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Degradation of Crude Oil Film on the Surface of Seawater: the Role of Luminous, Biological and Aqutorial Factors

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Abstract

Samples of water were collected from the port of Gdynia and the Gulf of Gdansk (Southern Baltic Sea), and were artificially covered by oil film and stored at a constant temperature. One part of samples was stored in darkness and the second batch was placed under artificial light. Change in the composition of oil on the water surface was determined by means of gas chromatography. Results indicate a greater rate of degradation for the film which covered port water than water from the Gulf of Gdansk. It was revealed that light decreases the rate of biodegradation of an oil film.

Keywords: crude oil, seawater, oil film, biodegradation, photooxidation

Introduction

Intensive sea traffic results in a constant danger of oil contamination in the sea environment. About 77 million tons of oil (mainly crude oil) were transported across the Baltic Sea in 1995 [1], in 1996 - 133 million tons, and in 1997 - 144 million tons [2]. Therefore, there is a high probability of oil appearing in the sea - in any case, several hundred illegal oil discharges in the Baltic Sea are registered by HELCOM [3] every year.

A number of investigations which focus on solving the problems of degradation of oil are reported in scientific literature, e.g.: cleaning port sediments [4], bioremediation and the search for biodegradation coefficient in chosen environments [5, 6], biodegradation of various types of oil [7, 8], identification and isolation of crude oil degrading bacteria [9, 10], effectiveness of bioremediation components used to fight oil spills [11, 12, 13], documentation (GC, HPLC, GC-MS, UV, IR) of progress of oil degradation [14, 15]. Other problems concerned with activity of bacteria degrading oil include: determining self-cleaning ability in different regions by means of investigations of oil biodegradability in sea waters [16, 17], creating biodispersants by marine organisms [7], investigating relations between occurrence of particular types of bacteria and degradation of various types of hydrocarbons [18,19], searching for easily degradable oils [20, 21], and seasonal changes of biodegradability abilities [22].

Photooxydation of oil substances in seawater has also been investigated [23, 24], but there is still a lack of knowledge about the interaction of light and degrading bacteria in oil film.

Rate of oil biodegradability in seawater depends mainly on the degree of oxygenation and occurrence of biogenes [25, 26]. In accordance with data from the 1970s [27], water in the Gulf of Gdansk (Southern Baltic Sea) shows greater ability to biodegradate than water from the open sea. At the same time a relatively high level of oil pollution is observed in the Gulf of Gdansk, in comparison with open sea waters. The oil concentration in the Gulf of Gdansk ranges from 4 to 6 $mg \cdot dm^{-3}$, while in open seawater of the Baltic, 0.5-1.5 $mg \cdot dm^{-3}$ [28].

The first form of presence of oil in the sea environ-

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ment is usually concerned with a thin layer covering the water surface. Then oil is dispersed and transported into a bulk of water and sediments. But how long does the oil film last on the surface as visible spots and how do their chemical and physical parameters change? Despite vast knowledge about long-term transformations and degradation of oil pollutants in the sea environment, the quick changes of features of thin oil film during the first few days after discharge or vessel accident are not well recognised. Especially, there is no knowledge of significance of photochemical and biological processes in fresh oil film degrading and if the solar radiation influence bacteria ability to degrade oil on the water surface.

The aim of the research described in this paper is to widen knowledge about chemical transformations of oil films, which cover the sea surface and potential dependencies/connections between place/position of oil film and rate of its degradation in various light expositions. To achieve it, laboratory tests using probes of seawater artificially covered by oil film, stored at stabilised temperature, humidity, air motion and light intensity were made. Analyses using gas chromatography have been used as a method for determination of n-alkane distribution in oil and determination of biodegradability rate.

Method

Twenty one glass containers of volume 800 ml were filled with three types of sea water: from the Gulf of Gdansk (collected from the Gdynia Pier), from the Gdynia-Port and artificially-prepared sea water. The natural water was collected during five days in the middle of April 1999 and mixed. The temperature of both types of water was 9°C. Artificial seawater was prepared by dissolving main sea salts in distilled water [29] to achieve ion composition similar to natural water of salinity 7.5 PSU. Solution of crude oil *(Romashkino* type) in *n-hexane* was spread on the surface of these samples. Oil film of 10 μm thickness on surfaces of the samples was created this way. Some samples were stored in darkness, some under artificial light (60 W/m^2) at constant water temperature (15°C) and air temperature (12°C). Characteristics of light were spectrally similar to solar radiation. First analyses were made after 0.5 hour, the next after 2 days and final after 8 days. Oil film for analyses was collected after water removal by rinsing the glass container with pure hexane. Analyses of oil composition were made by means of gas chromatography using capillary column, 40 m x 0.32 mm ID covered with stationary phase SPB-5 of film thickness 0.25 μm. Chromatographic analysis conditions were as follows: carrier gas: hydrogen 0.9 bar; temperature program: 60°C, 10 min.; 60-275°C at 4°C/min.; 275°C, 15 min. Injection technique: on-column. Detector: FID, 290°C.

Amount of *phytane* (2,6,10,14-C_{20}) with respect to amount of *octadecane* (n-C_{18}) was treated in this experiment as a measure of biodegradation intensity [30, 31]. Expression (1) as an indicator of biodegradation intensity was applied.

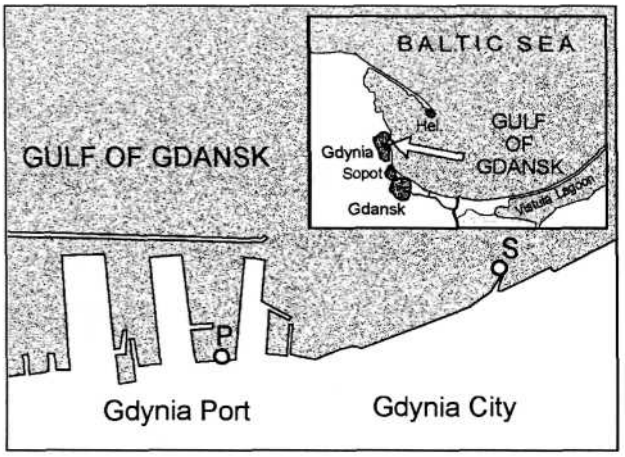

Fig. 1. Locations of natural water sampling (port water - at point *P* and sea water - at point *S).*

$$b = \frac{p}{o} - \frac{p_o}{o_o} \qquad (1)$$

where:
p - phytane content in the sample
o - octadecane content in the sample
p_o - phytane content in the reference sample
o_o - octadecane content in the reference sample

Pristane and *phytane* (izoprenoids) are regarded as biodegradation resistant with comparison to other chain hydrocarbons. At the same time izoprenoids evaporate to the atmosphere and dissolve in water similar to n-alkanes with the comparable number of carbon atoms in the chain. On the other hand, *hopane* is considered to be a more stable tracer for assessment of bioremedi-ation effectiveness of oils in subsurface forms, in sediments and beaches [32, 8]. Also, it is known that in sediments, izoprenoid *pristane* is degraded similarly like *heptadecane* [33]. Due to molecules of *hopane,* which are large and heavy (consisting of 30 atoms of carbon), they are relatively resistant to aeration and dissolving. Therefore, to assess biodegradability of fresh oil film floating on sea surface, *phytane* should be chosen.

Results

Gas chromatograms of fresh and aged oil film were made (always for two samples of identical history). The chromatogram of an oil film sampled after 30 minutes from the water surface as a reference for chromatograms was used. This basic chromatogram (Fig. 2) contains the peaks for relatively light n-alkanes (the maximum falls to n-C_{15}), as well as peaks for *pristane* and *phytane.* Figure 3 illustrates changes of amounts of particular aliphatic hydrocarbons in the chromatogram, which occur after 2 and 8 days of exposure to light, for samples with natural seawater. This figure reveals a fast decrease of short-chain n-alkane amounts. The maximum on that distribution falls to n-C_{21} for oil aged by 2 days, and to n- C_{26} for film aged by 8 days.

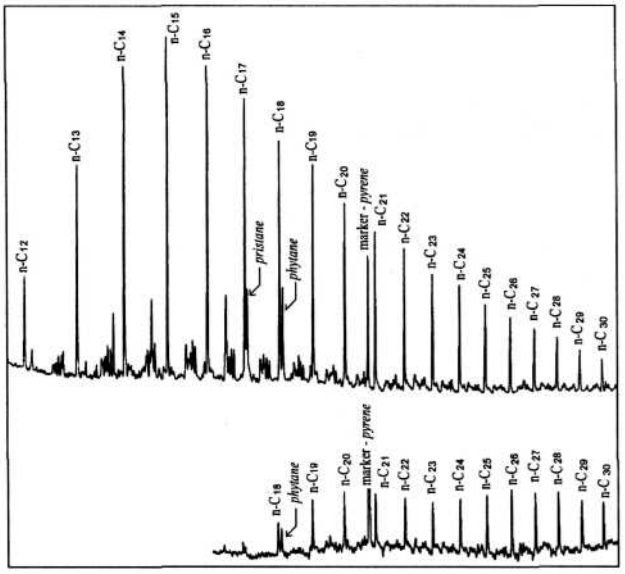

Fig. 2. Examples of oil film chromatograms: at the beginning of the experiment (upper) and after 8 days for the port water stored in darkness (lower).

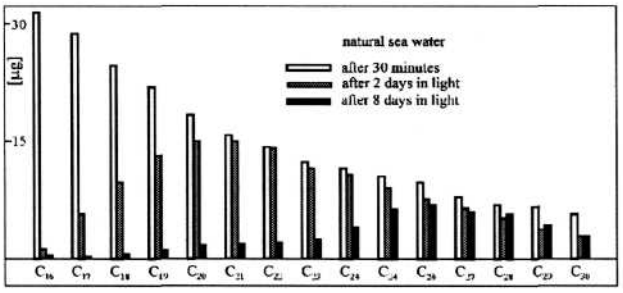

Fig. 3. Distribution of n-alkanes amount in oil films after various periods of time on the surface of illuminated natural seawater.

Figure 4 illustrates changes in oil film composition after 8 days in darkness. A change in composition of oil in the film and intensity of that change depends on the type of water. Rapid decrease of amount of short-chain n-alkanes were observed in the film covering port water. The shape of distribution for that film is not regular (it looks like a combination of two distributions with maxima at n-C_{20} and n-C_{27}).

If samples were stored in the light (Fig. 5), maximum depends on the kind of water as follows: for the artificial seawater - at n- C_{22-28}, for the natural seawater - at n- C_{26} and for the port water - at n- C_{22}

Changes of the composition of darkened films with respect to illuminated samples, for various types of water are indicated at Figure 6. For illuminated seawater (Fig. 6a) maximum of n-alkanes amount distribution occurs at a number of carbon atoms between 25 and 28, while for dark samples - from 18 to 21. In the case of port water (Fig. 6b), for illuminated samples, the maximum occurs in the range of number of carbon atoms from 21 to 24, while in dark samples, the bimodal distribution occurs with maxima from 19 to 21 and from 26 to 28. In the artificial seawater samples (Fig. 6c) the shapes of distribution are similar to the one for natural seawater.

Discussion

At the beginning of the experiment the distribution of hydrocarbons (Fig. 2) was obviously identical in every sample. During the first several tens of hours, evaporation is the main reason of the short chain n-alkanes loose. The aeration phenomenon is apparent at Figure 3 as the difference between distribution at the beginning and after two days. However, differences between distribution for the 2nd day and the 8th day should be considered as caused mainly by light and bacteria activity. Several days were enough for degrading the oil film, which covered natural seawater in the great scale - mainly low molecular compounds disappeared almost completely.

The tests carried out proved that the fate of the oil film depends to a great extent on the origin of water and light conditions. Transformations of chemical composition of oil in dark samples happened due to the activity of bacteria, whereas in illuminated samples the phenomenon of photooxidation must also be taken into consideration. In darkened samples degradation is less

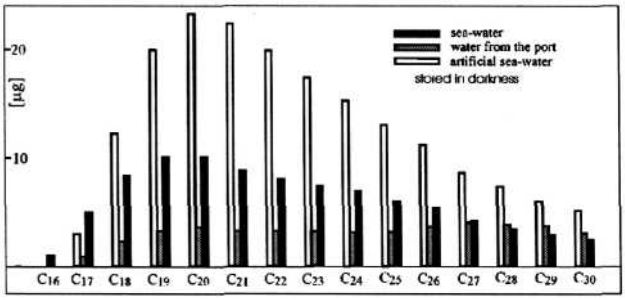

Fig. 4. Distribution of n-alkanes in oil films after 8 days on the surface of dark water.

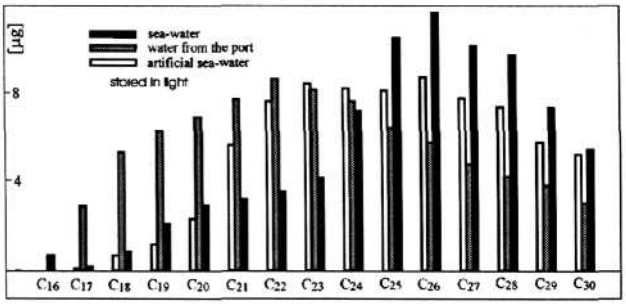

Fig. 5. Distribution of n-alkanes in oil films after 8 days on the surface of illuminated water.

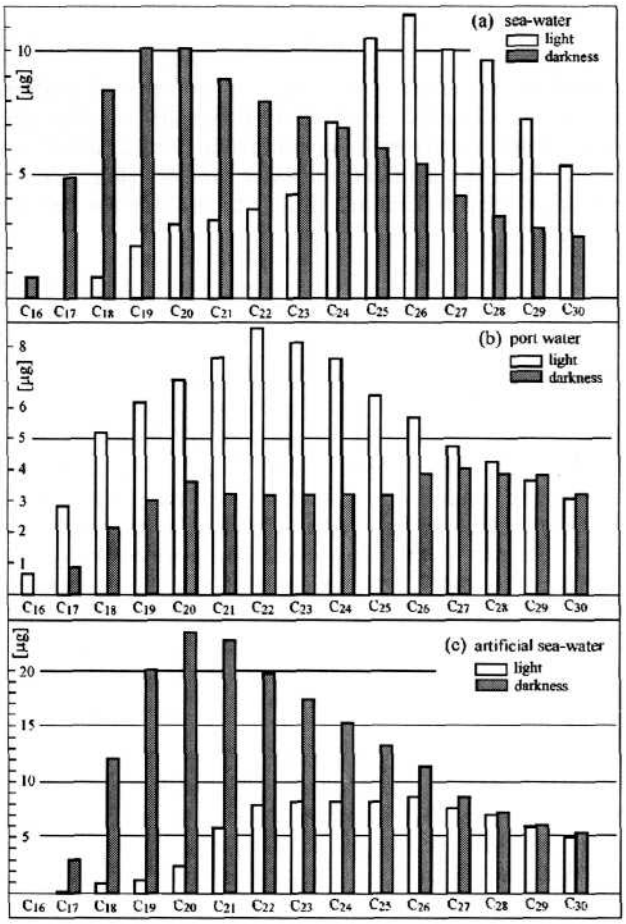

Fig. 6. Distribution of n-alkanes in oil films after 8 days on the surface of illuminated water (white columns) and dark water (grey columns).

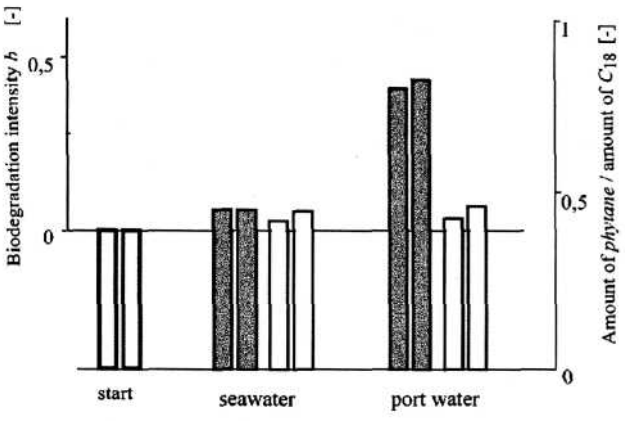

Fig. 7. Changes of biodegradation intensity determined in oil films after 8 days (in darkness - the grey rectangles, illuminated - the white ones).

intensive for artificial seawater (Figure 4). This situation can be explained by the activity bacteria, which are able to activate enzymatic apparatus towards oil degradation. Such bacteria are able to exist in large amounts in port waters as a result of oil chronicle pollution. It should have been expected that the illumination of samples would add a photooxidation factor. This, however, does not happen since, as shown in Figures 5 and 6b, a decrease in the amount of short chain n-alkanes in port waters is to a great extent slowed down when compared with the rate of degradation in dark samples. It is known that solar radiation plays the role of an inhibitor of activity of microorganisms in the sea surface layers [34]. Therefore, one could draw a conclusion that strong light also decreases activity of bacteria in the illuminated oil film.

Taking into consideration the rate of *phytane* amount to the amount of *octadecane* (biodegradation intensity *b* expressed by (1)) it is shown that in the case of dark samples, biodegradation was the most intensive for port water and least intensive for natural seawater (Figure 7). This phenomenon is caused by the increased amount of oil degrading bacteria existing in chronically polluted port waters in relation to open sea waters. Factor *b*, in the case of seawater, has lower values in illuminated samples than in dark samples - which additionally confirms that light inhibits biodegradation of thin oil films.

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