OPTICAL PROPERTIES OF CRUDE OIL DETECTED IN SEAWATER

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Abstract

The effects of crude oils entering marine environment have been investigated since early 1960s when oil pollution became a subject of global environmental concern. Extraction and transportation of crude oils have been contributing to water pollution especially in closed water basins, such as the Baltic Sea. It was estimated that yearly oil input to the Baltic Sea amounts to 21-70 thousands of tons, which is twice higher than in the North Sea and three times higher than in the North Atlantic. Growing pollution loads into the Baltic Sea created a demand for multifarious studies on the environmental effects of oil products. In this study, we focus on bio-optical and ecological aspects of the presence of crude oil in seawater. Dispersed oil droplets occur in seawater as the result of contaminated river inflows, bilge water discharges and as the consequence of mechanical and chemical dispersion of oil spills. Their optical properties depend on oil type, concentration and size distribution. We present further results obtained from the developed fluorescence-based method for determination of the crude oil concentration in natural Baltic seawater and for evaluation of the oil droplets size by applying vacuum filtering. The results have been measured for the samples collected in Southern Baltic Sea during several ship cruises in 2012. We discuss the application of vacuum filtering in the fluorescence analyses in the context of laboratory, in situ and remote detection of dispersed oil.

Keywords: crude oil, marine ecology, fluorescence, seawater, oil pollution

1. Introduction

In early 1960s, oil pollution became a subject of global environmental concern. The effects of crude oils and their products entering marine environment include i.e. biological effects on marine life, socio-ecological effects on water quality and optical effects on radiative transfer study in seawater [3]. Rising oil demand have been increasing offshore extraction and transportation of crude oils. On the other side, the development of economy have been increasing the onshore usage of oil products in industry and agriculture, loading pollution to the rivers and then to the seas and oceans (Fig. 1). Such activities contribute significantly to water pollution especially in closed water basins, such as the Baltic Sea. Currently 14-18% of ships on the Baltic Sea are tankers, carrying 166 million tonnes of oil at any time [5]. The amount of extracted oil, tanker traffic, the amount of transported oil, as well as oil loads on oil terminals have increased continuously within last 40 years (Fig. 2). It was estimated that yearly oil input to the Baltic Sea amounts to 21-70 thousand of tons, which is twice higher than in the North Sea and three times higher than in the North Atlantic (data from 1989-1993). Over 3 million tons of oil is reloaded every year in the oil terminals on the Baltic Sea [6].

In this study, we focus on bio-optical and ecological aspects of the presence of crude oil in seawater. Oil products occur in marine environment usually as oil droplets suspended in seawater as the result of contaminated river inflows, bilge water discharges and as the consequence of mechanical and chemical dispersion of oil spills [9, 12]. Surface oil films, which occur accidentally, amount to about 2% of total oil pollution in the Baltic Sea, and due to wave-induced mechanical dispersion, they tend to transform quickly into water-in-oil emulsion called the "chocolate mousse", which lasts up to 100 days and it is further transformed into oil-in-water emulsion [1].
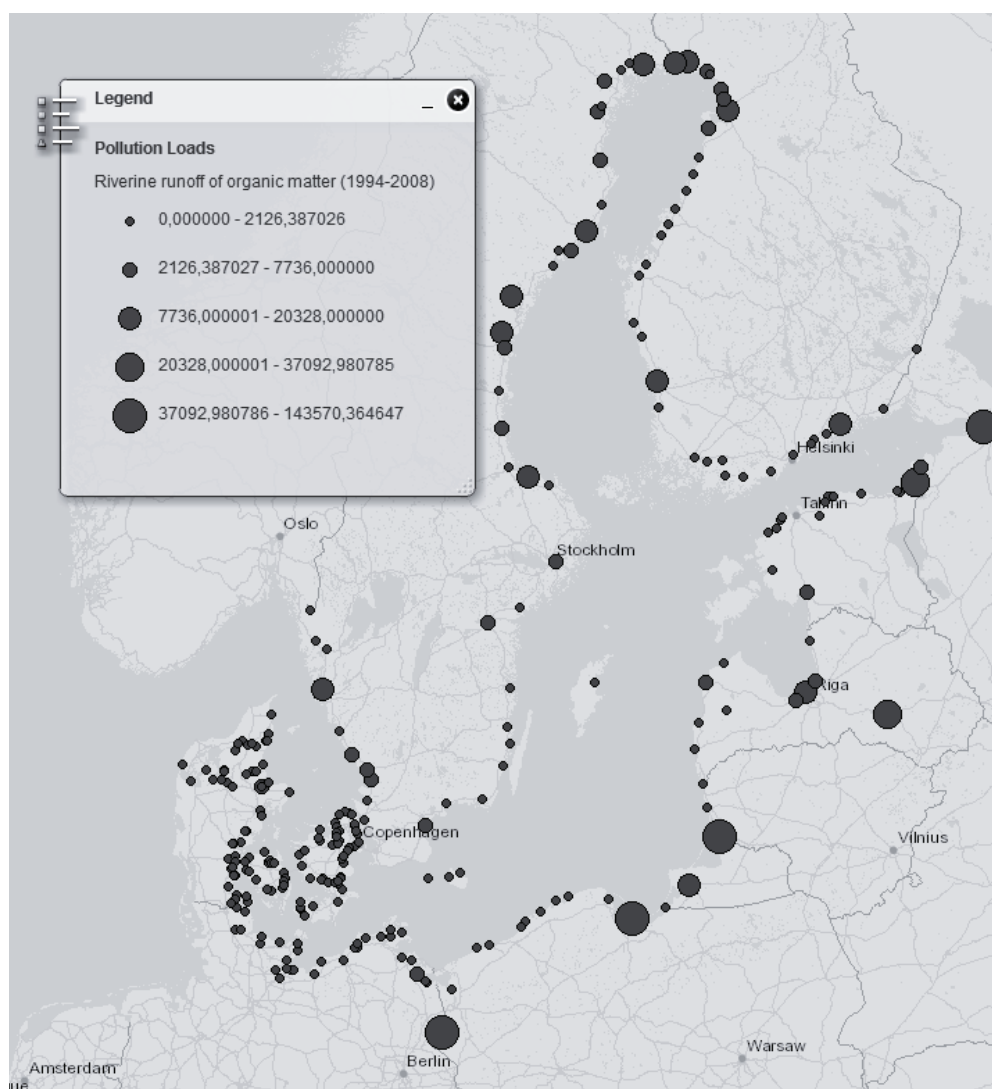
Fig. 1. Riverine pollution loads (containing land-based oil products) in the Baltic Sea (HELCOM, 2014, data from 1994-2008)

Oil products have the ability to fluoresce in the range from ultraviolet to infrared. The possibility of using fluorescence to detect and identify crude oil was reported in the early 1970's. Currently oil pollution in seawater is examined using methods based on aromatic hydrocarbon fluorescence measurements, e.g. [2, 7, 8], however, it is monitored irregularly regarding time and space [10].

2. Material and method

Seawater samples were collected in Southern Baltic Sea during several ship cruises in 2012 on-board r/v Oceania from the Institute of Oceanology of Polish Academy of Sciences (Fig. 3). Three stations, P104, ZN2c and ZN2 represent the region of the Gulf of Gdansk. Four other stations, P15, P16, W1 and W2 are placed in the near-shore and coastal area.

Reference samples were prepared in the form of crude oil solutions in n-hexane in the volume concentration of 5 ml/l. Three types of crude oil were used as reference oil products:

a) *Petrobaltic* (PB) extracted offshore in the Southern Baltic in the Polish Exclusive Economic Zone (EEZ),

b) *Romashkino* (RU) extracted onshore in Tatarstan, Russia,

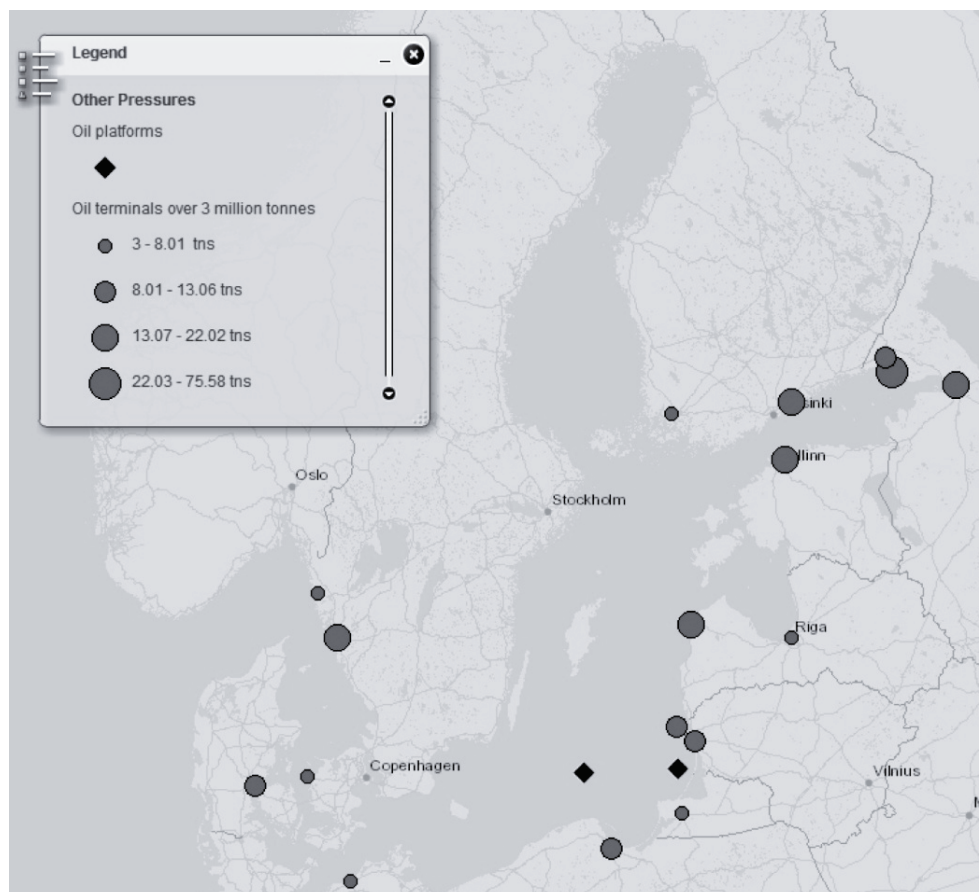c) *Flotta* (FL) extracted offshore in the North Sea in British EEZ.

Fig. 2. Oil pollution endangered areas on the Baltic Sea: main oil terminals and their volumes and oil rigs (HELCOM, 2014)

2.1. Filtering and extraction of samples

A part of each sample was extracted in n-hexane, using 15 ml of n-hexane for 1200 ml of seawater. After extraction all samples were shaken for 20 min on laboratory shaker 358S and stabilized for 24 hours in room temperature.

Another part of samples were filtered using vacuum filtering system with a qualitative fast-flow cellulose filter, called hereafter "standard filter" (FS), with the permeability in the range of 7-12 µm (Macherey-Nagel GmbH, MN 617). Then the filters were extracted in n-hexane using the same proportions as for unfiltered samples (U), shaken and stabilized alike.

2.2. Fluorescence measurements

Determination of hydrocarbon content in these samples was carried out using comparative fluorescence method [11] on spectrofluorometer Shimadzu RF-5301PC. All samples were excited separately by single light wavelength of 260 nm, and the emission of fluorescence signal was measured in the range of 270-600 nm.

3. Results

The intensity of fluorescence signal carries the information about the concentration of a substance extracted in a solvent. Although many substances show linear correlation between fluorescence intensity and concentration, this correlation usually works only for a certain range of concentrations, for specific excitation-emission wavelengths and is unique for every compound. It is relatively easy to search for such correlations for simple chemical compounds; however,

it becomes more laborious for complex chemical structures. Crude oil is a mixture of many kinds of hydrocarbons, including polycyclic aromatic hydrocarbons (PAHs), and characteristic admixtures. Their complexity requires a profound study of every type of crude oil in order to understand the process of fluorescence and to apply the knowledge in oil pollution sensing.
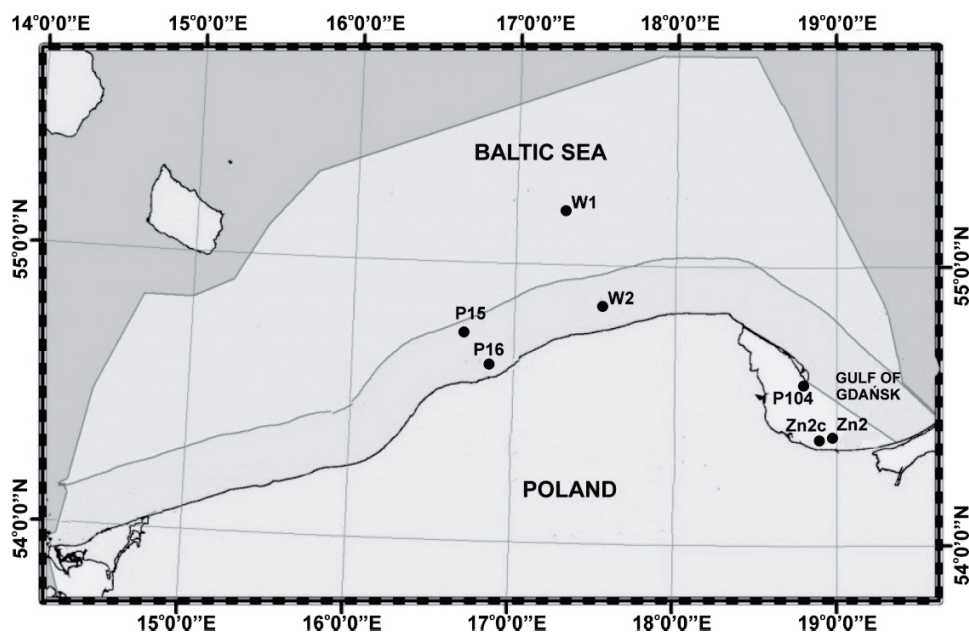

Fig. 3. Map of stations for sample collection in the Gulf of Gdansk

The shape of fluorescence spectra contains the cumulative information about the types of hydrocarbons included in a specific crude oil. However, it has to be noted that chemically different hydrocarbons may have similar fluorescence properties, therefore comparison of the shape of fluorescence spectra do not always allow us to distinguish between crude oils. Nevertheless, this method still deliver useful information about the type of oil which in correlation with other data can be crucial for optical detection of oil.

In this section, we present fluorescence spectra collected for natural seawater samples. Spectra registered for the filters are marked by FS, and spectra registered for the filtrates are marked by P. A representative range of fluorescence intensities and shapes for filters and filtrates is shown in the Fig. 4. The comparison of collected spectra to the spectra of reference crude oils is presented in the Fig. 5.
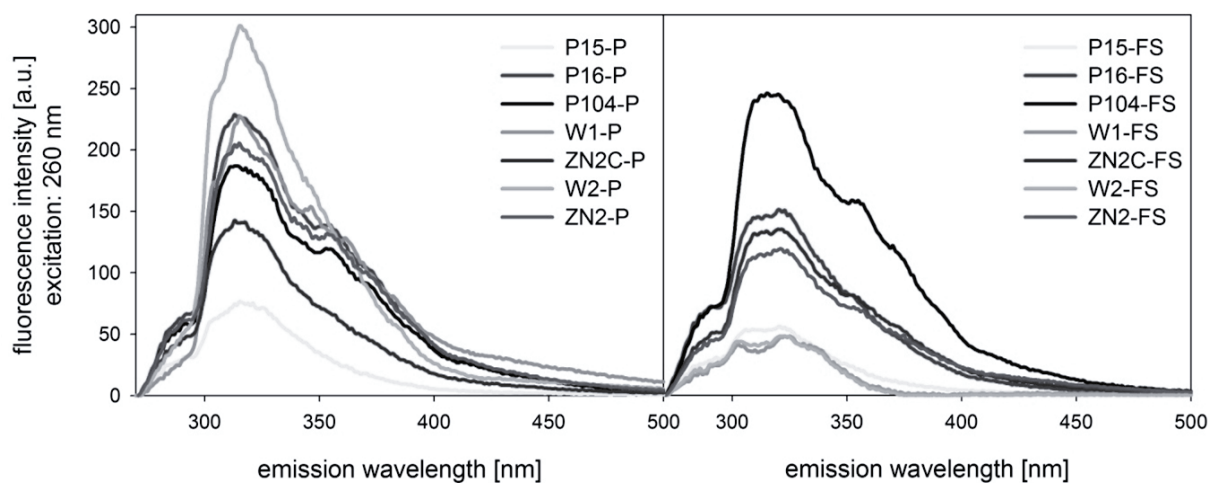

Fig.4.   Examples of fluorescence spectra of extracted filters (FS) and filtrates (P) obtained from natural seawater samples collected in the Southern Baltic Sea
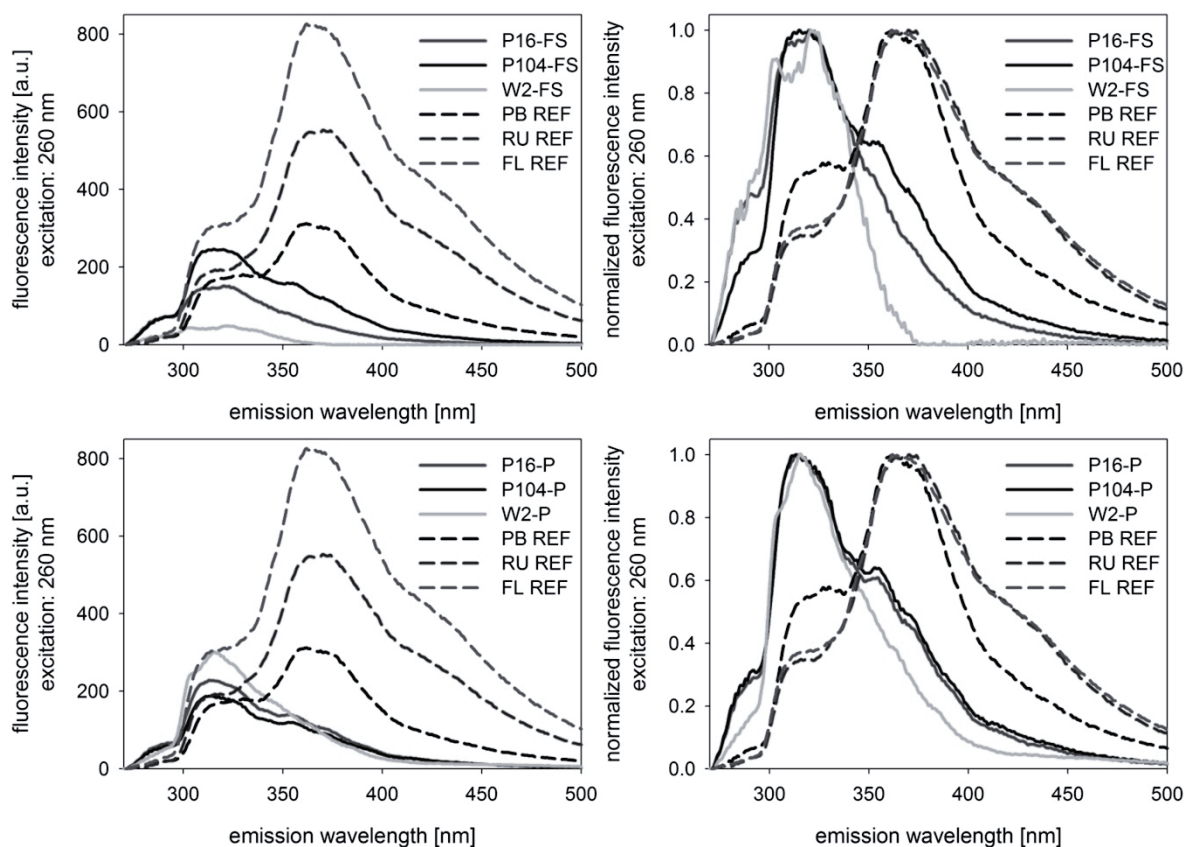
Fig. 5. Upper graphs: Comparison of fluorescence spectra obtained for extracted filters FS to reference crude oil extracts: Petrobaltic (PB REF), Romashkino (RU REF) and Flotta (FL REF), Lower graphs: Comparison of fluorescence spectra obtained for filtrates P to reference crude oil extracts

4. Discussion

The comparison of different parameters of fluorescence spectra for seawater samples and reference samples allows us to find and understand the correlations between them and to apply these correlations in algorithms and models for determination of oil type and concentration in any sample. Concentration of fluorescent hydrocarbons present in oil products was proved linearly proportional to fluorescence intensity for relatively low concentrations [11]. We observed the highest concentration on the filter for station P104 and in the filtrate for station W2.

Vacuum filtering was applied to seawater samples in order to separate the signal from large oil particles and coagulates from smaller particles. Applied filter FS showed the best concentration correlation in another study [4]. Stations W1 and W2 are the examples of small oil droplets domination, while station P104 shows the opposite situation.

Spectra of seawater samples show the content of oil products with different hydrocarbon composition than reference crude oils (see Fig. 5). This may be caused simply by the presence of another type of oil or by the processes of weathering of crude oils including volatilization, photo-oxidation and solution of lower molecular weight components. Fluorescence spectrum of the filters from stations W1 and W2 have a remarkable double-peak shape, different from other stations. This can be caused by the input of different type of hydrocarbons from the nearby harbour or ship origin pollution.

Stations P15 and P16 represent respectively the far-shore coastal area and the near-shore coastal area. Oil concentration is typically lower when we increase the distance from the seashore, both for the filters and filtrates. By comparison, of the intensity of their fluorescence spectra we can see that both samples contain similar proportion of large and small oil particles, and small particles predominate, which is typical for the stable coastal regions, not affected directly by fresh waters inflow.

5. Summary

In the presented study, we collected and analysed a unique set of fluorescence spectra for natural seawater samples. Although the method is time consuming and labour intensive, it still delivers valuable and irreplaceable data. While we are trying to improve *in situ* fluorescence techniques and increase the sensitivity of remote oil detection, collection of point data of seawater remains priceless. Application of vacuum filtering improves the time and extraction efficiency.

Acknowledgements

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