SURFACE MICROLAYER STUDY IN THE SEA LAKE (ROGOZNICA LAKE, MIDDLE ADRIATIC)

S. Frka, Z. Kozarac *, B. Ćosović

Rudjer Bošković Institute, Center for Marine and Environmental Research, 10002 Zagreb, Croatia - * kozarac@rudjer.irb.hr

Abstract

Sea-surface microlayers were studied using electrochemical methods, monolayer techniques and Brewster angle microscopy (BAM). Microlayer samples (ML) and the underlying seawater (ULW) were collected from a Middle Adriatic eutrophicated sea lake Rogoznica in different seasons and different conditions from March 2001 till nowadays. ML were studied in an original sample without any pretreatment and as *ex-situ* reconstructed films after previous extraction with organic solvents of different polarity. Content of surface active substances in ML and ULW was determined by alternating current voltammetry. Enrichment factors were calculated. The elastic properties of different ML were estimated from surface pressure measurements. BAM was used for optical characterization and visualization of ML.

Keywords: Rogoznica Lake, sea surface microlayer, electrochemical methods, monolayer technique, Brewster angle microscopy.

The sea surface microlayer is the upper 1 to 1000 μm thick boundary layer between the sea and the atmosphere. This interface region is a subject of number unique and dynamic, non-equilibrium processes such as wind stress, water transpiration, solar energy flux and atmospheric inputs. The exchange of gaseous and particulate material between the atmosphere and the ocean in this microenvironment is of fundamental importance. The sea surface microlayer is generally enriched in different natural and anthropogenic organic substances, which concentrate in the surface microlayer because of their surfactant nature, hydrophobic properties, and possible association with floatable particles, vertical diffusion mechanisms or bubbles scavenging. In this area large vertical gradients exist and physical, chemical and biological properties are most altered relative to subsurface water. Adsorbed organic substances change the physicochemical properties of natural interface, depending on the nature of organics, i.e., the nature of polar groups, architecture of the hydrophobic chain, ionic strength, pH and temperature. Although the physical and chemical properties of sea-surface microlayers have been studied extensively, knowledge is still lacking about the morphology, chemical composition and rates of surface film formation, alteration and disappearance.

In the study of the sea surface microlayer related to the morphology of natural films, relationship between the concentration and type of substances and the properties of films regarding the exchange between the film and subsurface, the main location of sea surface microlayer sampling was eutrophicated Rogoznica Lake (Middle Adriatic). Since 1994 in Rogoznica Lake investigations of seasonal variations of temperature, salinity and concentration of dissolved oxygen as well as vertical distribution of dissolved organic matter, surface active substances, phytoplankton and reduced sulphur compounds have been performed(1). Since steep cliffs shelter the lake and there is practically no wind effect on the water mixing, Rogoznica Lake represents a convenient model system for natural surface microlayer study. The sea surface microlayer was investigated from March 2001 till nowadays, in different seasons and under different weather condition. Original microlayer sample has been fractionated by extraction with organic solvents of different properties (*n*-hexane, chloroform and dichloromethane). The extracts have been successfully used for the studies of *ex-situ* reconstructed films. Investigation of the original microlayers as well as of *ex-situ* reconstructed films was performed using electrochemical methods, monolayer technique and Brewster angle microscopy (BAM)(2).

Phase sensitive alternating current voltammetry (*out-of-phase* signal) was used for quantification of adsorbable surface active substances (SAS) in original microlayers (ML) and underlying water samples (ULW) collected at ~0.5 m depth, expressed as equivalent amount of the selected standard tert-octylphenol ethoxylate (T-X-100)(3). Seasonal variability of SAS concentrations during the investigated period is shown in Table1. The mean SAS value of 1.2 mgl^{-1} was determined for ML samples and 0.12mgl^{-1} for ULW samples. Observed enrichment factors (EF) are several times higher than those found in the Northern Adriatic Sea (1.6-2.2)(4) and in May they reached the highest values. Generally, the concentrations of SAS of ML determined in May-October period were higher from those in winter season what could be related with the periods of more extensive phytoplankton activity in the Rogoznica Lake(1).

The *ex-situ* reconstructed microlayer films were studied by modified electrochemical method. The method is modified in the sense that the organic solvent extract of natural surface film was spread onto electrolyte solution and transferred from the air-water interface to the mercury surface by vertical dipping the electrode through the film. The capacitance of the film was determined by ac. voltammetry (*out-of-phase* signal). The obtained results for reconstructed microlayers were compared with those for model lipid monolayers. To our knowledge the method has not been used for the characterization of natural aquatic films until present.

Table 1. Seasonal variability of SAS concentrations in microlayer (ML) and underlying water samples (ULW) and enrichment factors (EF) in Rogoznica Lake.

Date sampled	SAS/mgl^{-1} eq. T-X-100 ML	ULW	EF
March 2001	0.71	0.11	6.4
May 2001	1.60	0.06	26.7
October 2001	0.71	0.19	3.7
February 2002	0.60	0.17	3.5
May 2002	3.80	0.22	17.3
January 2003	0.29	0.08	3.6
April 2003	0.48	0.08	6.0
August 2003	1.40	0.11	12.7
October 2003	1.30	0.27	4.8

Additional characterization of the structure of marine films was carried out by ac. voltammetry (*in-phase* signal) using an electrochemical probe. Redox processes of cadmium, as a potential pollutant in natural waters, were chosen as an indicator of the permeability of different films adsorbed at the mercury electrode. Results show a strong inhibition of cadmium reduction and oxidation in the presence of adsorbed films.

Monolayer studies, particularly measurements of surface pressure-area (π-A) isotherms, have been applied for comparison of physical states and elastic properties of different microlayers. Brewster angle microscopy was used for optical characterization and visualization of original microlayers and reconstructed films. BAM images have been recorded under surface pressure control to correlate the morphology and the monolayer phase state of the natural microlayers and *ex-situ* reconstructed films.

References

1 - Ciglenečki I., Kodba Z., Viličić D, Ćosović B., 1998a. Seasonal variation of anoxic conditions in the Rogoznica Lake. *Croatica Chemica Acta*, 71: 217-232.

2 - Kozarac Z., Ćosović B., Frka S., Mőbius D., Hacke S., Complex methodological approach to the studies of natural microlayers at the air/water interface. *Colloids and Surfaces A*, 219: 173- 186.

3 - Ćosović B., Vojvodić V., 1998. Voltammetric Analysis of Surface Active Substances in Natural Seawater. *Electroanalysis*, 10: 429-434.

4 - Marty J. C., Žutić V., Precali R., Saliot A., Ćosović B., Smodlaka N., Cauwet G., 1988. Organic matter characterization in the Northern adriatic sea with special reference to the sea surface microlayer. *Marine Chemistry*, 25: 243-263.