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Seasonal Fluctuations In Co, Ni, Cu, Zn, Cd, Pb Concentrations In Surface Microlayers And Subsurface Water Of Two City Ponds

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Abstract. We owe the knowledge concerning the surface water microlayer to the wide research into marine environment and relatively scarce research done into inland city ponds ecosystems. The surface microlayer is a very thin, several hundred micrometers thick layer at the contact of water and atmosphere. This important form of air-water exchange ecotone, which constitutes the surface microlayer of water, is a specific environment as to its chemical and physical characteristics and is different from subsurface waters. It can absorb chemical substances like heavy metals, phytoneuston and bacteria in larger quantities in comparison to lower parts of the water. This characteristic feature results, among others, from the processes of transport at the contact of hydrosphere-atmosphere and also transport within the very area of surface water microlayer. The paper describes transport processes of six heavy metals: Co, Ni, Cu, Zn, Cd, Pb from subsurface water to surface water microlayer and vice versa, analyzed in a one year cycle. The transport of chemical substances under consideration was described on a basis of experiments made during the period of one year at five city pounds in Słupsk (Polish Pomerania). During the research, samples of the surface water microlayer were collected by means of application of the Garrett mesh technique. At the same time, samples of subsurface water were collected and tested as to the content of the same parameters as the surface microlayer. Samples were sampled in month intervals. The concentration of aforementioned heavy metals was measured by mass spectrometry method and used Perkin Elmer Elan DRC aparature.

Key words: surface microlayer , heavy metals, pond

Introduction

We owe the knowledge concerning the surface water microlayer to the wide research into marine environment and relatively scarce research done into inland city ponds ecosystems.

The surface microlayer is a very thin, several hundred micrometers thick layer at the contact of water and atmosphere (Estep et al. 1985, Trojanowski et al. 2001). This surface microlayer of water bodies is a unique chemical and physical environment, different from subsurface water (Hillbricht-Ilkowska and Kostrzewska-Szlakowska,, 2004, Antonowicz and Trojanowski 2010). This important form of air-water exchange ecotone, which constitutes the surface microlayer of water, is a specific environment as to its chemical and physical characteristics and is different from subsurface waters. Compared to subsurface waters, the surface microlayer is enriched in natural and anthropogenic compounds and microorganisms. It depends of physico-chemical phenomena described in papers: Norkrans (1980), Antonowicz and Trojanowski (2010).

It can absorb chemical substances like heavy metals, phytoneuston and bacteria in larger quantities in comparison to lower parts of the water. Concentrations of various chemical and microbiological components found in this microlayer usually exceed their concentrations in subsurface water (Trojanowski et al. 2001). Among other things, markedly higher concentrations were found for heavy metals (Maki and Hermasson 1994), phosphorus and nitrogen compounds (Trojanowski et al. 2001, Mudryk et al. 2003), fatty acids, esters, alcohols (Kozarec et al. 2003), chlorophyll (phytoplankton) (Antonowicz 2008b) as well as microorganisms (Mudryk et al. 2003, Hillbricht-Ilkowska A. and Kostrzewska-Szlakowska I., 2004, Antonowicz et al. 2008d). This characteristic feature results, among others, from the

processes of transport at the contact of hydrosphere-atmosphere and also transport within the very area of surface water microlayer.

The aim of study is a compare variability of enrichment factor for study metals in surface microlayer of water of analyzed ponds.

Materials and Methods

A two eutrophic ponds is localized in north Poland in Słupsk city: pond L 54º27'32.86"N 17º02'27.21"E and pond T 54º26'59.84"N 17º02'23.46"E. Samples of the surface microlayer and subsurface water from the ponds were collected for eight mounts in 2007-2008 year. Samples of surface water were collected by two methods: The Garrett method (SML) was used to collect the surface microlayer with a thickness of 250 – 300 μm (Garrett 1965) (Fig. 1). Subsurface water (SSW) was collected at a depth of 15 cm from the water surface by immersing the container.

Fig. 1. Sampling of surface microlayer of water by Garrrett net.

At the same time, samples of subsurface water were collected and tested as to the content of the same parameters as the surface microlayer. The concentration of aforementioned heavy metals: was measured by mass spectrometry method and used Perkin Elmer Elan DRC aparature. Chemical analyses: the concentration Co, Ni, Cu, Zn, Cd, Pb was measured by mass spectrometry method and used Perkin Elmer Elan DRC aparature.

Statistical analysis: 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:

$$EF_{PM} = C_{SML}/C_{SSW}, EF_{SM} = C_{SM}/C_{SSW}$$

where: C_{PM} or C_{SM}– concentration of the analyzed component in a respective surface microlayer;
C_{SSW} – concentration of the same component in subsurface water (Guitat 2004), counting in terms of the

$$EF = \text{partial val} \frac{\sum \left(\frac{C_{SML1}}{C_{SSW1}} + \frac{C_{SML2}}{C_{SSW2}} + \ldots + \frac{C_{SMLi}}{C_{SSWi}} \right)}{i}$$

where: successive unit indexes were calculated according to individual partial values,
e.g. C_{SML1} – concentrations in season *1* in microlayer PM or SM, C_{SW1} – concentrations of a component at the same hour and at the same sampling station in the subsurface water layer and analogously the 2nd results up to the *i*-th result.

Results and Discussion

Processes in the interface between water basins and land is of importance for the flow of material from terrestrial to aquatic ecosystems. Usually, only horizontal transport is considered (Sődergren 1993). The process of accumulation of substances in the surface microlayer varies in time [Norkrans 1980].

The presented study describes transport processes of heavy metals: Co, Ni, Cu, Zn, Cd, Pb from subsurface water to surface water microlayer and *vice versa,* analyzed in almost one year cycle. On the figure 2 was presented seasonal dynamic of coefficient enrichment.
Dissolved substances like heavy metals ions, particles and microorganisms are transported to this unique zone by simple diffusion, drifting in gas bubbles, convection movements from bottom deposits and subsurface water, while at the same time the surface microlayer is supplied by the atmospheric precipitation, dusts and aerosols [Norkrans 1980, Trojanowski et al. 2001]. All the above - mentioned processes lead to the accumulation of chemical substances and mikroorganizms.

In presented study concentration of analyzed heavy metals was higher in surface microlayer than in subsurface water. Mean coefficient enrichment in years 2007 – 2008 was in ponds L: Co =1,94, Ni = 1,25, Cu = 1,54, Zn=1,37, Cd=2,75, Pb=1,80 and in pond T: Co =1,74, Ni = 2,44, Cu= 1,93, Zn=1,88, Cd=5,75, Pb=5,94. The present study showed that the concentration of heavy metals in city ponds was much greater in surface microlayer than in subsurface water layers. A similar phenomenon was mentioned by many authors (Lion and Leckie 1981, Antonowicz and Trojanowski 2010, Trojanowski and Antonowicz 2011). Thus, a study of the composition and properties of the microlayer may reveal a horizontal transport of material via the pond ecotones which up to now no has been fully recognised.

Conclusion

1. The surface microlayers of analyzed ponds show higher ability to accumulate heavy metals compounds than subsurface water.
2. There are a seasonal fluctuation in concentration of heavy metals in both analyzed layers.

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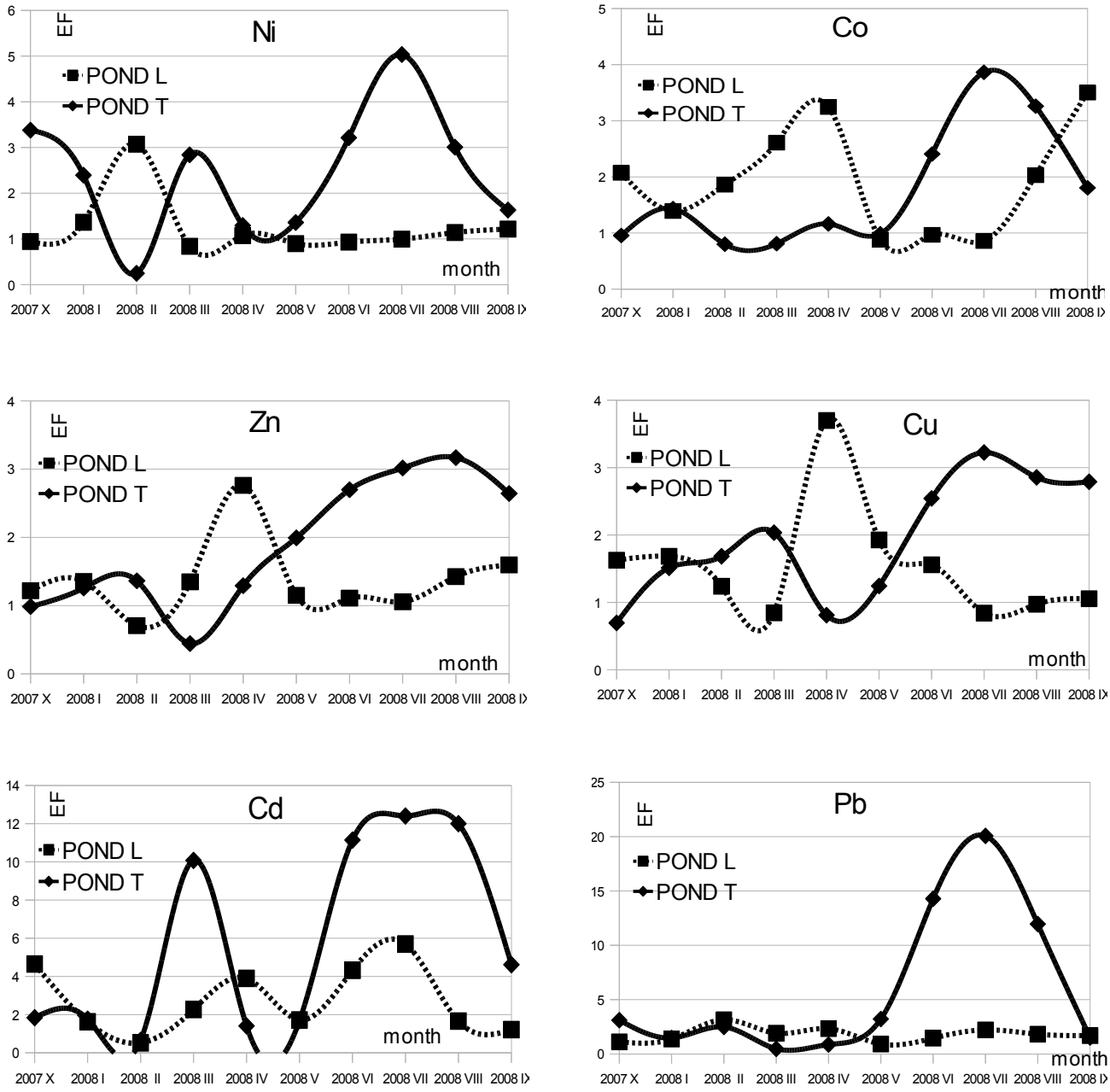

Fig. 2. Seasonal dynamic of coefficient enrichment for analyzed metals: Ni, Co, Cu, Zn, Cd, Pb in two city ponds in Słupsk (solid line – pond T, dotted line – pond L).

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