Article

Seawater Fluorescence Near Oil Occurrence

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Abstract: Petroleum and its related products pose a serious pollution risk to the world’s seas and require a simple, rapid detection method. This is a difficult task if the pollution is under the water surface. One common approach to oil detection is excitation-emission spectroscopy (EEMs) of seawater exposed to oil for analyzing the fluorometric index (Fl_o/w) as a potential indicator of oil presence in the marine environment. In this paper, Fl_o/w was determined for both natural seawater and samples of the same water, but exposed to a relatively small portion of oil. The water samples were collected from the coastal and port waters of the Gdynia region (Southern Baltic Sea) from five stations, four times at two-week intervals. Fl_o/w indicates the changes between seawater sampled from the marine environment and the same seawater polluted with oil substances. Moreover, the obtained Fl_o/w values do not depend on the point and time of sampling. In all cases of seawater exposed to oil, significantly higher Fl_o/w values were observed than for unpolluted seawater. Moreover, the detection of oil by analyzing the value of Fl_o/w is efficient if the oil-to-water weight ratio is close to or above 5 × 10^{-6}.

Keywords: oil in seawater; oil fluorescence; oil detection; seawater fluorescence; excitation-emission spectra; fluorometric index

1. Introduction

Oil pollution can enter marine waters from various sources, such as stormwater drainage from cities, untreated waste disposal from factories and industrial facilities, as well as unregulated recreational boating, onshore air pollution or natural seeps and by the heavy traffic in marine transport. The challenge is the prevention, detection, and removal of spills [1]. The ability to detect oil in the aquatic environment depends on the oil form and weathering state, the amount of oil in seawater and the spatial scale of the oil spill. When oil is visible on the surface of seawater, space-borne remote sensing detection, or airborne detection [2,3] are the most effective methods to assess the scale of the spillage. The advantage of remote sensing is the ability to observe events in remote and often inaccessible areas such as oil spills from ruptured pipelines. Moreover, remote sensing data through multi-temporal imaging allow obtaining information about the oil movement rate and direction, which is crucial in oil spill control. Remote sensing is based on a wide range of devices such as infrared video, photography from airborne platforms, thermal infrared imaging, and laser fluorosensors. In oil spill detection, airborne or space-born optical sensors are useful. After a very large oil spill in the Gulf of Mexico in 2010, various space-borne remote sensors were tested as possibly suitable for oil pollution detection and oil slick tracking [4–8]. However, during darkness and under poor weather conditions, only Synthetic Aperture Radar (SAR) is reliable [2,9].

When oil is invisible in an optical range, there is a broad spectrum of methods available for oil detection, such as ultraviolet, infrared or Raman spectroscopy [1,10,11] and sensitive methods based on fluorescence phenomenon [12,13]. Submersed oil (for example, oil-in-water emulsions) to a small extent manifests itself in the above-water upward radiance field, although detection is possible under certain lighting and weather conditions [14] or using underwater sensors [15].
Fluorescence spectroscopy also seems to be a sensitive method to study the complex structure of hydrocarbons with aromatic compounds responsible for oil fluorescence. However, seawater exhibits its own fluorescence spectra due to the presence of natural seawater components, referred to as Dissolved Organic Matter (DOM) [16], Fluorescent Dissolved Organic Matter (FDOM) [17], Coloured Dissolved Organic Matter (CDOM) [18,19], phytoplankton [20] and pigments [21]. It was found that the fluorescent properties of seawater in the ultraviolet (UV) range change after contact with even a small amount of oil. The fact that the shape of the spectra of seawater fluorescence changes after contact with oil has already been demonstrated [13] in studies of the ultraviolet field (excitation from 200 to 340 nm, emission 240–500 nm). Thus, the problem to be solved now is how to identify water that has been in contact with oil, based on fluorescence spectra.

The research described in this paper involves situations in which oil appears in the marine environment, but visual perception is unlikely. The oil may be invisible when it enters the water in small amounts but can become a threat over time. These events can occur, for example, in the case of unsealing underwater pipes [22], oil leaking during port trans-shipment [23], or leaks from wrecks [24,25]. Fuel leaks or lubricating oil from ships cannot be ruled out even if they operate faultlessly, or when a failure was not noticed by the ship’s crew. In some parts of the sea, there may be natural seepage from the bottom of the sea [26–28].

The paper reports on a study of the effectiveness of fluorometric index \( (FI_o/w) \) for water sampled from the sea at different points sampled several times in the warm season. It is, therefore, a continuation and extension of the authors’ previous paper [29] that includes water from only one place. In the present paper reports on a study extracted from excitation-emission fluorescence matrix spectra (EEMs), fluorometric index \( (FI_o/w) \) for water sampled from the sea in five stations located along the coastal and port waters of the Gdynia region (Southern Baltic Sea) collected at four times in summer season (June and July) in this area.

2. Materials and Methods

2.1. Seawater Sampling and Combining with Oil

Seawater samples were taken at the seaside (near Gdynia Port, Gulf of Gdansk in the Southern Baltic Sea, Poland) and in two points of the Port of Gdynia (Figure 1a). Seawater samples were collected from a 1 m depth into 1-L glass bottles, four times every two weeks in June and July (warm summer season): at the beginning of June \( (T = 10.7 \, ^\circ C \) and salinity 7.2 PSU), the middle of June \( (T = 14.6 \, ^\circ C \) and salinity 7.4 PSU), the end of June \( (T = 15.9 \, ^\circ C \) and salinity 7.2 PSU) and the middle of July \( (T = 16.1 \, ^\circ C \) and salinity 7.0 PSU). For the test, the warm summer season was selected due to the high content of phytoplankton and blooms of cyanobacteria (usually observed in June, July, and August when the temperature of the Baltic Sea is the highest, about 17–20 °C). The components could have a significant influence on the oil fluorescence in seawater due to the fluorescence of oil being partially covered in an area where chlorophyll or Colored Dissolved Organic Matter strongly absorbs light radiation [13,30–32]. Moreover, the presence of individual species of cyanobacteria may affect the succession of phytoplankton in the aquatic environment [33].

Crude oil Petrobaltic extracted from the Baltic Sea shelf (light crude, with American Petroleum Institute (API) gravity 43–44° and sulfur content 0.12%) was used as material for the laboratory contamination of seawater. A small droplet of oil was placed on a slice of aluminum foil and was then weighed and inserted into a seawater sample (Figure 1b) to reach the desired oil-to-water ratio \( (r_o/w) \) —explains the ratio of weighted oil to a certain amount of seawater. Six samples polluted by oil with an oil-to-water ratio \( (r_o/w) \) in the range of \( 0.5 \times 10^{-6} \) to \( 500 \times 10^{-6} \) were prepared (the use of the unit “ppm” has been abandoned because the actual concentration of oil substances that have passed into the oil is unknown). The studied seawater before fluorescence measurements was exposed to the added oil for one day.
2.2. Measurements

A Hitachi F-7000 spectrofluorometer was used to determine the excitation-emission spectra (EEMs). Measurements were performed for excitation wavelengths ranging from 200 nm to 480 nm with an excitation sampling interval of 5 nm, whereas the emission wavelengths were changed from 260 nm to 700 nm with an emission sampling interval of 5 nm. The excitation slit was established as 10 nm, the emission slit 10 nm, the integration time 0.5 s, and the photomultiplier tube voltage was 400 V.

The EEMs were determined for seawater sampled from the sea environment and seawater exposed to Petrobaltic-type crude oil for various oil-to-water ratios. Measurements were performed at a stabilized temperature of 20 °C. Rayleigh scattering to yield a digital matrix of EEMs was removed (if the excitation wavelength and emission wavelengths were equal, and the emission wavelength was two times higher than the excitation wavelength).

3. Results and Discussion

3.1. Fluorometric Index (FI) Determination Procedure Using EEMs of the Seawater before and after Combining with Oil

The EEM spectra were determined for natural seawater and oil-polluted seawater samples for several oil-to-water ratios: 0.5 × 10⁻⁶, 5 × 10⁻⁶, 50 × 10⁻⁶ and 500 × 10⁻⁶ from five stations at four sampling times in June and July. Figure 2 presents examples of EEMs for natural seawater samples at five stations (Figure 2a) and polluted by oil for an oil-to-water ratio of 50 × 10⁻⁶ (Figure 2b) in the middle of July. The EEM spectra of natural seawater in Figure 2a indicates the presence of the main peak in the UV-range positioned at an excitation wavelength from 200 nm to 280 nm (centered at 225 nm) corresponding to an emission wavelength from 300 nm to 450 nm centered at 355 nm (see Table 1). The detected peaks are well-linked to the tryptophan-like seawater component [30]. The position of the main peak at 355 nm in natural seawater was determined for five stations at four sampling times, and the peaks ranged from 350 nm to 360 nm except for one sample from at the end of June—whose peak was centered at 390 nm. In Figure 2, it is visible that the EEMs of natural seawater changes when oil is present in natural seawater. In the EEMs of seawater polluted by oil (Figure 2b), the main peak centered at 340 nm for the emission wavelength corresponds to the excitation wavelength at 225 nm (see Table 1) for all analyzed stations. Moreover, the position of the peak at 340 nm for polluted seawater was also determined for five stations at four sampling times.
Figure 2. Examples of normalized EEM spectra of natural seawater samples (a) and the same samples polluted by oil for an oil-to-water ratio of $50 \times 10^{-6}$ (b) in five stations indicated in Figure 1a in the middle of July.
Table 1. Major fluorescent peaks of natural seawater and the same samples polluted by oil for an oil-to-water ratio of $50 \times 10^{-6}$ with their wavelength-independent maxima for five stations (numbered as in Figure 1a) in the middle of July.

| Station | $E_{\text{max}}$ [nm] ± (5 nm) | $E_{\text{max}}$ [nm] ± (5 nm) |
|---------|-------------------------------|-------------------------------|
| #1      | 225/355                       | 225/340                       |
| #2      | 225/350                       | 225/340                       |
| #3      | 225/350                       | 272.5/335                    |
| #4      | 225/350                       | 225/340                       |
| #5      | 225/360                       | 225/340                       |

The position of peaks in EEMs caused by the presence of oil in the natural seawater is significant to detect the presence of oil in the sampling area. However, taking into account the need to detect oil quickly and easily, a better solution would be to find a sensitive indicator of the presence of oil in a defined sea area, which could be used to construct a specialized fluorosensor. Based on EEMs of natural seawater and seawater polluted by oil, a fluorometric index $FI_{o/w}$ was proposed, which uses a specific wavelength for both natural unpolluted seawater and the same seawater but having contact with oil [29]. Formula (1) described the $FI_{o/w}$ definition as the quotient of the fluorescence intensity at the emission wavelength for seawater polluted by oil to the intensity at the emission wavelength for natural seawater corresponding to the detected excitation maxima for both natural seawater and seawater polluted by oil.

$$FI_{o/w} = \left[ \frac{I(\lambda_{\text{Emission of seawater polluted by oil}})}{I(\lambda_{\text{Emission of natural seawater}})} \right]_{\lambda_{\text{Excitation}}}$$

(1)

The specific excitation and emission wavelengths for $FI_{o/w}$ definition were selected based on the EEMs of natural seawater and seawater polluted by oil (see Figure 3). The main peaks detected for the same excitation wavelength at 225 nm (the red line in Figure 3) correspond to the emission wavelengths for these peaks detected for natural seawater at 350 nm (the green line in Figure 3) and seawater polluted by oil at 340 nm, respectively (the purple line in Figure 3). Therefore, $FI_{o/w}$ was calculated as the quotient of the fluorescence intensity at a 340 nm emission wavelength and the intensity at 355 nm, while the excitation wavelength remained equal to 225 nm (Formula (2)).

$$FI_{o/w} = \left[ \frac{I(\lambda_{\text{Em}=340})}{I(\lambda_{\text{Em}=355})} \right]_{\lambda_{\text{Ex}=225}}$$

(2)

where $I(\lambda_{\text{Em}=340})$ describes the fluorescence intensity corresponding to the emission wavelength for polluted seawater (340 nm) and $I(\lambda_{\text{Em}=355})$ describes the fluorescence intensity corresponding to the emission wavelength for natural seawater (355 nm) linked to the same excitation wavelength ($\lambda_{\text{Ex}=225}$) for both kinds of seawater (225 nm).

3.2. Fluorometric Index of Different Origin Sea Waters

Using Formula (2), $FI_{o/w}$ was calculated for natural seawater and seawater contaminated by oil from all stations in the considered time and for all oil-to-water ratios. The non-normalized data of EEM spectra of natural seawater and seawater polluted by crude oil were used for calculations. The results of $FI_{o/w}$ calculations are presented in Table 2 for natural seawater and in Table 3 for seawater polluted by oil (for chosen oil-to-water ratio equal to $50 \times 10^{-6}$) from all stations at different times. Moreover, the results for several oil-to-water ratios for seawater contaminated by oil for the selected station #1 at four different times are presented in Table 4. $FI_{o/w}$ values for polluted seawater achieved higher values above 1 (about 1.4) than for natural seawater below 1 (about 0.93). This creates an easy way to
accurately identify seawater pollution. Moreover, $FI_{o/w}$ values do not depend on the time of sampling, and $FI_{o/w}$ is independent of the oil concentration.

**Figure 3.** EEM spectra for natural seawater from the station (#1) (a) at the beginning of June and the same seawater contaminated by oil for an oil-to-water ratio of $50 \times 10^{-6}$ (b).

**Table 2.** Fluorometric index ($FI_{o/w}$) calculated by formula 2 for uncontaminated seawater.

| Station | Date              | $FI_{o/w}$ [-] |
|---------|-------------------|----------------|
| #1      | Beginning of June | 0.90           |
| #2      | Middle of June    | 0.93           |
| #3      | End of June       | 0.91           |
| #4      | Middle of July    | 0.94           |
| #5      |                   |                |

**Table 3.** Fluorometric index ($FI_{o/w}$) calculated by formula 2 for seawater from five sampling stations taken at different times and contaminated by oil for an oil-to-water ratio of $50 \times 10^{-6}$.

| Station | Date              | $FI_{o/w}$ [-] |
|---------|-------------------|----------------|
| #1      | Beginning of June | 1.42           |
| #2      | Middle of June    | 1.33           |
| #3      | End of June       | 1.37           |
| #4      | Middle of July    | 1.42           |
| #5      |                   |                |

**Table 4.** Fluorometric index ($FI_{o/w}$) calculated by formula 2 when seawater was sampled at station #1 contaminated by oil for different oil-to-water ratios.

| $r_{o/w}$  | Beginning of June | Middle of June | End of June | Middle of July |
|------------|-------------------|----------------|-------------|----------------|
| $0.5 \times 10^{-6}$ | 1.33           | 1.18           | 1.09        | 1.27           |
| $5 \times 10^{-6}$  | 1.39           | 1.26           | 1.38        | 1.32           |
| $50 \times 10^{-6}$ | 1.42           | 1.33           | 1.37        | 1.42           |
| $500 \times 10^{-6}$ | 1.41           | 1.37           | 1.39        | 1.40           |
In each case, the amount of contaminant in relation to water was 5:100,000 (r<sub>o/w</sub> = 50 × 10<sup>-6</sup>). The average FI<sub>o/w</sub> value for natural water was 0.925 (standard deviation 0.023), while for contaminated water, it was 1.381 (standard deviation 0.044).

### 3.3. Fluorometric Index Compared to the Degree of Contamination

The results of the test described in Section 3.2 indicate that the value of FI<sub>o/w</sub> shows whether the water is in contact with oil contamination. To determine to what extent the amount of oil pollution affects the possibility of its detection based on the FI<sub>o/w</sub> value, tests were carried out for seawater collected at sampling point #1 (the end of the pier in Orłowo) at four different times contaminated by oil with an oil-to-water ratio r<sub>o/w</sub> from 0.5 × 10<sup>-6</sup> to 500 × 10<sup>-6</sup>. The results are presented in Figure 4. A distinct increase in FI<sub>o/w</sub> already exists for r<sub>o/w</sub> = 0.5 × 10<sup>-6</sup>. Beginning with r<sub>o/w</sub> = 0.5 × 10<sup>-6</sup>, the FI<sub>o/w</sub> value ceases to depend on r<sub>o/w</sub> (stabilizes at the level closed to 1.4).

![Figure 4](image)

**Figure 4.** Value of fluorometric index FI<sub>o/w</sub> for seawater exposed to various amounts of oil for various sampling dates. The internal graph shows FI<sub>o/w</sub> for only small r<sub>o/w</sub> values with a stretched scale. The letter U indicates the values of the index for uncontaminated seawater.

### 4. Conclusions

The fluorometric index FI<sub>o/w</sub> was defined as a tool for oil pollution detection in seawater in such a manner that the oil pollution present in the sea is manifested by an increase in FI<sub>o/w</sub>. In the authors’ previous paper, the effectiveness of FI<sub>o/w</sub> was tested for seawater polluted by various kinds of oils and various oil-to-water ratios for one sampling point. The tests performed earlier and statistical calculations indicated a high similarity in the values of FI<sub>o/w</sub> independent of both the kind of oil and oil-to-water ratio.

In the paper, the test of the effectiveness of FI<sub>o/w</sub> was expanded, corresponding to different sampling points and several sampling times. The results presented in this paper concern seawater collected from five different stations in coastal waters four times during the summer season in the Baltic Sea (June–July) and seawater polluted by oil for different oil-to-water ratio (0.5–500 × 10<sup>-6</sup>). For the tests, only one oil was used (Petrobaltic-crude oil), taking into account the independence of FI<sub>o/w</sub> from the kind of oil. The results indicate the FI<sub>o/w</sub> value, starting from a certain threshold amount
of oil (in this case it the oil-water-ratio is about $5 \times 10^{-6}$), ceases to increase despite increasing the dose of this contamination for five different stations in coastal waters. The rising effect of FI$_{o/w}$ in the case of contact of water with oil was observed in each of the twenty examined cases. In summary, the results indicate the independence of FI$_{o/w}$ index from the time and point of sampling. By treating this fact as a good prognostic of the effectiveness and universality of the method, it is possible to extend the research to include water collected in other seasons and from a wider area. Moreover, the wavelengths proposed for the FI$_{o/w}$ index could be used in the future to design and build sensors for oil detection.

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