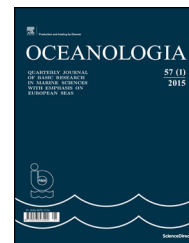




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ORIGINAL RESEARCH ARTICLE

Spectrophotometric studies of marine surfactants in the southern Baltic Sea[☆]

Violetta Drozdowska^{a,*}, Marek Józefowicz^b

^a *Institute of Oceanology, Polish Academy of Sciences, Sopot, Poland*

^b *Institute of Experimental Physics, University of Gdańsk, Gdańsk, Poland*

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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 Leba 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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* Corresponding author at: Institute of Oceanology, Polish Academy of Sciences, Powstańców Warszawy 55, 81-712 Sopot, Poland. Tel.: +48 58 7311801; fax: +48 58 5512130.

E-mail address: drozd@iopan.gda.pl (V. Drozdowska).

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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.

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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 (Kowalczyk et al., 2010) causing the need to develop local algorithms and measurement procedures (Darecki and Stramski, 2004; Kutsner, 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; Kowalczyk 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 (Uścińowicz, 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 Stupsk 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

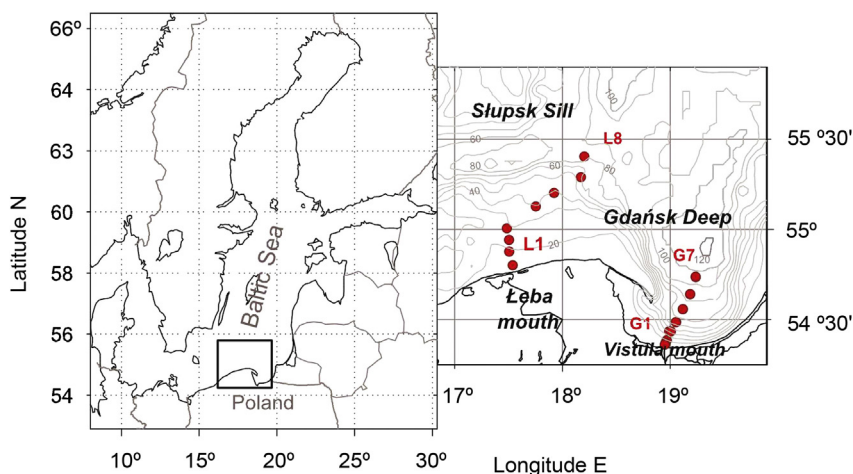


Figure 1 The location of monitoring stations along transects from the Vistula and Łeba mouths to Gdańsk Deep and Stupsk Sill, respectively; a research cruise of r/v Oceania in November 2012.

several to 15%. Furthermore, the interference of in situ measurements of CDOM fluorescence by particles was studied by Belzile et al. (2006) who estimated a possible error in fluorescence signal retrieval in less than 4%. The similar experiment, performed to assess the impact of suspended solids on measurements accuracy of the CDOM fluorescence intensity in the Baltic Sea (Kowalczyk et al., 2010), revealed that the presence of particles in water can reduce the CDOM fluorescence signal by 35%. Taking into account the above conclusions, for the purposes of the study of surfactant, the all studied samples were analyzed without filtration.

2.2. Laboratory setup

Spectrophotometric and spectrofluorometric measurements of seawater samples were carried out in 24 h after collection without any previous treatment at room temperature using a 1 cm high sensitivity quartz cell. The steady-state spectroscopic measurements were carried out using the Shimadzu UV-2401 PC Spectrophotometer and Shimadzu RF-5301 PC Spectrofluorometer with 5 nm bandwidth in both excitation and emission, respectively. The fluorescence was observed perpendicularly to the direction of the exciting beam (Józefowicz et al., 2007). Firstly the base-line was corrected for an artificial seawater (salinity 7) sample. The absorption spectra of the samples were measured in a spectral range of 200–500 nm, with an artificial seawater used as a reference. The fluorescence spectra were excited at three different wavelengths: 260, 310 and 335 nm and recorded in a spectral

range from 280 to 600 nm, respectively. The all measured fluorescence spectra possess two distinct emission bands with maxima centered at about 380 and 445 nm, assigned to the components described in Table 1. Finally, the fluorescence excitation spectra, observed at 380 and 445 nm, were recorded in a spectral range from 220 to 500 nm. The analysis of the fluorescence excitation spectra confirms the existence of the spectral bands coming from the components shown in Table 1. Decomposition of the measured spectral curves into several spectral bands (reported in Kowalczyk et al., 2009) results from the fitting to the Gaussian Curves by the least squares method.

3. Results and discussion

It is well known that the steady-state absorption and fluorescence spectra of water samples give reliable information about a type and concentration of different chromo- and fluorophores contained in marine organic matter. It is reported by Coble (2007) that variability of the excitation and emission (EEM) spectra indicates the presence of several types of fluorophores manifested by characteristic spectral bands. Briefly, they are assigned to the humic-like (the bands are marked as A and C), the marine humic-like (M) and the protein-like (B and T) fractions of dissolved organic matter (Babichenko, 2001; Blough and Del Vecchio, 2002; Kowalczyk et al., 2009; Parlanti et al., 2000).

The absorption, fluorescence excitation and fluorescence spectra were analyzed assuming the presence of the basic

Table 1 Description of chromophoric/fluorophoric compounds of dissolved organic matter contained in studied seawater samples (Coble, 1996; Coble et al., 1990; Fellman et al., 2010; Kowalczyk et al., 2009; Parlanti et al., 2000).

Excitation and emission maxima [nm]	Peak name	Probable sources	Description
ex. 310/em. 380	M	Marine, autochthonous, microbial processing	Low molecular weight, common in marine environments associated with biological activity but can be found in wastewater, wetland, and agricultural environments
ex. 260/em. 460	A	Terrestrial	High molecular weight and aromatic humic, widespread
ex. 335/em. 440	C	Terrestrial	High-molecular-weight humic, widespread

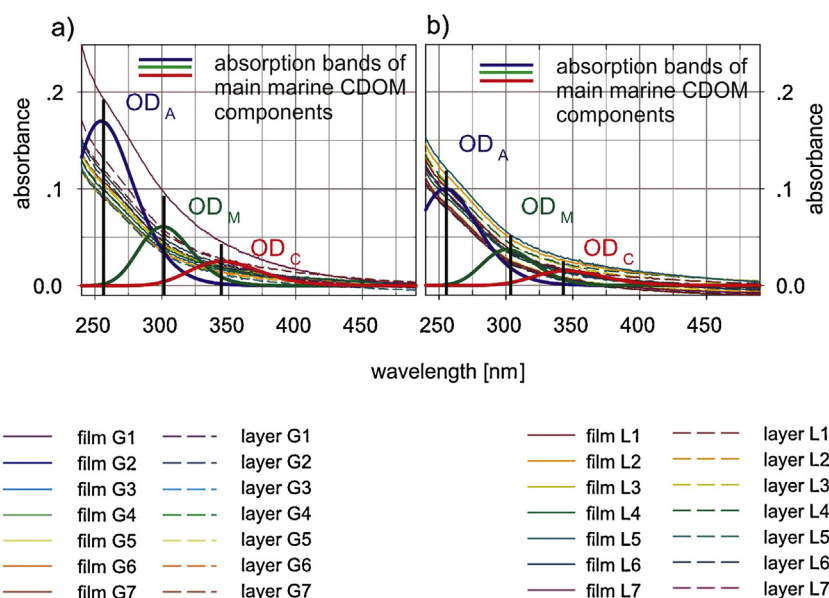


Figure 2 The absorption spectra of the samples taken along the Vistula (a) and Łeba (b) transects. As the examples, the absorption spectra of G1 and L1 are deconvoluted into three spectral bands assigned to the main fractions of marine CDOM: A, M and C; see [Table 1](#).

fractions of CDOM in the waters of the Baltic Sea ([Kowalczyk et al., 2005](#)) collected in [Table 1](#). Taking into account the above, the absorption spectra, in the units of energy ([Korshin et al., 1997](#)), were decomposed into three spectral bands by fitting to the three Gaussian Curves. As it is seen in [Fig. 2](#), the absorption spectra, presented in the units of wavelengths, consist of three partially overlapping bands that correspond to the absorption of the fractions: A, M, and C (compare [Table 1](#)). Obviously, the presented values of the absorbances of the analyzed absorption bands indicate the higher concentration of CDOM fractions in the Gdańsk and Łeba coastal waters. The ratio between the values of absorbance (optical density (OD)) for the Vistula and Łeba mouths is about two ($OD_A(\text{Gdańsk})/OD_A(\text{Łeba}) \approx 2$, see [Fig. 2](#)). The explanation can be purifying of the Łeba waters by the Łebsko Lake just before entering the sea.

As can be seen in [Fig. 2](#), the concentration of marine surfactants significantly depends on the distance from the river mouth. To obtain more conclusive information on the role of different types of chromophores in the studied regions, the analyzed absorption spectra are normalized in a way that each of the areas under the absorption curves was normalized to unity (100%). The relative changes in absorbance (optical density described by the ratio $OD_A/OD_M/OD_C$ (relative proportions of the fractions A (260 nm), M (310 nm), and C (335 nm), respectively)) are analyzed as a function of a distance from a river mouth. The graphical presentation of the absorbance value (optical density (OD)) corresponding to the three main fractions of seawater CDOM: OD_A , OD_M and OD_C and the relative changes in absorbance described by the ratios $OD_A/(OD_A + OD_M + OD_C)$ and $OD_M/(OD_A + OD_M + OD_C)$ and $OD_C/(OD_A + OD_M + OD_C)$, analyzed as a function of a distance from the Vistula and Łeba mouths is illustrated in [Figs. 3](#) and [4](#). Analyzing data assembled in [Figs. 3](#) and [4](#), in connection with a graphical presentation of the locations of monitoring stations (see [Fig. 1](#)) it follows that waters of the Vistula bring into the Gulf of Gdańsk much more terrestrial

runoff in comparison to the waters of the Łeba (the presence of the Łeba Lake causes filtering the water flowing into the sea). Additionally, it should be noted that small variations in percentage composition of the three main fractions of CDOM observed as a function of distance from the Łeba mouth (small changes between coastal and open waters, see [Fig. 4](#)) clearly show that the Łeba estuary waters form a more spectrally homogeneous column in comparison to the Gulf of Gdańsk waters. Analyzing the recorded spectra as a function of a distance from the river mouths, it is also evident that for both studied transects, the absorption spectra undergo visible changes for the samples collected close to the river mouth only. Upon increasing a distance from a land, the absorption spectra become similar to these recorded in the open sea. [Figs. 3](#) and [4](#) clearly show that for the large distance (≥ 20 km) from the river mouths the studied samples are spectroscopically nearly the same.

The percentage value of participation of the selected fractions, i.e., A, M, and C in the absorption spectrum indicates a higher concentration of A fraction at a depth of 0.5 m as well as at a surface film for all investigated systems (see [Figs. 3](#) and [4](#)). The major observation that can be made suggests that for all studied samples humic fraction (A) of DOM plays dominant role ($\sim 60\%$) whereas the contribution of the M and C components is significantly smaller and equals 20 and 15%, respectively. Furthermore, analyzing the absorption spectra of seawater samples collected close to the land (G1, L1, see [Figs. 1](#) and [2](#)), it has been found that the values of absorbance corresponding to the three main fractions of CDOM are higher in a film than in a depth of 0.5 m in the Vistula estuary. Not such a behavior is observed for the Łeba mouth water. This behavior is understandable in terms of the presence of the Łeba Lake at the mouth of the river to the sea.

In order to obtain more insight about the different types of optical active components in seawater, the steady-state fluorescence and fluorescence excitation spectra of the investigated samples were analyzed. The fluorescence

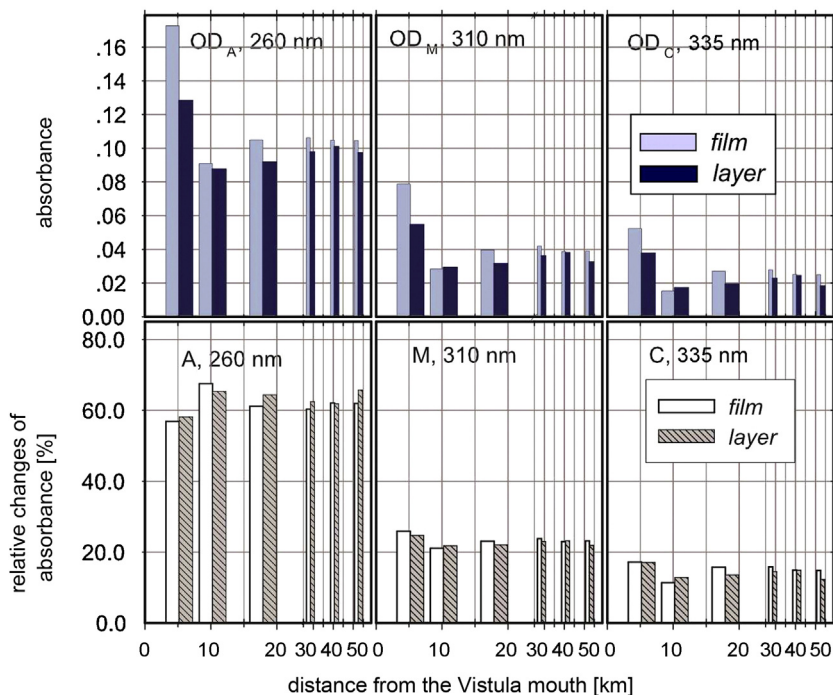


Figure 3 Graphical presentation of the absorbance value (optical density (OD)) corresponding to the three main fractions of seawater CDOM: OD_A , OD_M and OD_C (a) and the relative changes in absorbance described by the ratios $OD_A / (OD_A + OD_M + OD_C)$ and $OD_M / (OD_A + OD_M + OD_C)$ and $OD_C / (OD_A + OD_M + OD_C)$ (b), analyzed as a function of distance from the Vistula mouth. In order to better visualize the changes in the first 20 km from the Vistula mouth X-axis has been extended in this section.

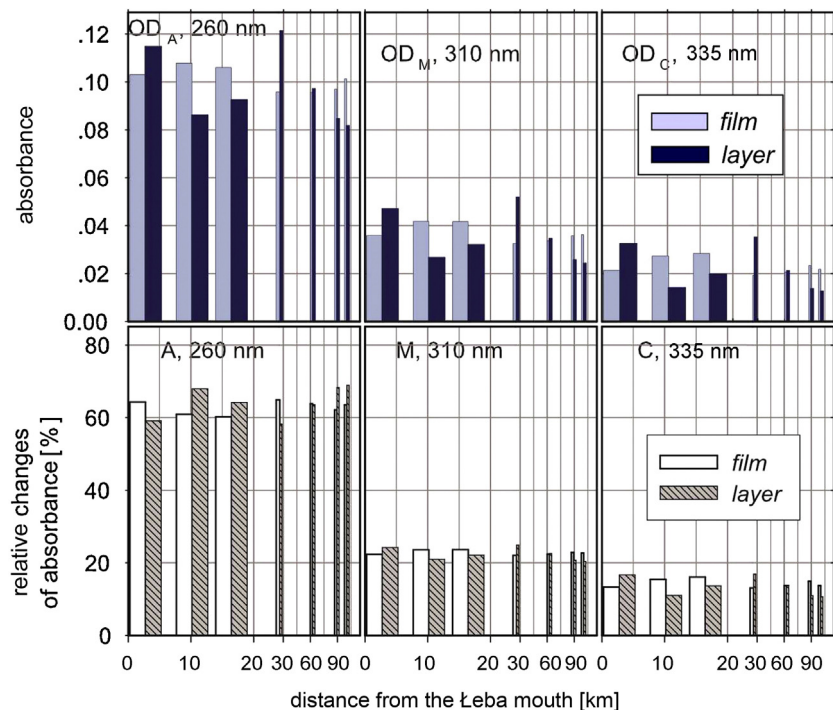


Figure 4 Graphical presentation of the absorbance value (optical density (OD)) corresponding to the three main fractions of seawater CDOM: OD_A , OD_M and OD_C (a) and the relative changes in absorbance described by the ratios $OD_A / (OD_A + OD_M + OD_C)$ and $OD_M / (OD_A + OD_M + OD_C)$ and $OD_C / (OD_A + OD_M + OD_C)$ (b), analyzed as a function of distance from the Łeba mouth. In order to better visualize the changes in the first 20 km from the Łeba mouth X-axis has been extended in this section.

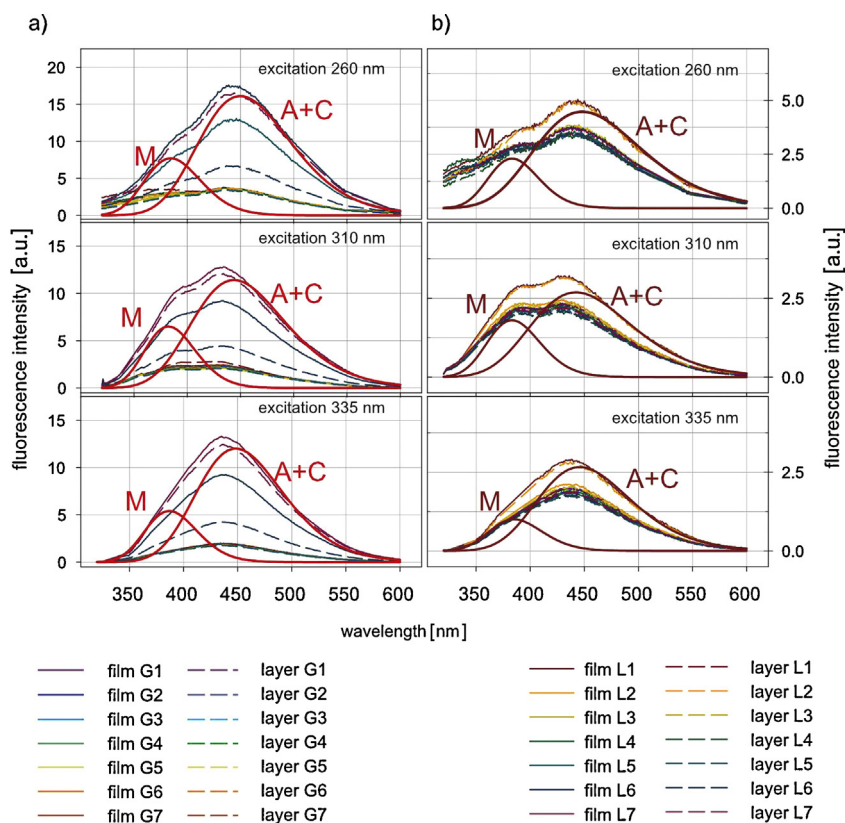


Figure 5 The fluorescence spectra of the investigated seawater samples taken along the Vistula (a) and Łeba (b) transects recorded for the three different excitation wavelengths: 260, 310 and 335 nm. As the examples, the fluorescence spectra of G1 and L1 are deconvoluted into two spectral bands corresponding to the main fractions of marine CDOM – M (380 nm), A + C (450 nm).

spectra were measured for the excitation wavelengths: 260, 310 and 335 nm. It is important to remember that selected wavelengths correspond to the maxima of the absorption bands marked as A, M, and C, respectively (Table 1). For all investigated samples, the fluorescence spectrum consists of two partially overlapping bands with the maxima at 380 and 450 nm. The analyzed spectra were deconvoluted by the least square method into two Gaussian Curves with maxima at 380 nm and 450 nm (see Fig. 5). These results confirm that investigated samples form a spectrally inhomogeneous system with M (centered at 380 nm), A (at 460 nm), and C (at 440 nm) fractions.

It is clear from Fig. 5 that the intensity of the fluorescence spectrum recorded for samples from the Gulf of Gdańsk yields several times higher values than for samples from the Łeba transect. This demonstrates significantly higher concentration of emitting FDOM molecules in the Gulf of Gdańsk in comparison to the Łeba transect. Quantitative analysis of the fluorescence spectra of the investigated samples confirms the hypothesis about the influence of the Łebsko Lake on the concentration and spatial distribution of different types of fluorophores dissolved in seawater.

For samples collected along the Łeba transect as well as in the Gulf of Gdańsk, the fluorescence spectra (obtained in all studied λ_{exc}) indicate the presence of the humic-like fraction (A) of FDOM as a major emitting component with smaller contributions of M and C components. It is found that the

intensity ratio of the fluorescence bands assigned to the A, M, and C components strongly depends on the excitation wavelengths. Nevertheless, for all studied excitation wavelengths the emission of fluorophores assigned to the humic and land origin fractions (A and C) plays a dominant role. Analyzing the fluorescence spectra obtained at a different distance from the Łeba and Vistula mouths, it is found that the fluorescence intensity of the bands: A + C – land origin and M – marine origin versus a distance from the Vistula and Łeba mouths are very well fitted by the exponential functions (Figs. 7 and 8). Along the Łeba transect the concentration of emitting FDOM molecules in a film and in a depth of 0.5 m slightly decreases with increasing a distance from a river mouth, whereas along a transect from the Vistula mouth toward the Gdańsk Deep the concentration of FDOM molecules decreases much faster. The difference between the decay constants is understandable taking into account differences in concentrations of fluorophores and salinity values (Ahel and Terzic, 2003).

Moreover, analysis of the fluorescence spectra confirms the presence of greater quantities of FDOM molecules in a film that in a depth of 0.5 m (see Figs. 7 and 8). Additionally, it is clear from Figs. 7 and 8 that waters of the Gulf of Gdańsk are more enriched in terrestrial and anthropogenic molecules of DOM in comparison to the waters along the Łeba transect.

In order to confirm the interpretation of the steady-state absorption measurements, i.e., different types of

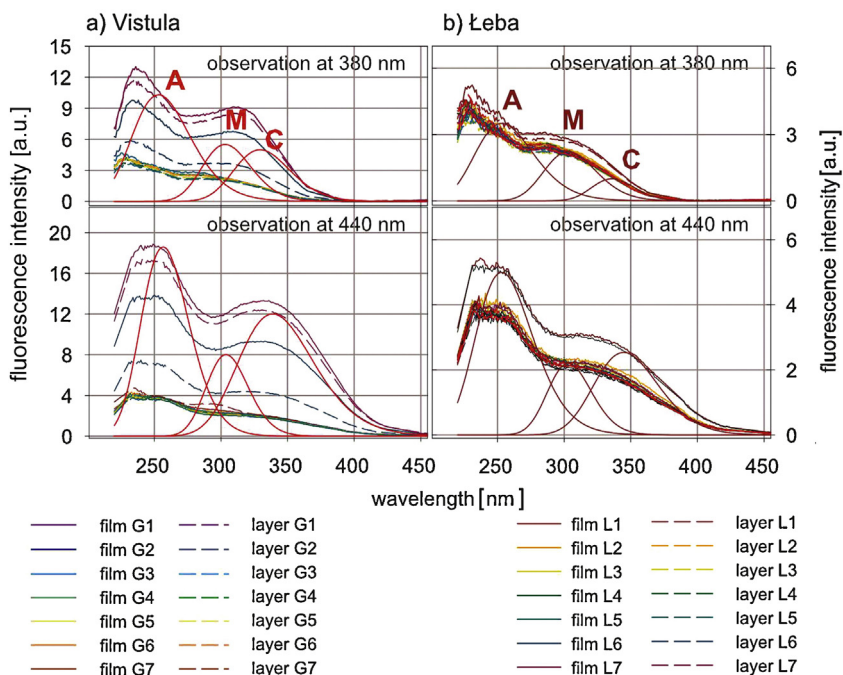


Figure 6 The fluorescence excitation spectra of the investigated seawater samples taken along the Vistula (a) and Łeba (b) transects. As the examples, the fluorescence excitation spectra of G1 and L1 are deconvoluted into three separated bands centered at about 260 nm (A), 310 nm (M) and 340 nm (C).

fluorophores in the ground state, the fluorescence excitation spectra were also monitored. Fig. 6 presents the observation-wavelength dependence of the fluorescence excitation spectra of the investigated seawater

samples. The major observation that can be made confirms the presence of the mentioned above fractions in the excitation spectra i.e. a fluorescence excitation spectrum is composed of three bands, centered at

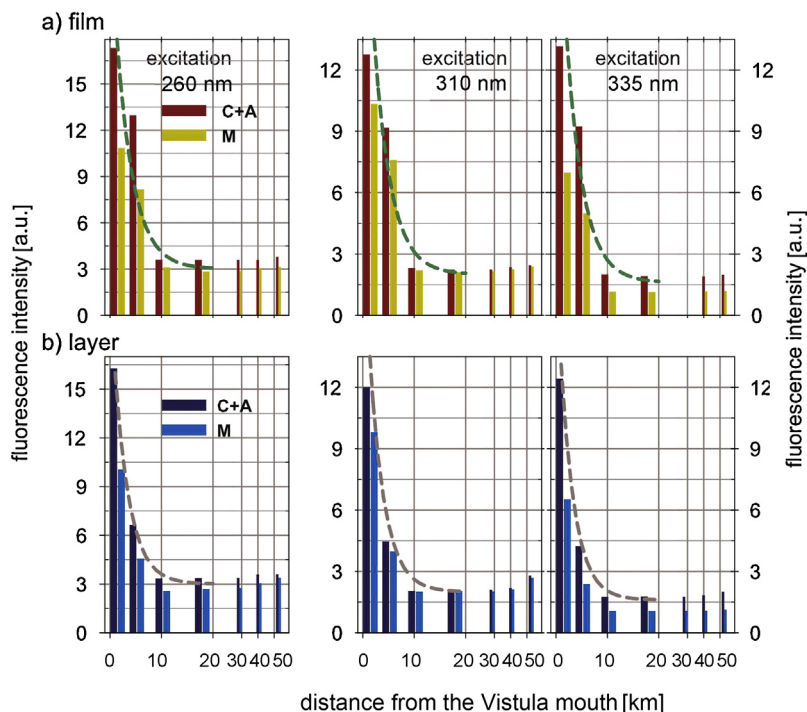


Figure 7 Graphical presentation of the fluorescence intensity changes of the three main fractions of seawater (A, M, and C) in a surface film (a) and a depth of 0.5 m (b) analyzed as a function of distance from the Vistula mouth; dashed lines represent exponential decrease of concentration of fluorophores in the first 20 km. In order to better visualize the changes in the first 20 km from the Vistula mouth X-axis has been extended in this section.

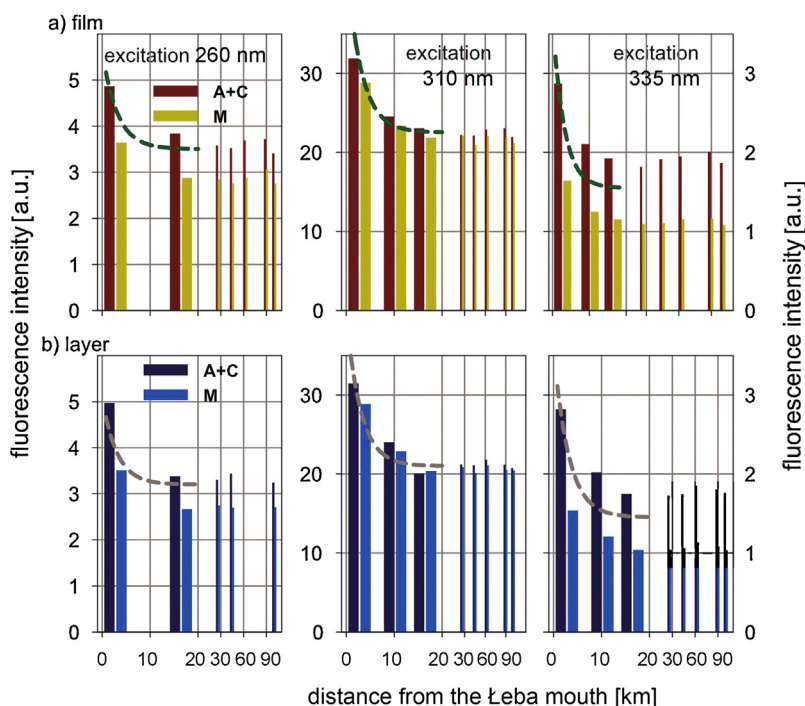


Figure 8 Graphical presentation of the fluorescence intensity changes of the three main fractions of seawater (A, M, and C) in a surface film (a) and a depth of 0.5 m (b) analyzed as a function of distance from the Łeba mouth; dashed lines represent exponential decrease of concentration of fluorophores in the first 20 km. In order to better visualize the changes in the first 20 km from the Łeba mouth X-axis has been extended in this section.

about 260 nm (A), 310 nm (M), and 340 nm (C), respectively.

4. Conclusions

Spectrophotometric and spectrofluorometric studies of seawater samples collected from a surface film and a layer at a depth of 0.5 m in the Vistula and Łeba estuary waters during a November research cruise enabled to create a method for fast detection of the main fractions of CDOM entering the Southern Baltic with riverine waters and their propagation in a surface layer. Analyzing the data obtained from the steady-state absorption and fluorescence measurements, one can state that:

- All studied samples form a spectrally inhomogeneous system with M, A and C fractions of marine CDOM (Coble, 2007; Kowalczyk et al., 2005).
- The participation of the respective fractions strongly depends on the distance from a river mouth and on the salinity and geomorphology of an estuary.
- The waters of the Vistula bring into the Gulf of Gdańsk much more terrestrial runoff in comparison to the waters of the Łeba.
- The small spectral changes of the three main fractions of seawater CDOM observed in absorption spectrum analyzed as a function of a distance from the Łeba mouth clearly show that the Łeba estuary waters form more spectrally homogeneous column in comparison to the Gulf of Gdańsk waters.

- The fluorescence intensity of the bands: A + C – land origin and M – marine origin versus distance from the Vistula and Łeba mouths are very well fitted by exponential functions. The difference between the decay constants is understandable taking into account the different concentration of fluorophores.
- For all investigated samples the humic fraction (A) of DOM plays a dominant role in the absorption spectrum, whereas the contribution of the M and C components is significantly smaller. The M fraction appeared more abundant in the Łeba estuary waters than in the Gulf of Gdańsk (Fig. 6). The C fraction was present in both estuaries in the smallest quantity.
- The surface microlayer is composed of the same CDOM and FDOM molecules as bulk water.
- For both studied transects the higher values of absorbance (optical density) and fluorescence intensity were observed in a surface film than in a depth of 0.5 m.
- The Vistula plays dominant role in optical properties of surface waters of the Gulf of Gdańsk while along the Łeba transect, which is characteristic for the coastal waters of the southern Baltic Sea (Cieśliński, 2013), a permanent mixing of the river and seawater masses as well as their organic components takes place.

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