

FLUORESCENCE OF NATURAL SEAWATER EXPOSED TO OIL POLLUTION

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Abstract

The natural seawater contains both dissolved and suspended organic substances originating from natural sources and human activities – like the marine transport fleet among other. To specify the type and quantity of vitally valid as well as dangerous for properly functioning marine ecosystems substances complicated and sophisticated chemical instrumentation and methodologies must be used. Only a small number of seawater components it is possible easily to determine their concentrations – for example, the salt content is determined directly in the bulk of water through simultaneous measurement of electrolytic conductivity and temperature of water. It is worth to search similarly quick method for oil substances directly in the seawater. Taking into account seawater organic pollutants originating from natural sources inter alia crude oils, the presence of refinery petroleum substances due to their fluorescence in ultra-violet light can be determined based on fluorescence spectroscopy. The aim of this paper is to search fluorescence features of oil substances dissolved in natural seawater based on excitation-emission spectroscopy. In the paper fresh and oily contaminated seawater taken from the coastal area of the Baltic Sea were used. As an oil pollution ‘Petro-baltic’ oil were applied. The natural seawater, at first was laboratory exposed to low extremely amount of oil and then it was examined by fluorescence under UV light. The seawater from vicinity of Gdynia (Poland) were tested as fresh and after artificially contaminated by different amount of oil (from 0.5 to 500 ppm). Spectrofluorometer Hitachi F-7000 FL was applied to measure excitation-emission spectra (EEMs). Low amounts of oil (up to several ppm) cause increasing of main peak in excitation-emission spectra (EEMs). Addition of larger amounts of oil results in appearance new peaks, which originate from fluorescence of soluble fractions of oil artificially added to examined water. These specific features of oil describe the spectroscopic signatures of oil, which is the basis to development operational method of the source of oil pollution identification.

Keywords: marine fleet exploitation, seawater, oil pollution, fluorescence spectroscopy

1. Introduction

Permanent developing the intensity of the transport activity on the surface waters (like maritime routes, rivers, lakes, inland canals) is inextricably linked to the use of different driving systems, among which various types of combustion engines dominates. This results in a continuous inflow to marine waters the unintentional chronic (technological) petroleum substances, which marine environment has to “consume”. Added to this are deliberate illegal discharges from ships as well as shipwrecks – among of those the most harmful to the environment are tanker catastrophes.

The issue of residence oily substances in seawater has a nature of multiple kinds. Apart from environmental damage, the most important are two aspects, namely, at the first – detection of those substances in both discharge waters from the vessels and in marine waters masses and at the second – disruption of the technical methods of tracking of the natural processes in marine waters. To investigate marine water masses among various physical testing media (electromagnetic waves) only light can be used because other kinds of radiation (ultraviolet, infrared, radio waves) are absorbed in the water on a short-path. One of optical methods, which can be used, is fluorescence, the more that all products derived from petroleum show fluorescent properties [1-3, 6].

In this paper, tests on fluorescence features of natural marine water exposed clearly to define

various small amounts of exemplary crude oil (*Petrobaltic*, extracted from the Baltic Sea area) are described. Based on excitation-emission spectroscopy wavelength-independent fluorescence maxima for pure seawater and seawater contaminated by crude oil for various oil concentration were determined.

2. Method

2.1. Oil samples preparation in seawater

To prepare *Petrobaltic* crude oil samples as a solvent seawater from Baltic Sea from Gdynia-Orłowo coast was used. The pure seawater samples were taken in the middle of May. First, four individual samples of seawater were prepared. Next, four individual oil concentration in n-hexane were prepared. Then the hexane was evaporated to obtain the appropriate amount of oil. Next evaporated oil from each n-hexane sample was added to seawater sample. Finally, crude oil was diluted in seawater for each individual oil concentration (see Tab. 1).

Tab. 1. '*Petrobaltic*' oil amount in the water samples

<i>Petrobaltic</i> (P)	Ps1	Ps2	Ps3	Ps4
c [ppm]	1	10	100	500

2.2. Measurement

Excitation-emission spectra of crude oil *Petrobaltic* samples dissolved in seawater in three-dimensional plane (3D) were measured using spectrofluorometer Hitachi F-7000 FL [3, 5]. EEMs for the solvent – pure seawater and for each concentrations of oil in seawater were measured in 1×1 cm quartz cuvette.

To measure EEMs of pure seawater and oil seawater samples the following measurement parameters were applied: excitation wavelength from 200 nm to 340 nm with excitation sampling interval 5 nm, emission wavelength from 260 nm to 450 nm with emission sampling interval 5 nm, excitation slit 5 nm, emission slit 5 nm, integration time 0.5 s and photomultiplier tube voltage 400 V.

Firstly, EEM spectra for used solvent – pure seawater at a stabilised temperature 20°C were performed. Next, EEM spectra of seawater exposed on crude oil *Petrobaltic* for particular four oil's concentrations were measured, also at a stabilised temperature 20°C.

Further, to obtain the real EEMs of crude oil after it contacts with seawater each data of measured oil samples diluted in seawater and particular four oil's concentration were corrected by subtraction the spectra of pure seawater.

3. Results

At first, EEM spectra for pure seawater sample from Baltic Sea coast – Gdynia-Orłowo were measured. Obtained EEMs in three-dimensional plane (3D) – (left) and in two-dimensional plane (2D) – (right) are presented in Fig. 1. The EEM spectra indicate the presence of main peak in UV-range, which is especially visible in two-dimensional plane (right chart in Fig. 1). Moreover, the intensity of natural seawater is low; it is clearly visible in three-dimensional plane (3D) – (left chart in Fig. 1).

Next, EEMs of seawater exposed into crude oil *Petrobaltic* were measured. In Fig. 2 EEM spectra in 2D plane for crude oil after it contacts with seawater for different oil concentration potentially found in seawater environment, changing from the lowest oil concentration – 1 ppm to the highest oil concentration 500 ppm, were presented. Moreover, based on measured EEMs of

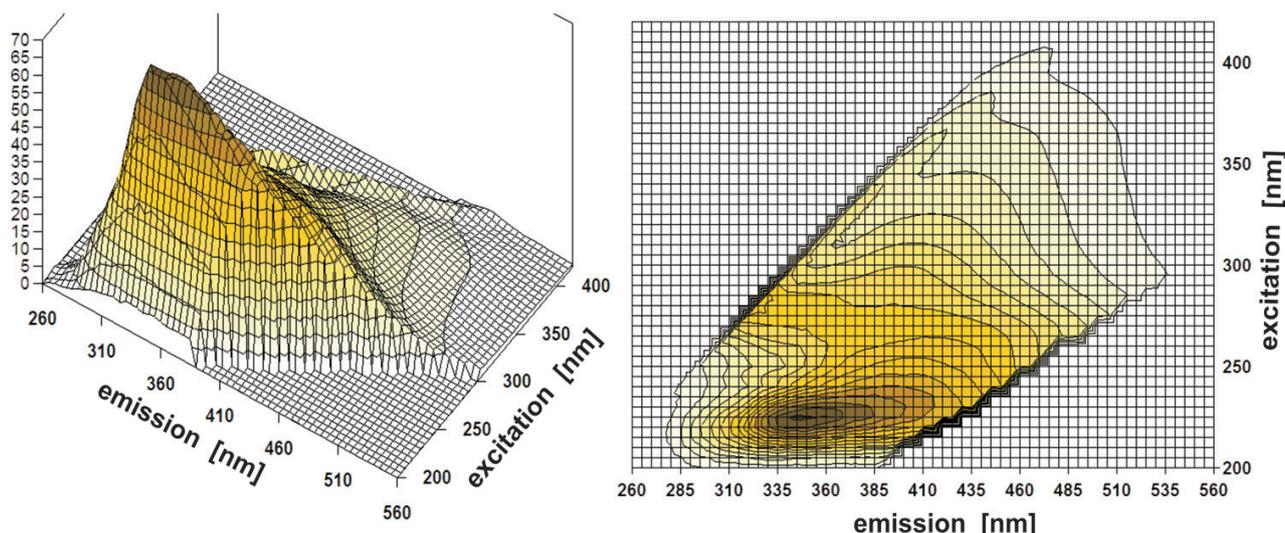


Fig. 1. EEM spectra of exemplary natural seawater (Baltic Sea, Poland, the Gdynia-Orłowo walking pier, seawater samples were taken on May 15, 2015)

pure seawater and seawater exposed to crude oil the EEMs of crude oil after it contact with seawater were determined. In Fig. 2 are presented results where fluorescence of natural seawater components was removed. In Fig. 2 is visible the changing of EEMs of crude oil after it contact with seawater when the oil concentration is changing. The intensity of crude oil fluorescence increases already for small amount of oil pollution in seawater – 1 ppm, and for higher oil concentration the significant increase of fluorescence intensity is observed in Fig. 2.

Main information of considered samples is fixed in normalized EEM spectra. Therefore, EEM spectra for each measured samples were normalized. In Fig. 3, normalized EEMs both for seawater exposed to crude oil with seawater components and without seawater, components are presented. Based on EEMs, the wavelength independent maximum for seawater samples, exposed to crude oil was determined and it is presented in Tab. 2.

Tab. 2. Wavelength-independent fluorescence maximum for seawater exposed to small portion of crude oil ‘Petrobaltic’ (for individual oil amount)

	Ex _{max} [nm] / Em _{max} [nm]		
	Peak 1	Peak 2	Peak 3
Ps1	230 / 350	–	270 / 330
Ps2	225 / 340	220 / 295	275 / 335
Ps3	225 / 340	220 / 295	275 / 335
Ps4	225 / 340	220 / 295	275 / 335

4. Discussion

Obtained results indicate that the natural seawater shows fluorescence due to certain diluted chemical compounds and suspended particles. Fluorescing chemical compounds are usually marine and inland organisms and flora decomposition products [4, 7-9]. Fig. 1 shows EEMs charts determined for natural water sampled from the sea. The most strong fluorescence is observed for excitation by UV light in vicinity of 230 nm. Therefore, to observe only oil component all fluorescence intensities were reduced by intensities for unpolluted water. Unfavourable however physically justified is that EEMs shape depends on amount of oil to which water is exposed. Certainly, concentration of oil substances in water is closely linked with amount of oil added to water. Fig. 2 confirms increasing of fluorescence intensity with amount of oil increasing.

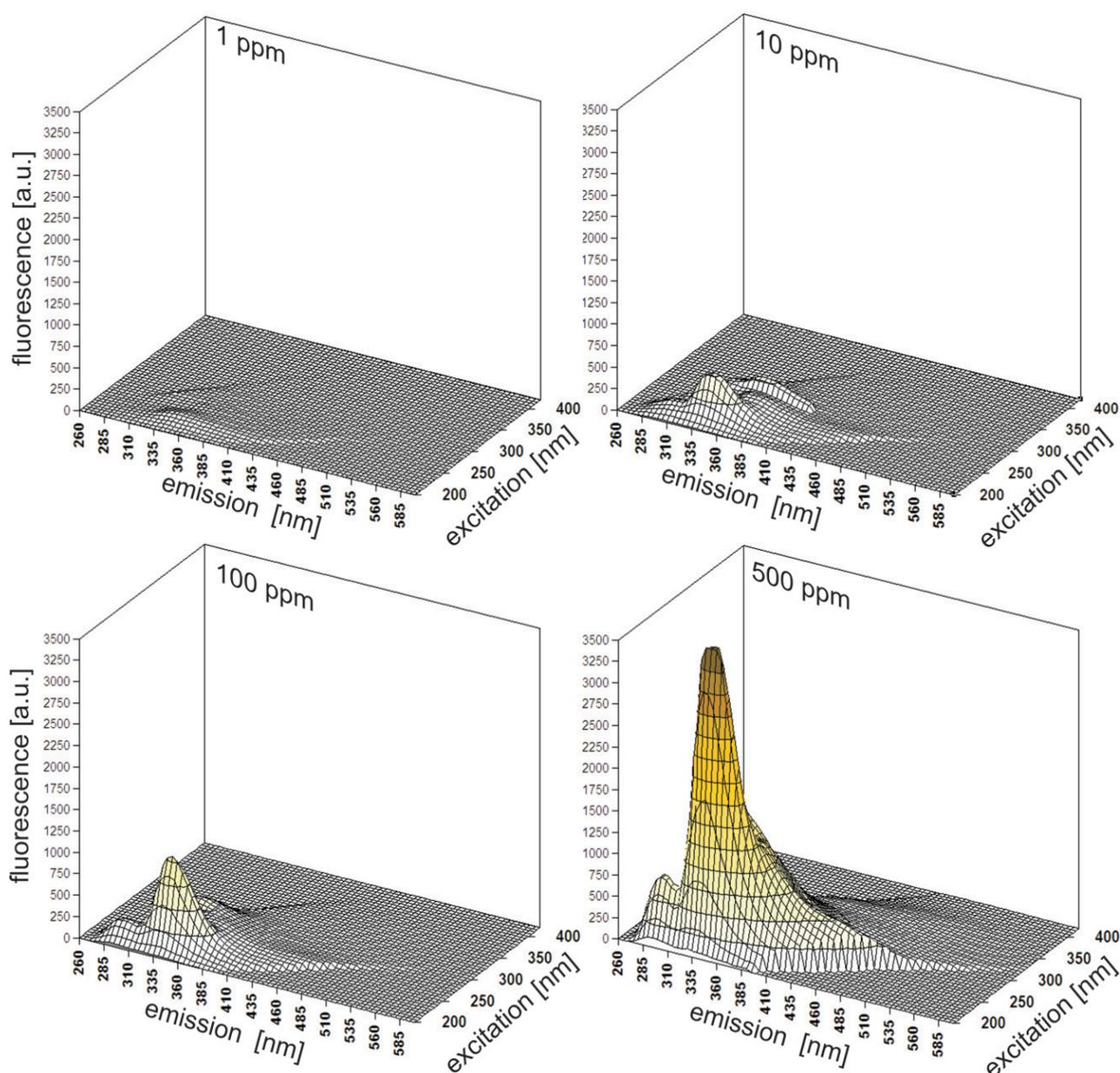


Fig. 2. Excitation-emission spectra of seawater caused by oil-component (fluorescence of natural seawater components were deducted)

In Fig. 3 is evidenced that the shape of EEMs for various amount of oil differs slightly. The main peak for low amount of oil is situated at excitation wavelength 230 nm and emission wavelength 350 nm, whereas is shifted towards shorter emission 240 nm (excitation is stable). However, it is noticeable appearance of new peaks when the amount of oil increases (excitation 220 and 275 nm, emission 295 and 330 nm). Also in Fig. 3, comparison of EEMs in two cases when fluorescence of seawater is taken into consideration and fluorescence of seawater was removed for low amount of oil natural fluorescence overlaps oil-component. That means that natural components of seawater can disturb EEMs originated from oil dissolved in water.

Results presented above demonstrate the possibility of using fluorescence spectroscopy to detect of oil substances directly in the natural seawater, but to establish operational fluorescence method to oil in water detect further extended tests should be performed, especially for various types of oil and in natural seawater in various seasonal phases of phytoplankton development. Likewise, the region of the sea may prove to be significant (for example for the reason of rivers inflow).

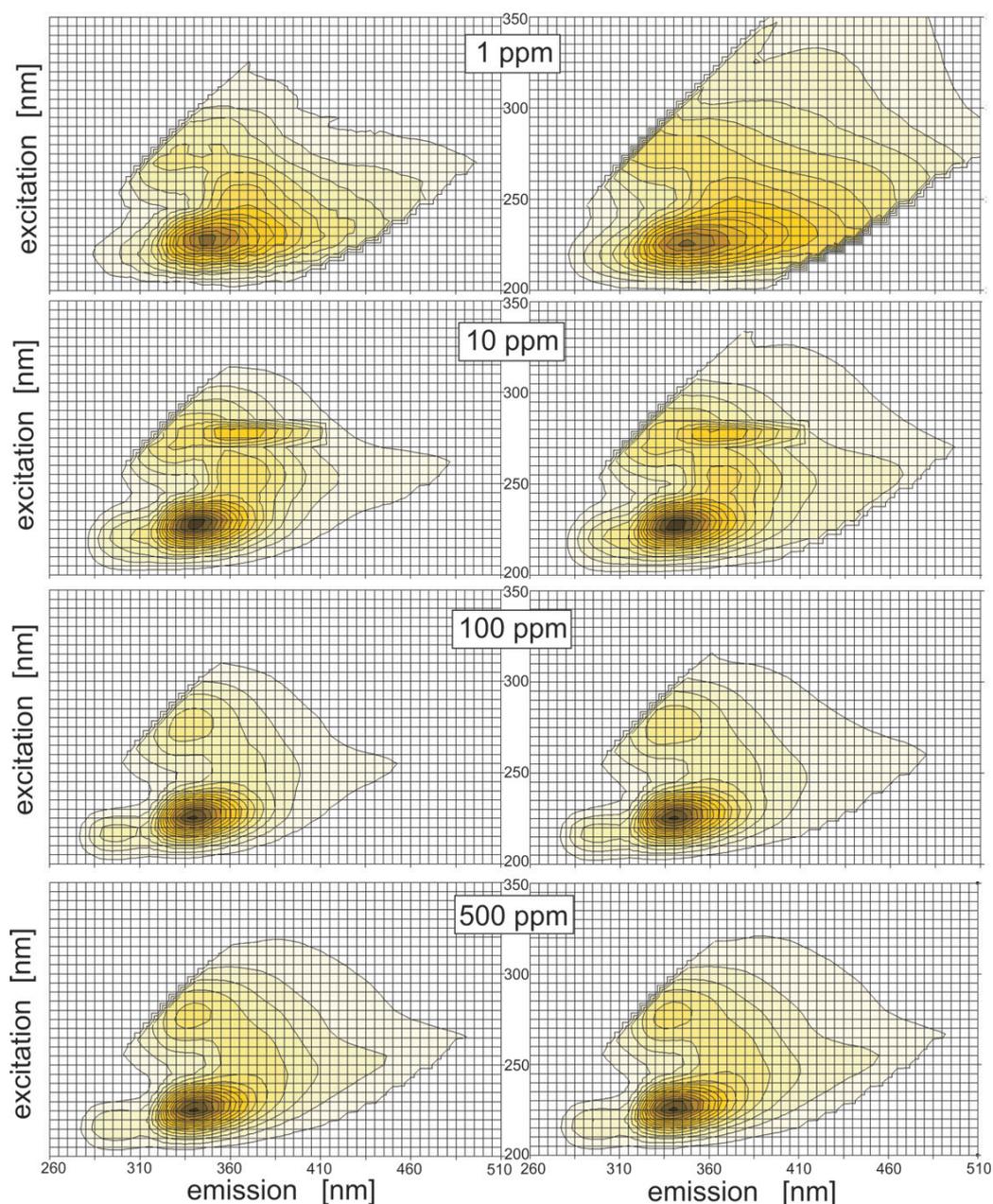


Fig. 3. Normalized excitation-emission spectra of seawater caused by oil-component (left) and caused by both oil and natural components of seawater (right)

In the oceanography, oil substances are considered as a one of alien substances in the surface waters, which can disturb optical methods of the remote monitoring of biological processes in the bodies of water. Therefore, knowledge of the optical features of an oil substance in the natural waters can be also useful in interpretation models of images of surface waters in the world.

4. Conclusions

Obtained results indicate that seawater fluorescence intensity strongly increased after exposition to oil pollution. Moreover in the shape of EEM spectra is clearly visible the difference between EEMs of pure seawater and seawater contaminated by oil. The difference is already observed for small amount of oil pollution in seawater. Additionally, when the natural seawater components are removed from EEM spectra oil fluorescence peaks are detected after it contacts with the natural seawater.

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