSW layer the lowest cadmium concentration was recorded in the spring (Fig. 2). Tukey’s test preceded by the analysis of variance only in the SSW layer showed significant differences in analyzed concentrations and even then they occurred solely between autumn and spring (ANOVA, df = 44, $F = 2.87$, $P < 0.05$).

Mean lead concentration in subsurface water of Lake Jasień was 1.76 mg dm$^{-3}$.
Surface microlayer in eutrophic lake

Table 1. Concentrations of cadmium, lead and manganese (μg dm⁻³) in surface microlayers of different thickness: PM (80–115 μm) and SM (250–300 μm) and in subsurface waters, SSW (20 cm below surface) of Lake Jasień. Data for three 1–3 sampling stations (see Fig. 1). Arithmetic mean values for four years (X), minimum (MIN) maximum (MAX), standard deviation (SD) and enrichment factor (EF – see formula 1).

<table>
<thead>
<tr>
<th></th>
<th>Cd</th>
<th>Pb</th>
<th>Mn</th>
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<tr>
<td></td>
<td>X MIN MAX SD</td>
<td>X MIN MAX SD</td>
<td>X MIN MAX SD</td>
</tr>
<tr>
<td>PM</td>
<td>0.97 0.17 2.38 0.74</td>
<td>2.56 0.97 4.60 1.14</td>
<td>97.5 25.2 323.2 76.6</td>
</tr>
<tr>
<td>SM</td>
<td>0.68 0.09 1.35 0.53</td>
<td>2.31 0.96 8.47 1.92</td>
<td>168 118.5 251.0 61.3</td>
</tr>
<tr>
<td>SSW</td>
<td>0.38 0.01 0.89 0.34</td>
<td>1.96 0.82 4.13 0.99</td>
<td>59.2 14.7 261.0 63.1</td>
</tr>
<tr>
<td>1PM</td>
<td>0.93 0.02 1.98 0.62</td>
<td>2.46 2.89 1.10 4.40</td>
<td>1.73 76.7 21.8 118.7</td>
</tr>
<tr>
<td>2PM</td>
<td>0.61 0.05 1.12 0.38</td>
<td>1.94 2.47 1.53 4.10</td>
<td>0.62 1.55 54.7 18.7 94.1</td>
</tr>
<tr>
<td>3PM</td>
<td>0.44 0.01 1.16 0.37</td>
<td>1.72 0.82 3.50 0.72</td>
<td>39.5 12.4 85.3 22.9</td>
</tr>
<tr>
<td>1SM</td>
<td>0.70 0.12 1.33 0.52</td>
<td>1.90 2.88 1.56 5.37</td>
<td>1.13 1.90 78.4 20.0 215.0</td>
</tr>
<tr>
<td>2SM</td>
<td>0.79 0.01 1.85 0.60</td>
<td>1.60 2.47 1.26 5.32</td>
<td>1.17 1.63 50.5 14.7 123.2</td>
</tr>
<tr>
<td>3SM</td>
<td>0.70 0.05 0.96 0.35</td>
<td>1.61 0.82 3.27 0.66</td>
<td>39.9 11.6 91.3 29.5</td>
</tr>
</tbody>
</table>

Table 2. Concentrations of cadmium, lead and manganese (μg dm⁻³) in surface microlayers (see Table 1) and subsurface waters of Lake Jasień. Cumulated data for each element from all years and stations. Enrichment factors (EF) – see formula (1).

<table>
<thead>
<tr>
<th></th>
<th>Cd</th>
<th>Pb</th>
<th>Mn</th>
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<tbody>
<tr>
<td></td>
<td>PM</td>
<td>SM</td>
<td>SSW</td>
</tr>
<tr>
<td>Cd</td>
<td>0.88</td>
<td>0.69</td>
<td>0.44</td>
</tr>
<tr>
<td>EF</td>
<td>2.61</td>
<td>1.95</td>
<td>1.76</td>
</tr>
<tr>
<td>Pb</td>
<td>2.77</td>
<td>2.63</td>
<td>1.62</td>
</tr>
<tr>
<td>EF</td>
<td>1.57</td>
<td>1.62</td>
<td>1.69</td>
</tr>
<tr>
<td>Mn</td>
<td>84.21</td>
<td>73.08</td>
<td>46.18</td>
</tr>
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</table>

Table 3. Correlation coefficients between the mean values of metal concentration in samples collected from surface microlayers (PM, 80–115 μm and SM, 250–300 μm in thickness) and in samples from subsurface waters (SSW–20 cm below surface), n = 48, all correlation coefficients were statistically significant, P <0.05.

<table>
<thead>
<tr>
<th></th>
<th>Cd</th>
<th>Mn</th>
<th>Pb</th>
</tr>
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<tbody>
<tr>
<td>SM/SSW</td>
<td>0.53</td>
<td>0.87</td>
<td>0.79</td>
</tr>
<tr>
<td>PM/SSW</td>
<td>0.76</td>
<td>0.83</td>
<td>0.51</td>
</tr>
</tbody>
</table>

(Table 3), ranging from 0.82 to 4.13 mg dm⁻³ (Table 1), and being similar at all the stations. No statistically significant differences were found in this lake between the sampling stations in subsurface water (ANOVA, df = 45, F = 0.76, P > 0.05). Much higher concentrations of this metal were observed in analyzed microlayers of surface water. Differences between lead concentration in the microlayers and in subsurface water were statistically significant. In turn, no differences were found between sampling stations, thus the mean lead enrichment factor for both microlayers, PM and SM, in Lake Jasień were very similar, amounting to approx. 1.6 (Table. 3). Seasonal variation in lead concentration in Lake Jasień presented in Fig. 3 was manifested in the proportional increase of this component from spring to autumn in all the analyzed layers. Only at sampling station 3 lead concentration was observed to decrease from the summer season to winter. After the autumn season in all cases a lower lead content was recorded in winter. Differences in lead concentration between seasons were slight and thus the analysis of variance did not show significant differences between seasons in Lake Jasień.

Subsurface waters of Lake Jasień contained from 11.6 to 261.0 mg dm⁻³ manganese and were characterized by the mean content of this component of 46.18 mg dm⁻³ (Table 2) at the negative ANOVA result calculated for individual sampling stations in layer SSW in relation to Mn concentration (df = 45, F = 1.13, P > 0.05). In turn, the concentration of this metal in microlayers was approx. two times higher, thus the enrichment factor for manganese in the surface microlayer PM.The
mean value of EF was equal to 2.25 and uniform at all sampling stations (Table 2). Greater differences between sampling stations were observed in microlayer SM: the mean value was equal to 1.69. The enrichment factor for surface microlayer SM at sampling station no. 1 was by 53% higher than that calculated for the other areas of the lake (Table 1). Seasonal variation in manganese concentration in Lake Jasień, presented in Fig. 4, shows lower concentrations of this element in the spring-summer season and higher values in the autumn-winter season for all sampling stations and in all analyzed layers (Fig. 4). Tukey’s test for layers PM, SM and SSW showed significant differences in manganese concentrations between the autumn and summer seasons; additionally, in layers SM and SSW between the winter and summer seasons, and in layer SSW, apart from those already mentioned, also a significant difference between autumn and spring (ANOVA, PM layer df = 44, F = 3.79, P < 0.05; SM layer F = 4.89, P < 0.01; SSW layer F = 7.12, P < 0.001).

Pearson’s correlation coefficient – r was calculated for analyzed heavy metals in each of the investigated layers. Results are presented in Table 3.

5. DISCUSSION

Heavy metals are cumulated in the surface microlayer and the EF value can be as high as 100 (Wurld and Obbard 2004). Such a huge discrepancy in the enrichment factor values is probably caused both by the type of metal and the adopted sampling technique (Hardy et al. 1990, Maki and Hermansson 1994, Wurld and Obbard 2004), as well as the type of the water body. Studies on contents of heavy metals in surface microlayers of lake waters are rare, whereas sea water was frequently investigated.

The mechanism of heavy metal accumulation in the surface microlayer is highly complex. The main mechanisms of enrichment for the surface microlayer were discussed in the introductory part of this paper.
The heavy metals are accumulated in the microlayer due to their binding to the microsuspension (coloids), e.g. proteins, carbon hydrates, etc. Also bacteria may produce organic components, which may provide the chelation effect for heavy metals dissolved in the surface microlayer (Wurld and Obbard 2004). Hunter and Liss (1981), as well as Lion and Leckie (1981) suggested that dissolved metals may be incorporated into the complexes of metal ions with organic ligands and may be found in this form in the surface microlayer. Cadmium is an exception in this respect, as in sea water it does not bond well with organic components to form complexes (Sadig 1992), which leads to higher concentrations of dissolved forms of cadmium in the surface microlayer and higher values of enrichment factors, which was also reported in studies by Hardy et al. (1985) and Hardy et al. (1990). Also Jickells (1994) and Migon and Nicolas (1998) in their studies established higher EF values for cadmium in comparison to other metals. Moreover, it was found that enrichment of the surface microlayer with heavy metals depends on pH, salination with chloride ions, as well as synergies and antagonisms between individual trace metals (Wurld and Obbard 2004).

Recorded mean values of enrichment factors for the surface water microlayer in the studied lake of heavy metals ranged from 1.60 to 3.48 (Table 1). Accumulation of heavy metals in the surface microlayer in the analyzed lake seems to be dependent on their concentrations in the subsurface water, as it was indicated by substantial values of correlation coefficients between metal contents in individual microlayers and their content in the subsurface water (Table 3).

The water in Lake Jasień exhibited a lower (1.5–2.5 times) capacity to accumulate Cd, Pb and Mn than in the estuary Lake Gardno, (Antonowicz 2008, Antonowicz and Trojanowski 2009) located at a distance of 100 km from the investigated lake. Higher enrichment factors (EF) recorded for surface microlayers of Lake Gardno (EF = 4.89 for Cd, EF = 3.83 for Pb and EF = 3.43 for Mn, and EF = 4.72 for Cd, EF = 2.75 for Pb and EF = 4.19 for Mn, respectively) were caused by its brackish character (Antonowicz and Trojanowski 2009, and author’s unpublished results). Obviously in Lake Gardno sea water plays a considerable role, resulting in the higher accumulation of heavy metals in the ecotone of the surface microlayer. Studies conducted in the Mediterranean Sea confirmed a high accumulation in the surface microlayer of marine waters where EF for Pb was 19 and for cadmium 55 (Migon and Nicolas 1998). In case of studies carried out in Chesapeake Bay for lead EF was recorded to be 43 (Hardy et al. 1990), while in studies conducted in the Puget Sound, Washington, it was 6–8 for cadmium and 26–65 for lead (Hardy et al. 1985). However, studies conducted in the Xiamen Bay (Chiny) may be an exception here, as this factor for cadmium fell within the range of as little as 1.1–1.6 (Hong and Lin 1990).

Zhang et al. (1998) and Zhang et al. (2003) in their studies found corresponding values of enrichment factors to those recorded in the analyzed Lake Jasień. They investigated the surface microlayer using different methods (including also the techniques used in this study) in order to observe the distribution of chemical substances within this microlayer. They concluded that the microlayer shows a difference in the vertical profile. In the thinnest layers collected using the glass plate method and ever a thinner microlayer, collected using methods with the application of teflon, the highest amounts of heavy metals such as Zn, Cd, Pb and Cu were found to be accumulated. In the other surface microlayer, such as PM, their accumulation of investigated heavy metals was usually higher.

6. CONCLUSIONS

Accumulation of heavy metals in the surface microlayers of the analyzed deep eutrophic lake is a regular phenomenon of high dynamics. Intensity of accumulation of these components in the surface water microlayer was higher than in the subsurface water. The thinner surface microlayer of lake water, i.e. the closer it is to the water-air boundary surface, the higher the accumulation of heavy metals. Enrichment factors recorded in waters of the study lake (Lake Jasień) were lower.
than in marine water investigated by other scientists. The main source of cadmium, lead and manganese in the surface microlayer is the subsurface water. In the surface microlayer of lake water a seasonal cycle is observed for changes in heavy metal concentrations. Fluctuations in concentrations of analyzed substances are not accidental, but are definitely periodical in character.

7. REFERENCES

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