

Determination of petroleum pollutants in coastal waters of the Gulf of Gdańsk

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Abstract

The paper presents an improved method of determining petroleum pollutants in water based on fluorescence, which allows the oil content to be estimated with an accuracy better than 50%. The method was used to measure the oil content in Gulf of Gdańsk seawater sampled at Gdynia-Orłowo between January 2006 and September 2008. The 174 measurements made during this period ranged from 1 to 120 $\mu\text{g kg}^{-1}$, but the majority did not exceed 20 $\mu\text{g kg}^{-1}$. The most probable level of contamination is c. 5 $\mu\text{g kg}^{-1}$.

1. Introduction

Petroleum substances (henceforth ‘oils’¹) have an adverse impact on the natural environment; this has been reported in many papers. A number of monographs (e.g. NRC 1985, GESAMP 1993) present comprehensive, albeit incomplete, lists of the relevant papers. The oils – many kinds of crude oil and petrochemical products – vary in their compositions and properties (Kajdas 1979, Petrov 1984). The variability of these oils is best reflected

¹According to the MARPOL Convention (IMO 1997), an ‘oil’ is any kind of crude oil and any petrochemical product (like fuel or grease oil) as well as a product of petroleum transformation in the marine environment. The Convention does not, however, treat vegetable fats as oils. The situation is different in American literature and in environmental protection practice, where petroleum, fats and any other oils are all referred to as ‘oils’.

by their fluorescence spectra – comparison of the total spectra allows even similar products of one kind to be distinguished (Stelmaszewski 2007a). Furthermore, the natural environment affects the oils, and fluorescence reflects these changes. Obviously, any differences in properties have their source in the diverse chemical constitution of petroleum.

Despite their differences in composition and properties, oils constitute a single class among a variety of marine pollutants. This legal status arises from the MARPOL Convention (IMO 1997). It is worth noting that oils were acknowledged to be a marine pollutant in the early 1950s, long before any other substances, at a time when coal was still the main energy source. The Convention imposes a duty to monitor the level of oil contamination. The above differences are the reason for the difficulties in perfecting a method for determining the concentration of an oil pollutant in any compartment of the environment. This is not a problem in the case of a large oil spill, but there is no really reliable technique of monitoring small-scale oil pollution in seawater (GESAMP 2007). There is no space here to review all the methods tried out, but one of them, the fluorescence technique, will be discussed briefly. Determining the concentration of petroleum contaminants by this means is not new – it was developed for monitoring seawater pollution back in the 1970s (Horning 1974, IOC 1984). It is based on the fact that fluorescence distinguishes mineral oils from other, similar substances like fats; the fluorescence of fats is very much less intensive, if it occurs at all. In this method, a hexane extract of a water sample is obtained and the intensity of light emitted by the extract measured. The wavelength of the exciting radiation is 310 nm, that of the fluorescence is 360 nm. This measurement is then compared with the intensity of luminescence of a reference compound – a solution of an artificially aged crude North Sea oil. Though still used in the 1980s, the method is no longer applied as it is not sufficiently accurate (GESAMP 1993) – the fluorescence of individual oils varies too much. In the case of the luminescence excited by 310 nm radiation, the intensity of light of 360 nm wavelength emitted by solutions of different oils of the same concentration varies over a range of values. But there is no other practicable method for monitoring the oil pollution of natural water, and the scarcity of data is solely due to this technique having been discarded.

In spite of this diversity of fluorescence properties, a novel means of significantly improving the fluorescence method has been successfully worked out. The present paper describes this improved method, which is applicable to all petroleum pollutants except pure aliphatic compounds, solvents and certain synthetic species. In addition, the paper states preliminary oil concentration measurements made by means of this method in the coastal waters of the Gulf of Gdańsk since the beginning of 2006.

2. Material and methods

Seawater was sampled from the end of the pier in Gdynia-Orłowo, about 200 m from the shore and over 100 m from the breaker line. A c. 1.5 dm³ bottle was filled with water sampled at a depth of 1 m. A fixed amount (c. 1.2 dm³) of water was extracted with hexane (10–15 cm³). Both the water and the hexane were weighed: the former accurate to 1 g, and the latter accurate to 0.01 g. The efficiency of the extraction of oil from water with hexane is > 98%. Throughout this process, the extracts were stored in darkness at a temperature < 5°C.

This improved method has resulted from studies of the luminescence properties of many different substances representing all types of oils. As it has already been presented in greater detail elsewhere (Stelmaszewski 2007b), only its key points will be given here. Photoluminescence can be described by a total spectrum. The total fluorescence spectrum is a function w of two variables: the wavelengths of the exciting radiation λ^{ex} and the luminescence λ^{f} . In the case of fluorescence excited by a ray of given wavelength λ^{ex} , the value of the differential dw :

$$dw = a\Psi dx \quad (1)$$

gives the fluorescence of wavelength λ^{f} emitted by an element of the luminophore volume of length dx in the direction of the exciting flux. In the equation, a denotes the linear absorption coefficient of the exciting radiation and Ψ the spectral internal efficiency of fluorescence (Kawski 1992). The above expression, which is a definition of the total spectrum, could also be presented as follows:

$$dw = \frac{dI^{\text{f}}}{I^{\text{ex}}}, \quad (2)$$

where dI^{f} is the intensity of radiation emitted by the luminophore element of length dx , and I^{ex} is the intensity of radiation exciting the fluorescence (Stelmaszewski 2004). Integration of equation (2) over limits appropriate to the measurement device requires absorption of the radiation to be taken into consideration. It enables w to be determined from measurements of the light intensity I^{f} emitted by the whole volume where fluorescence occurs, in relation to the intensity of the exciting radiation I_0^{ex} incident on the luminophore.

This work presents the measurements carried out using the *Fluorat-02 Panorama* spectrofluorimeter. In this device a narrow beam of exciting radiation (diameter = c. 1 mm; wavelength $\lambda^{\text{ex}} = 210$ nm) passes through the centre of a 1 cm long quartz glass cuvette. The measured fluorescence (wavelength $\lambda^{\text{f}} = 295$ nm) emerges from the entire length of the cuvette

perpendicular to the direction of the exciting flux. The fluorimeter measures the parameter F , which is proportional to the ratio of the luminescence intensity I^f and the intensity of the exciting radiation I_o^{ex} . Integration of equation (2) under the above conditions yields the formula:

$$w = F \frac{T_i^o \ln \frac{T_o^{\text{ex}}}{T^{\text{ex}}}}{T_o^{\text{ex}} - T^{\text{ex}}} \sqrt{\frac{T_o^f}{T^f}} - F_o, \quad \text{where } F = \frac{I^f}{I_o^{\text{ex}}}, \quad (3)$$

F denotes the measurement for the solution under investigation, F_o is the background measurement (radiation scattered in hexane), T^{ex} and T^f are the respective transmissions of the exciting and emitted radiations through the solution tested, and T_o^{ex} and T_o^f are the respective transmissions through the solvent.

The test extract is subjected to measurements in order to determine the value of function w according to equation (3). The concentration C of petroleum in the water is determined by comparing w with the spectral function w_{ref} of a reference solution of concentration C_{ref} :

$$C = \frac{w}{w_{\text{ref}}} \frac{m}{M} C_{\text{ref}}, \quad (4)$$

where M denotes the mass of water tested, and m is the mass of the solvent². The relative mass concentration, i.e. the mass of oil in relation to the mass of water, is the result of the test.

The relative uncertainty of the method is the sum of the relative uncertainties of the values appearing in equation (4)

$$\frac{\Delta C}{C} = \frac{\Delta w}{w} + \frac{\Delta w_{\text{ref}}}{w_{\text{ref}}} + \frac{\Delta m}{m} + \frac{\Delta M}{M} + \frac{\Delta C_{\text{ref}}}{C_{\text{ref}}}. \quad (5)$$

In consequence of the accuracy of measurements, the relative uncertainties of most of the results are no greater than 10%. The most significant source of uncertainty is the reference compound itself. The test was carried out for more than fifty oils representing different types of petroleum. It demonstrated that the parameter w of their solutions of the same concentration did not differ from the average (the value obtained by averaging the functions of all the oils tested) by more than 40% (Stelmaszewski 2007b), and that the differences for most kinds of oil do not exceed 25%. This average value thus seems to be the most suitable for a reference. As previously, North Sea

²This determination is based on the linear relation between the concentration and the value of w . It is true if the tested extract or solution fulfils the Lambert-Beer rule – a necessary precondition of equation (1). In the case of oils, only their hexane solutions of small concentration ($< 2 \times 10^{-5}$) behave according to this rule, so the results should be verified.

crude oil (artificially aged at a temperature of 120°C for 2 hours) was still the reference in the present measurements because the w of its solution almost reaches this average value – a difference of only 2%. After the accuracies of measurements have been taken into consideration, the relative uncertainty of the method can be assumed to reach 50%.

3. Results

The measurements were carried out from January 2006 to September 2008. The relative concentration of petroleum pollutants in the water ranged from 10^{-9} (limit of detection) to $> 10^{-7}$ ($120 \mu\text{g kg}^{-1}$). Most of the results (over 75%) did not exceed 2×10^{-8} , and only single samples had levels $> 5 \times 10^{-8}$. These highest concentrations may have been the effects of incidental oil spills.

All 174 results were divided into groups spanning $5 \mu\text{g kg}^{-1}$ (0–5, 5–10, 10–15 etc. $\mu\text{g kg}^{-1}$), and the number of results in each group was counted. Figure 1 illustrates the distribution of the results. The log-normal function $p(C)$ is the most suitable for describing this distribution:

$$p(C) = \exp\left(-\frac{1}{2}\left(\frac{\ln(C/C_o)}{\sigma}\right)^2\right), \quad (6)$$

where $C_o = 4.3 \times 10^{-9}$ and $\sigma = 9.6 \times 10^{-10}$. The most probable level of petroleum contamination of the Gulf of Gdańsk coastal water is about 5×10^{-9} .

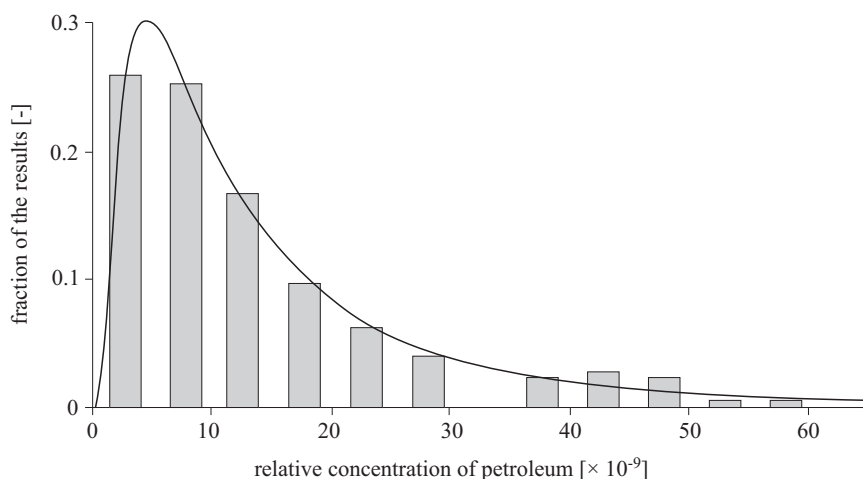


Figure 1. Distribution of the results (the line is a plot of the log-normal distribution function)

During this time some tests on the waters of the open Baltic Sea and Gulf of Gdańsk were carried out. These areas are evidently cleaner: only in a few samples did the oil concentration exceed 3×10^{-9} . The large majority of results were at a level of c. $1\text{--}2 \mu\text{g kg}^{-1}$ or even below the limit of detection; in some places no petroleum was found at all.

One may compare the current results with the concentrations of oil pollutants measured in the same sea area in the 1990s (Otremba & Stelmaszewski 1994). The previous results, though obtained with the earlier technique and therefore encumbered with great uncertainty, are the only available data concerning the same basin. The majority of those results ranged from 5 to $15 \mu\text{g dm}^{-3}$. Taking into consideration the fact that they may have been underestimated, comparison of the present results with the earlier ones indicates that the level of contamination may be decreasing.

The attempt to determine the seasonal variability of petroleum pollutant concentrations has been worthwhile. All the results of the entire test period were divided into twelve parts according to the months of the year, after which the mean concentration was calculated for each month. Figure 2 depicts this preliminary monthly variability of the oil concentration in seawater. It should be noted that this concentration was greater in winter than in the other months except June and July. At this time (June and early July 2006 and 2007) dredging operations to move sand from the sea bed to the beach were being carried out near the sampling area. This could be a reason for the elevated oil levels: the bottom sediments in this region

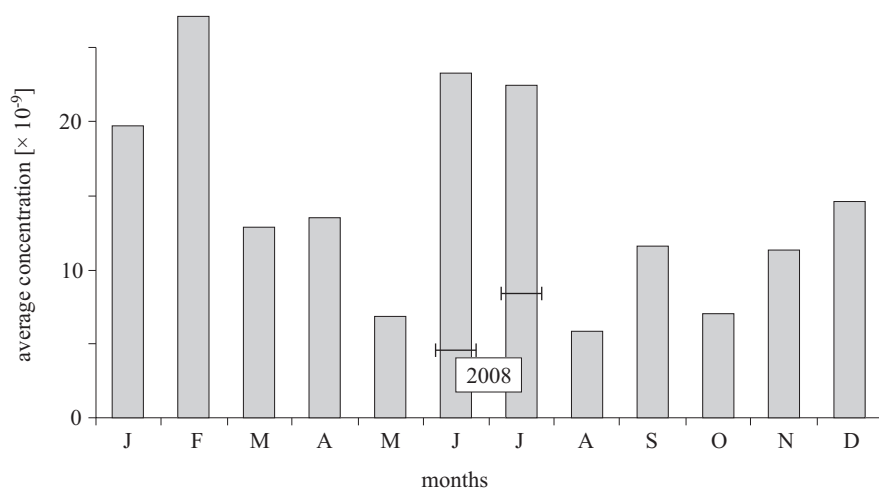


Figure 2. Average petroleum concentration in Gulf of Gdańsk coastal water in particular months of the test period from January 2006 to September 2008. The mean values in June and July 2008 are shown by lines on the respective columns

are strongly polluted with petroleum derivatives (Kaniewski et al. 2003). Measurements carried out in 2008 confirm that this was the case: the average concentration was 4.6×10^{-9} in June 2008 and 8.3×10^{-9} in July. Nonetheless, the limited period of testing and the continued inefficiency of the data prevent any far-reaching conclusions to be drawn.

4. Summary

These investigations enabled the oil pollution level of coastal seawater to be estimated. The results demonstrated the practicability of a method for the reliable investigation of seawater pollution with oil in a relatively simple and accurate manner, which allows for the gathering of a large number of data and for continuous monitoring.

The current studies should be continued and linked to the measurement of other parameters, like temperature, oxygen content or illumination, in order to discover possible relationships. The determination of oil pollution in rivers entering the sea is important, as is the extension of these measurements to other basins. However, comparison of results concerning the pollution of other sea areas is almost impossible at present owing to the lack of literature data.

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