

FLUORESCENCE PROPERTIES OF MECHANICALLY DISPERSED CRUDE OIL

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Abstract

Despite of numerous actions undertook by the global and local authorities towards protection of marine environment, oil pollution loads into the Baltic Sea still tend to increase and need to be continuously estimated in order to apply the legal regulations. There is a demand for multifarious studies on the environmental effects of oil products. 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. Oil content influences many environmental factors, like water quality and bio-optical parameters (e.g. water-leaving radiance, inherent optical properties, seawater fluorescence).

We present a unique study of the collected database of crude oil fluorescence spectra for better understanding the correlations between oil optical properties and its concentration, as well as for evaluation of the oil droplets size by the application of vacuum filtering using three filters of different permeability. Fluorescence spectra have been registered for oil-in-water emulsion samples prepared in the laboratory by mechanical dispersion. We discuss the optical properties of crude oil and the relationships between them in the context of potential remote detection of dispersed oil in seawater.

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

1. Introduction

Growing pollution loads into the Baltic Sea created a demand for multifarious studies on the environmental effects of oil products. The statistics show that yearly oil input to the Baltic Sea is in the range from several to several dozen thousands of tons [6]. Baltic Sea is considered to be one of the most ship-crowded areas covering about 15% of the world's marine traffic. It was estimated that at any moment it carries about 2000 ships, including c.a. 200 tankers transporting crude oil and other liquids. There is currently over 40 oil terminals on the Baltic Sea and their number is growing [7]. The map below shows the most oil pollution endangered regions in the Baltic Sea due to the high marine traffic (Fig. 1).

Oil is a luminescent medium which fluoresces in the range from ultraviolet (UV) to near infrared (NIR), including Photosynthetically Active Radiation (PAR) in the range of 400-700 nm. Oil products also absorb electromagnetic radiation in the range from UV to NIR. Crude oil is a complex mixture of paraffinic, naphthenic, aromatic and asphaltic hydrocarbons and admixtures such as minerals and salts [11, 13]. Crudes can be classified as "light" or "heavy", depending on the density parameter called American Petroleum Institute (API) gravity [1].

Optical properties of oil are important to investigate because optical methods in comparison with chemical analyses are generally less costly, much faster, sufficiently sensitive, and easy to apply both, in the laboratory and in field measurements [4, 9]. Moreover, optical methods are currently applied in remote detection of oil slicks and expected to enable remote detection of dispersed oil [8, 12]. Optical properties of oil-in-water emulsions depend on oil type, concentration and size distribution.

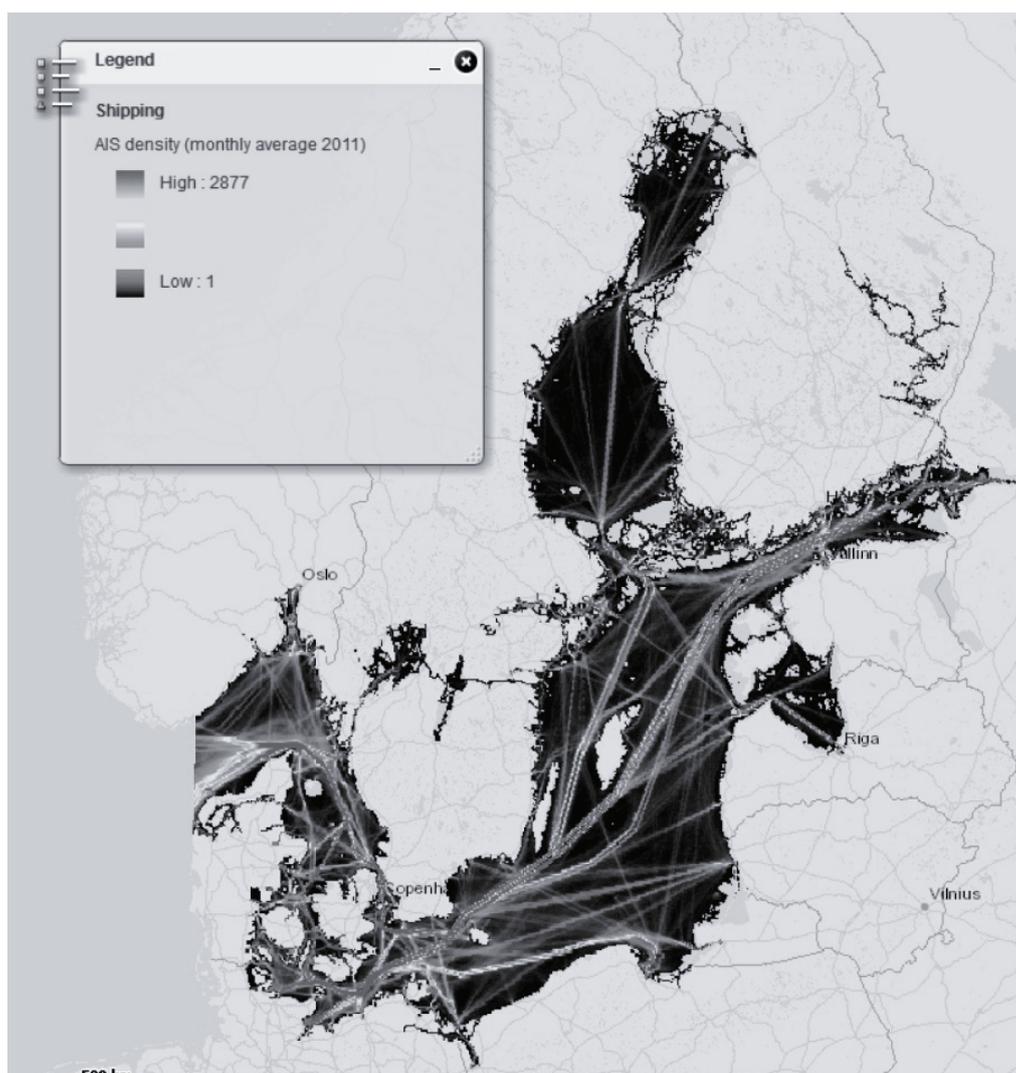


Fig. 1. Oil pollution endangered areas on the Baltic Sea: tanker traffic, main oil terminals and their volumes (1997-2002) and oil rigs

2. Material and method

Three types of crude oil were used as reference oil products:

- 1) *Petrobaltic* (PB) extracted offshore in the Southern Baltic in the Polish Exclusive Economic Zone (EEZ),
- 2) *Romashkino* (RU) extracted onshore in Tatarstan, Russia,
- 3) *Flotta* (FL) extracted offshore in the North Sea in British EEZ.

Reference samples were prepared in the form of crude oil solutions in n-hexane in volume concentrations of 1, 5, 10 and 15 mg/l.

2.1. Preparation of oil emulsions

Laboratory samples of mechanically dispersed oil-in-water emulsions were prepared in the laboratory in several-step experiment. First, reference crude oils were homogenized in demineralised water in the volume concentration of $(2 \pm 0.3)10^3$ mg/l using a laboratory homogenizer MPW-120 (run parameters: time – 10 min, rotation speed – 10.000/s). This procedure allowed us to obtain stable oil-in-water emulsions which were stored in glass bottles. We observed that not all amount of added crude oil emulsified, some sediment was visible on the inside of bottles. The sediment was made mostly of crude oil impurities and was estimated to no

more than 5% of the total crude oil concentration. Then the emulsions were diluted in demineralised water to the final volume concentrations of 1, 5, 10 and 15 ml/l. Total maximal uncertainty of the volume concentration of oil-in-water emulsion due to sampling procedure and sedimentation was no more than 19%.

2.2. Filtering and extraction of samples

A part of each sample was extracted in n-hexane, using 15 ml of n-hexane for 800 ml of laboratory sample. After extraction all samples were shaken for 20 min on laboratory shaker 358S and stabilized for 24 hours in room temperature.

Another parts of available samples were filtered using vacuum filtering system with different cellulose filters of permeability 0.45 μm (F45), 0.80 μm (F80) (CHEMLAND Poland) and a standard qualitative fast-flow 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.

2.3. Fluorescence measurements

Determination of hydrocarbon content in these samples was carried out using comparative fluorescence method [5, 10] on Hitachi F-7000 FL Spectrophotometer. All samples were excited separately by single light wavelengths of 240 nm, 260 nm, 280 nm and 320 nm, and the emission of fluorescence signal was measured in the range from excitation wavelength plus 10 nm to 600 nm.

3. Results

The parameters of fluorescence spectra carry the information about the type and concentration of a substance extracted in a solvent [3]. It is relatively easy to search for linear correlations between these parameters for simple chemical compounds; however it becomes more laborious for complex chemical structures. Crude oil is a mixture of various kinds of aromatic and aliphatic hydrocarbons characterized by different fluorescence properties. The complexity of crude oil composition AND chemical structure 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 [2]. Nevertheless, this method still delivers useful information about the type of oil which in correlation with other data can be crucial for optical detection of oil [5].

Laboratory samples were investigated for better understanding of fluorescence properties of specific crude oils. Below, we present representative fluorescence spectra collected for various combinations of three factors (Fig. 2):

- crude oil type: *Petrobaltic* (PB), *Romashkino* (RU), *Flotta* (FL),
- volume concentration of oil-in-water emulsion: 1, 5, 10, 15 ml/l,
- application of vacuum filtering: unfiltered (U) and filtered (F) oil-in-water emulsion samples.

4. Discussion

Comparison of different parameters of fluorescence spectra for 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. In the graph below we present a representative analysis of correlation between integral fluorescence and crude oil concentration (Fig. 3).

Integral fluorescence is a widely used parameter in concentration estimation. In our study we obtained the best linearity for the excitation wavelength 320 nm. This result encourages us to search a better linear correlation for even higher excitation wavelengths in future experiments.

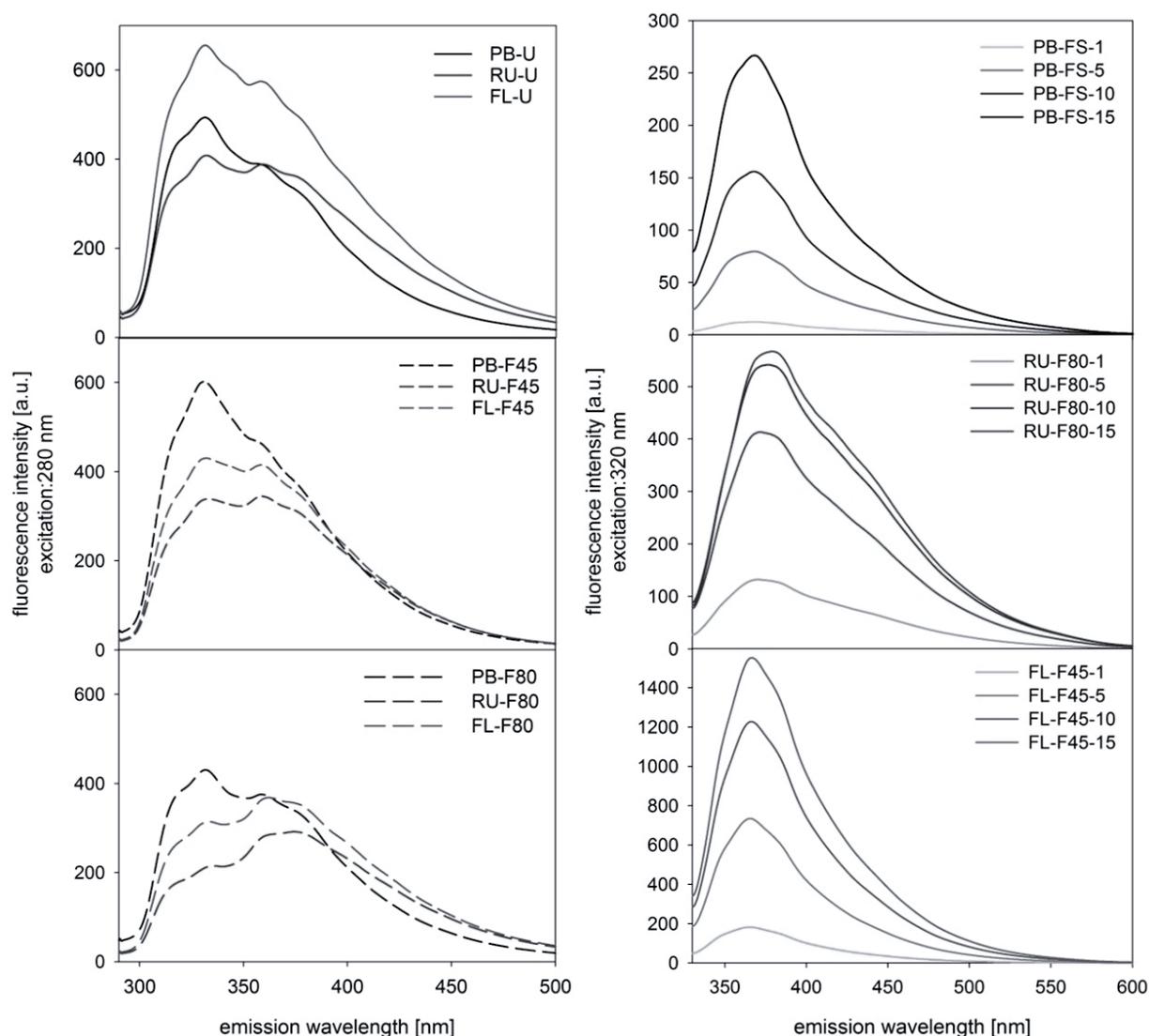


Fig. 2. Left graph: Fluorescence spectra for different crude oils at the same concentration of 1 ml/l: Petrobaltic (PB), Romashkino (RU) and Flotta (FL) obtained for unfiltered samples (U) and for samples filtered using 0.45 μm filter (F45) and 0.80 μm filter (F80). Right graph: Fluorescence spectra for different concentrations of crude oils (marked by a number of ml/l) obtained for samples filtered using standard filter (FS), 0.80 μm filter (F80) and 0.45 μm filter (F45)

In the whole experiments two sources of uncertainties were taken into account:

- 1) Single measurement uncertainty (due to sample preparation; see § 2.1.) stayed within 10% for the concentration of 10 ml/l. To minimize it we recommend analysing the summed integral fluorescence for all four excitation wavelengths instead of single spectra. This allowed us to reduce the uncertainty to 3.5%,
- 2) Fluorimeter uncertainty stayed within 4% for all samples.

4.1. Type of crude oil

Petrobaltic, as the representative of light crudes, has a different shape of fluorescence spectrum than heavy crudes *Romashkino* and *Flotta*. Although the similar shape of *Romashkino* and *Flotta* suggest similar hydrocarbon composition, the differences in signal intensity show that their proportions are different. Therefore, gathering of a large database of fluorescence properties of fresh and weathered oil products is crucial for proper oil type detection.

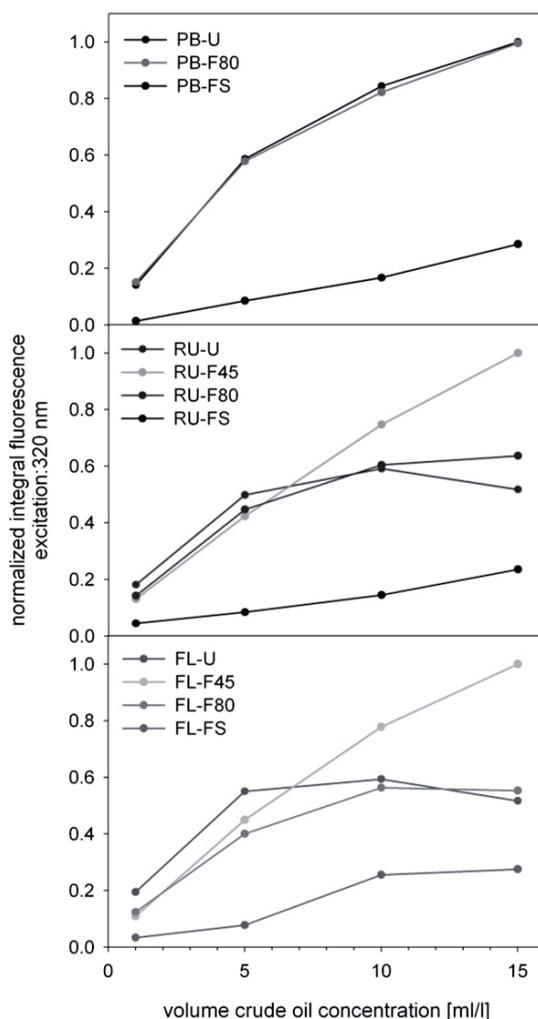


Fig. 3. Concentration dependence of unfiltered (U) and filtered (F) laboratory samples

4.2. Concentration dependence

Finding a linear correlation between crude oil concentration and a parameter of fluorescence spectra is very important for future determination of crude oil concentration in natural samples. In our experiment, the best concentration correlation was obtained for the excitation wavelength of 320 nm and for *Petrobaltic* crude oil. Lower excitation wavelength tend to correlate linearly only in a small range of crude oil concentrations (usually smaller than 10 ml/l). Due to crude oil chemical complexity, slopes and linear correlation coefficients are unique for every type of oil and they may also vary in time of oil exposure to atmospheric conditions.

Considering unfiltered oil emulsion samples good correlation was obtained only for *Petrobaltic* crude oil. Fluorescence signal for *Romashkino* and *Flotta* increased non-linearly up to 10 ml/l and then decreased for 15 ml/l. There is a need to perform a further experiment involving more crude oil concentrations in order to model those correlations mathematically. Observed non-linearity for unfiltered emulsion samples may be caused by the shift of the local maximum fluorescence intensity, which would be visible on the total excitation-emission matrix. It can be also caused by limited ability of emulsified oil to bond to the applied solvent. Further experiments will enable correct interpretation.

4.3. Application of vacuum filtering

Vacuum filtering was applied to laboratory samples in order to examine the new method designed to simplify the whole measurement process. We collected and compared fluorescence

spectra for unfiltered oil emulsions as well as oil emulsions filtered using three filters of different permeability (see § 2.2). The best concentration correlation was observed on standard filter FS for all applied excitation wavelengths, although the fluorescence signal was very low due to relatively large filter pores. A good correlation and a high signal were obtained for the filter F45, though only for the excitation wavelength of 320 nm. Filter F80 gave slightly better than unfiltered samples, however still non-linear results.

We observed that the vacuum filtering technique improves the crude oil – hexane extraction efficiency. It was estimated to increase for up to 40% for the concentration of 1 ml/l for all crude oils. At the concentration of 15 ml/l the extraction efficiency doubled for *Petrobaltic*, increased 6-fold for *Romashkino* and *Flotta* by the use of filters FS and F80 and 12-fold using filter F45.

The filter FS is supposed to contain only the largest oil particles and coagulates. The fluorescence signal of oil extracted on FS can be therefore a good measure of high concentrations of crude oils as well as samples containing weathered crude oil which tends to coagulate. Moreover, we find it worthy of examination to use FS as a first filter in a multistep filtering sample preparation process. Then possibly application of next filters, e.g. F80 and F45 would improve the linearity of concentration correlation and allow estimating the proportions of droplets of different size in the sample.

5. Summary

In the presented study we collected and analysed a unique set of fluorescence spectra for samples of oil-in-water emulsion prepared in the laboratory by mechanical dispersion. Oil in the form of dispersed droplets is most likely to be found in natural seawater, especially in estuarine and coastal areas. Oil emulsions were prepared for three different crude oils in four concentrations. Fluorescence method was applied to examine the correlations between the type and concentration of oil, and spectral parameters both for unfiltered samples and samples filtered using three filters of different permeability. This multistep experiment enriched our database of crude oil fluorescence properties and showed the direction for future investigations. We find it useful to apply vacuum filtering for the analyses of emulsified oil samples. Filtration process significantly increases extraction efficiency and allows gathering more information about the size structure of oil emulsion. This knowledge can be then applied in analysis of natural water samples and field measurements of oil pollution.

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