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ORIGINAL RESEARCH ARTICLE

Spectrophotometric studies of marine surfactants in the southern Baltic Sea☆

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Summary It is well known that surfactants in the southern Baltic Sea constitute the organic matter from riverine waters discharges as well as the secondary degradation products of marine phytoplankton excretion. They reach the surface microlayer by the upwellings and turbulent motions of water and in the membranes of the vesicles as well as from the atmosphere. To assess concentration and spatial distribution of marine surfactants in the southern Baltic Sea, the steady-state spectrophotometric and spectrofluorometric measurements of water samples taken from a surface film and a depth of 0.5 m were carried out. Water samples were collected during windless days of the cruise of r/v 'Oceania' in November 2012, from the open and the coastal waters having regard to the vicinity of the Vistula and Łeba mouths. In the present paper, fractions of dissolved organic matter having chromophores (CDOM) or fluorophores (FDOM) are recognized through their specific spectroscopic behavior, i.e., steady-state absorption, fluorescence excitation and fluorescence spectra. The steady-state spectroscopic measurements revealed the CDOM and FDOM molecules characteristic to both the land and marine origin. Moreover, the concentration and spatial distribution of marine surfactants significantly depend on the distance from the river mouth. Finally, higher values of absorbance and fluorescence intensity observed in a surface film in comparison to these values in a depth of 0.5 m clearly suggest the higher

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concentration of organic matter in a marine film. On the other hand, our results revealed that a surface microlayer is composed of the same CDOM and FDOM as bulk water.

1. Introduction

One of the characteristics of the Baltic Sea ecosystem as a semi-enclosed sea is the excessive input of anthropogenic organic matter coming with the riverine waters (Kowalczuk et al., 2010) causing the need to develop local algorithms and measurement procedures (Darecki and Stramski, 2004; Kutser, 2004; Ostrowska et al., 2012; Petelski et al., 2014). The anthropogenic organic matter compounds can be formed both by the development of biotechnological processes and by intensified agricultural activities in the catchment area of the Baltic Sea (Cincinelli et al., 2001; Petrovic et al., 2002), whereas the organic matter in the oceans takes its main source in the bacterial decomposition of the dead remains of marine organisms (Zutić et al., 1981). The molecules of organic compounds possess the parts that have different polarity, which can combine with other molecules to form, by electrostatic forces, the oval micelles or surface films (Liss and Duce, 1997; Leenheer, 1985). Depending on the chemical composition and structure, both natural and synthetic organic compounds may be dissolved or suspended in water and form a surface microlayer (Frew and Nelson, 1999; Soloviev and Lukas, 2006). As it was presented in many papers a surface layer can significantly affect the access of solar energy into the sea (Maritorena et al., 2000). Under the influence of light, temperature or other environmental factors the surface films would be more or less stable, as is determined by the chemical composition of the surface active molecules (surfactants) (Grzybowski, 2000; Upstill-Goddard, 2006).

It is well known that the steady-state spectroscopic studies are a versatile tool to establish the optical properties of the molecules of dissolved organic matter (DOM) in seawater (Hudson et al., 2007). Advanced spectrofluorometric research of Baltic surfactants and CDOM has been conducted at the Institute of Oceanology of the Polish Academy of Sciences for several years (Drozdowska, 2007a,b; Drozdowska and Fateyeva, 2013; Drozdowska et al., 2013; Kowalczuk et al., 2009; Schwarz et al., 2002). Despite the widespread use of the optical techniques no systematic and extensive studies have been carried out to explain the role of different types of fluorophores in surface microlayers in different regions of the Baltic Sea. The Baltic Sea is a catchment area of many Polish rivers; hence, the research of the riverine water propagation and their chemical composition in the surface layer over the Polish coastal zone of Baltic would be highly desirable.

The River Vistula is the longest Polish river that drains 100 times bigger area of land than another river flowing into the Baltic Sea — the River Łeba. The flow rate at the mouth of the Vistula is about 50 times higher than the flow rate of the Łeba (Cieśliński and Drwal, 2005). Additionally, it is important to remember that before the Łeba enters the Baltic Sea, it runs through the Łebsko Lake that purifies the river water. Furthermore, depending on the wind speed and direction the intrusions of seawater inland occur commonly and the sea has small stratification in this shallow region (Bednorz et al., 2013). Dynamic of the Vistula water inflow into the Baltic Sea has a peculiar property due to the profile of a bottom, since the depth along the Vistula transect increases 2—3 times faster than along the Łeba one (Uścinowicz, 2010). These contraries, describing two different estuaries, help to explain the differences between the optical properties of surface seawaters.

In the present paper, we have attempted to explore the concentration distribution of chromophoric and fluorophoric dissolved organic matter (CDOM and FDOM) in a surface film and at a depth of 0.5 m in coastal and open sea. The main goal of this work was to develop a rapid spectroscopic method to estimate the extent of the organic matter introduced into the Baltic Sea by two Polish rivers and determine the fractions of the organic matter. The next task was to detect the variability of CDOM or FDOM composition (surfactants) with the distance to the land and compare the types of the molecules occurring in surface films in two investigated regions: the Vistula and Łeba estuaries.

2. Experiments

2.1. Marine measurements and study area

Water samples were collected during a research cruise of r/v 'Oceania' in November 2012 in the southern Baltic Sea. The locations of monitoring stations were determined in two areas from a river mouth to open waters: from the Vistula and Łeba mouths to the Gdańsk Deep and the Słupsk Sill, respectively (see Fig. 1).

The meteorological conditions (a wind speed and direction) and salinity of water were recorded during sampling. In all cases, a wind direction was from the West and a speed about 5 m s^{-1}. Salinity of water at a depth of about 0.5 m increased with increasing a distance from the Vistula mouth in a range from 3.4 to 7.02 and oscillated in a range from 6.94 to 7.04 along the Łeba transect.

Seawater samples were taken from a surface film by a glass plate method (Harvey and Burzell, 1972) and from a depth of 0.5 m by a bathometer. For further analysis, the unfiltered samples were placed into dark bottles and stored at 4°C. It is well known that, filtration separates a particulate fraction from dissolved and colloidal ones. On the other hand, during filtration strongly-surface-active molecules or macromolecules might be retained on the filter by sorption processes (Ćosović and Vojvodić, 1998). Ćosović and Vojvodić (1998) reported that the filtration process of water from the northern Adriatic Sea is accompanied by a decrease of the concentration of surface active organic molecules by about