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Modeling of the Crude Oil Suspension Impact on Inherent Optical Parameters of Coastal Seawater

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Abstract

This paper presents the results of modeling of spectra of light scattering and absorption coefficients in sea water polluted with crude oil suspension. In the *Mie* theory, which has been applied for calculations, the results of the measurements of the size distribution spectra in artificial crude oil suspensions in sea water were used as well as the results of the measurements of the components of the complex light refraction index of crude oil from the Baltic Sea *(Petrobaltic* type). The comparison of the spectra obtained with those which are characteristic for the waters in the Gulf of Gdansk confirmed that the admixture of emulsion with about 2 ppm of crude oil doubles the light scattering coefficient. The same effect, with respect to the light absorption coefficient, is obtained when the concentration of the crude oil suspension is about 100 ppm.

Keywords: oil pollution, coastal seawater, optical parameters, light scattering, radiative transfer

Introduction

Crude oil pollution of water, together with natural environmental components take part in the creation of illumination conditions both in the water column and above the water surface. The impact of superficial forms of crude-oil-based substances on the radiation field above the sea surface had to some extent already been analyzed [1, 2]. This paper, on the contrary, describes the investigations of the impact of oil suspension on coefficients of light absorption and scattering in sea water from a coastal area, i.e. the Gulf of Gdansk in the Baltic Sea.

Crude oil suspension is created as a result of wavy motion of the free sea surface. This process is sometimes enforced by dispersants, which are used to fight accidental oil spills. The results of the studies of the impact of crude oil suspension on water optical properties may be very useful in order to improve the methods of detection of sea contamination with crude oil based substances, as well as to satellite imagery correction.

In order to determine the optical parameters of water polluted with crude oil the *Mie* theory, which describes the light scattering by spherical particles, may be applied [3, 4, 5]. In such cases it is necessary to know the following: complex coefficient of light refraction by the substance (oil) which creates suspension, suspension particle radii and the medium (water) refractive index. The calculations of optical parameters (i.e. specific scattering and absorption cross-sections) are firstly made for particular droplet radii and then the results obtained are averaged with respect to the size distribution of suspension droplets in the water.

In this paper the modeling of the optical parameters of crude oil suspension in the water has been described. The modeling process consists of two stages: first, experimental, which involves the preparation of input data for calcu-

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lations, i.e. spectrum of complex refractive index of crude oil, spectrum of refractivity of the seawater and oil droplets size distribution. In the second, computation stage, firstly spectra of specific light absorption and scattering cross-sections in the monodispersed suspension are derived. Then these cross-sections are recalculated to specific light absorption and scattering coefficients in the polydispersed suspension with the oil droplet size distribution taken into consideration.

Materials and Methods

In order to determine the most probable shape of oil droplet size spectrum a model oil suspension was made in the laboratory, through mechanical (mixer working at 600 rpm) oil dispersion in water. The distilled water with the addition of the components which secure chemical composition similar to natural sea water [6] of salinity 8 PSU was used. Oil dispersion was made in a dish of volume 10 dm^3, in which 8 dm^3 of water and 50 cm^3 of crude oil was placed. The oil-water system was stored for two weeks, which resulted in almost stable suspension. The number and sizes of suspension droplets were determined using

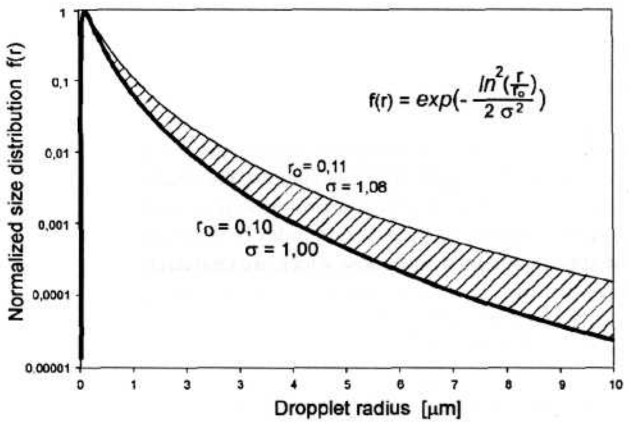

Fig. 1. Changes of size spectrum of crude oil suspension in sea water after one week of its creation (thin line) and after two weeks of stabilizing (thick line).

the microscope. The results of the microscope observations were used to determine the parameters of lognormal size distribution. Figure 1 presents the size spectrum of the suspension after one and two weeks of stabilizing. The area between the curves is the range of the changes of the size distribution during the second week of suspension stabilization. It has been assumed that the suspension, which was stabilized in such a way has a size distribution similar to that of the oil droplets, which are basically permanent (until their bio- and photodegradation) in the water.

Spectra of the components of a complex coefficient of light refraction *m* (refractive index - the real part, absorptive index - the imaginary part) of crude oil type *Petrobaltic* have been determined experimentally. The oil was centrifuged from the studied suspension and its refractive index and light absorption coefficient were measured in the range of wavelengths from 400 nm to 700 nm. The real part of the light refraction index was determined using the Abbe refractometer with stabilized temperature. The oil absorption coefficient (which was determined using the spectrophotometer) was recalculated to absorptive index [7]. The spectra of both components of the complex light refraction index are presented in Fig. 2.

Analogous spectra of both the real and imaginary parts of the light refraction index of natural sea water are presented in Fig. 3. Spectra of the real part of the light refraction index in the water, similar to crude oil, were derived experimentally. The spectrum of the imaginary part of the light refraction index *k* for the ocean water have been taken from works of Morel and Prieur [8] and Shifrin [9]. The values of *k* for water (Fig. 2) and oil (Fig. 3) differ by a magnitude of several orders. This justifies the assumption, which was made in the *Mie* theory about the lack of light absorption in the medium in which the suspension droplets are placed.

During the calculations of the optical properties of the suspension, firstly scattering c_{ss} and absorption c_{sa} cross-sections are calculated. They describe the ratio of proper oil droplet cross-sections and their volumes. The specific scattering and absorption cross-sections describe the efficiency of the light scattering and absorption by these droplets in the suspension made of droplets of uniform radii r. The optical properties of the suspension, which consists of droplets of various radii (polysdispersed dispersion) are described by the specific scattering b_s (1)

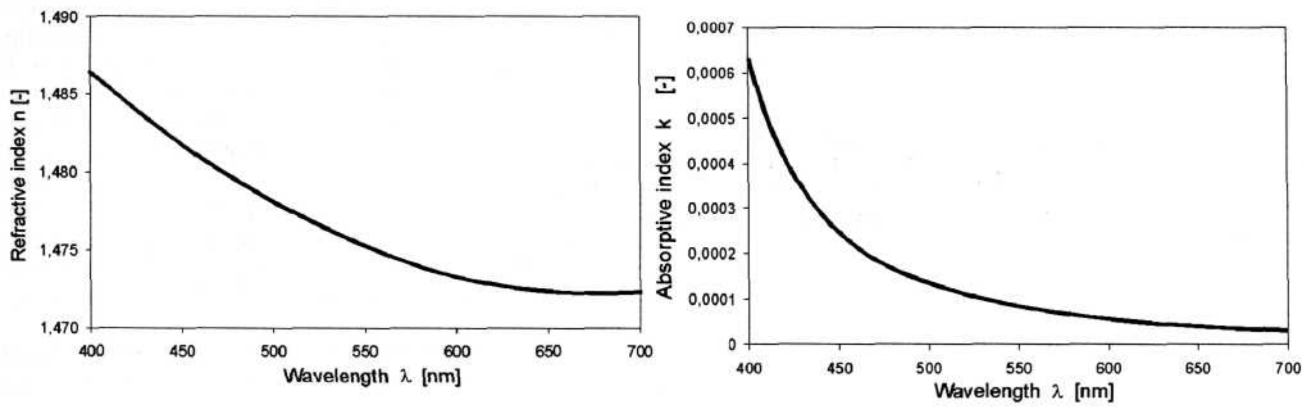

Fig. 2. Components of a complex coefficient of light refraction *m* of the crude oil type *Petrobaltic* (after Otremba [7]).

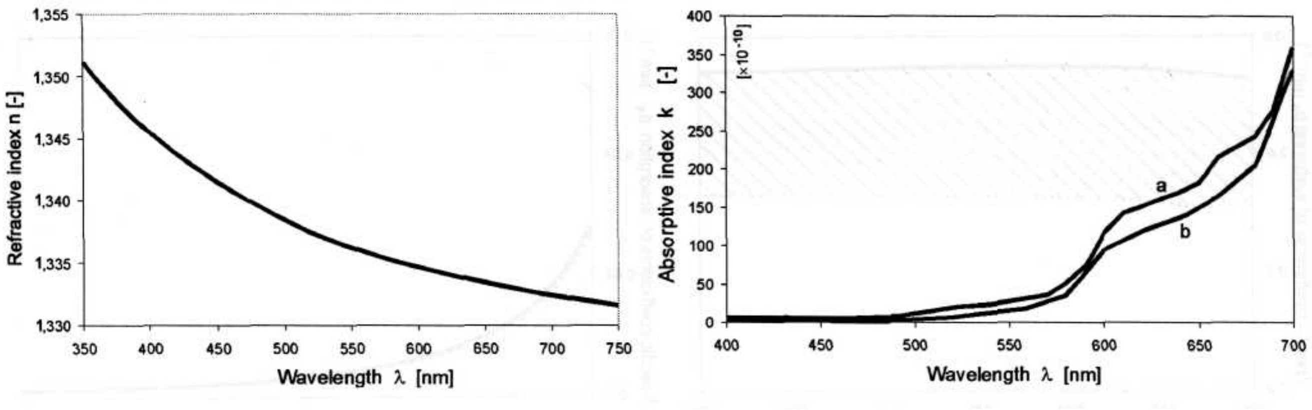

Fig. 3. Components of a complex coefficient of light refraction *m* of the seawater. On the left - spectrum of refractive index of water of salinity 8 PSU (own results), on the right - typical spectra of the absorptive index of the seawater: curve *a* - after Morel and Prieur [8], curve *b* - after Shifrin [9].

and absorption a_s coefficients of the medium (2). They are obtained through the averaging of the specific cross-sections using oil droplet size distributions, derived earlier (Fifrl).

$$b_s = \int_{r_{min}}^{r_{max}} f(r)\, v(r)\, c_{ss}(r, m)\, dr \tag{1}$$

$$a_s = \int_{r_{min}}^{r_{max}} f(r)\, v(r)\, c_{sa}(r, m)\, dr \tag{2}$$

where v(r) is volume of the oil droplet.

Knowledge of the specific light scattering coefficient b_s specific absorption coefficient a_s and the volume concentration of oil in the suspension p facilitates the derivation of both the scattering coefficient *b* (3), and the absorption coefficient *a* (4), as well as the light attenuation coefficient *c* (5) of the medium, i.e. the physical value which is measured in the water column using the so-called *beam transmittance meters.*

$$b = b_s\, \rho \tag{3}$$

$$a = a_s\, \rho \tag{4}$$

$$c = a + b \tag{5}$$

Results

The values of the specific scattering cross-sections c_{ss} and specific absorption cross-sections c_{sa} were derived using the *Mie* theory for different wavelengths, from 400 nm to 700 nm, every 10 nm and for different suspension droplet radii, from 50 nm to 20 μm, every 50 nm. The results of these calculations are illustrated in Fig. 4. The specific scattering cross-section $c_{ss}(\lambda,r)$ has a clear maximum for

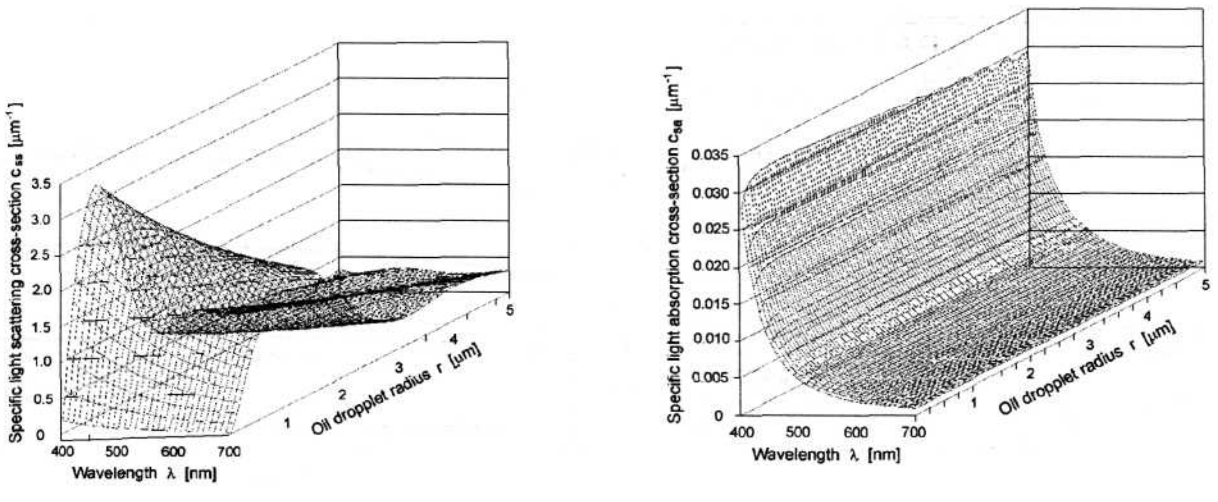

Fig. 4. Spectrum of the specific attenuation cross-section (left graph) and specific absorption cross-section (right graph) of the suspension of crude oil type *Petrobaltic* in Baltic water.

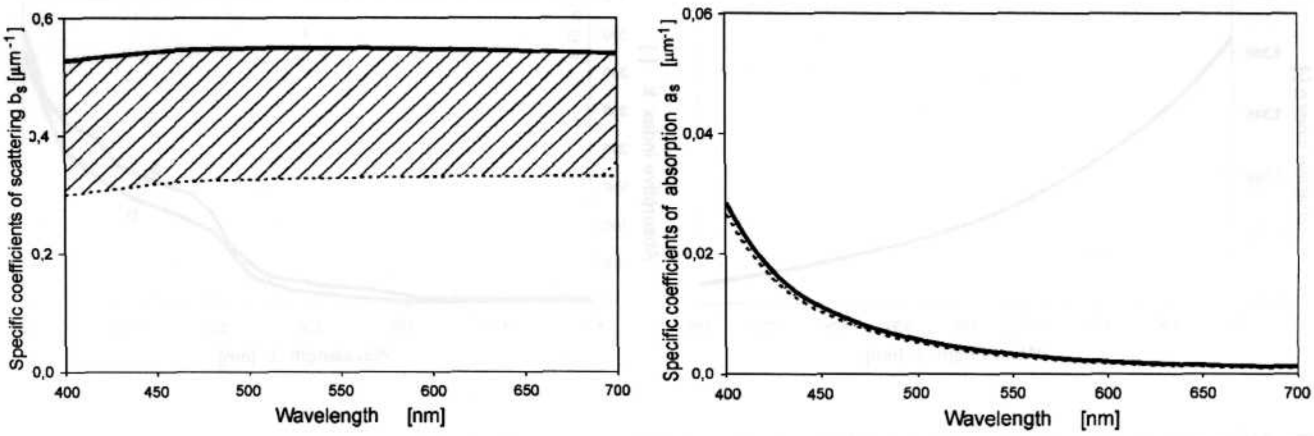

Fig. 5. Spectra of specific absorption (left) and scattering (right) coefficients of suspension of crude oil *Petrobaltic* after one week stabilization (thick line) and after two weeks (thin one).

droplet radii comparable with the light wavelength. The shape of the specific absorption cross-section $c_{ss}(\lambda,r)$ to a great extent reflects the shape of the spectrum of the absorption coefficient in the crude oil. The specific absorption cross-sections have values of a magnitude of two orders lower than the specific scattering cross-sections.

The calculated values of scattering and absorption cross-sections were transformed using formulae 1 and 2 to emulsion-specific absorption a_s and scattering b_s coefficients, which determine the optical properties of the polydispersed oil suspension in the water. Spectra of emulsion scattering and absorption coefficients are presented in Fig. 5, where the dashed line denotes the unstable suspension (one-week-old), and the thick solid line denotes the stable suspension (two-week-old). The value of the specific scattering coefficient b_s depends on the size spectrum (they are bigger, when the emulsion is stable for a longer period of time), and to a small extent on the light wavelength. The values of the specific absorption coefficient a_s decrease quickly with the increase of light wavelength. The shape of this spectrum to a small extent depends on the size distribution of suspension droplets.

If the crude oil concentration in the suspension is known, then in accordance with dependencies 3 and 4 the values of the specific scattering b_{sp} and absorption a_{sp} coefficients can be recalculated to emulsion scattering b and absorption a coefficients.

Discussion

The results of modeling of light scattering and absorption coefficients by the suspension of crude oil in the water (Fig. 5) facilitate evaluation of the input of the oil emulsion to the change of the value of the scattering and absorption coefficients of the natural sea water. Figure 6 presents the exemplary spectra of the absorption and scattering coefficients measured in the Gulf of Gdansk, which were used to calculate their spectra for the oil suspension. The value of the scattering coefficient of the dis-

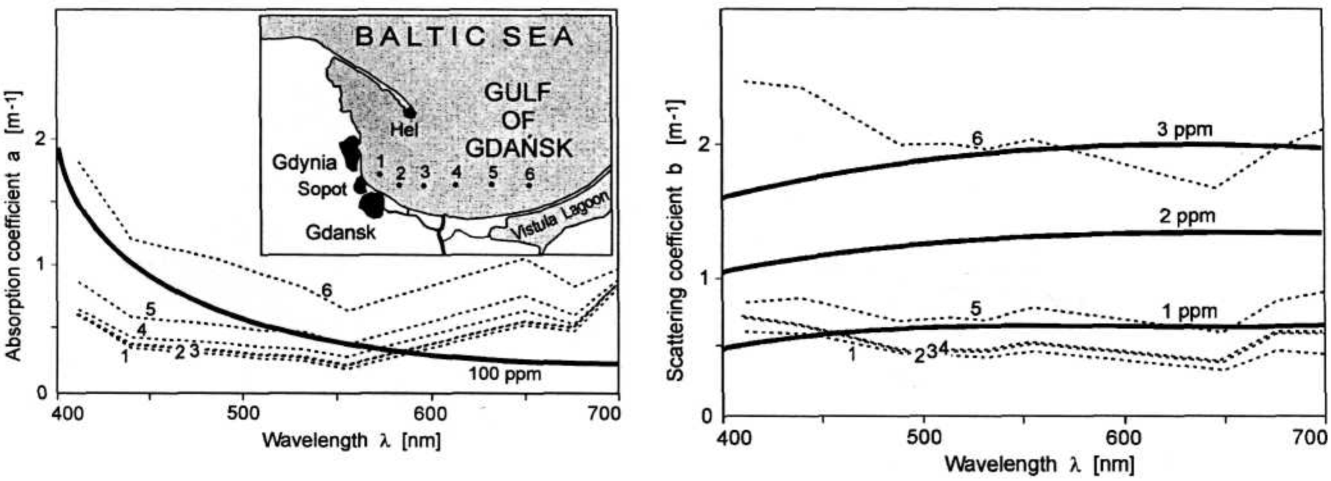

Fig. 6. Spectra of real optical parameters of the oil suspension.(solid lines) versus the measured real water optical parameters from various regions of the Gulf of Gdansk (dashed lines). Data on waters from the Gulf of Gdansk were collected during measurements on 24 April 1999 within the scope of the EU MAST III programme (MAS3-CT97-0085), "BIOCOLOR".

persed oil is close to the value of this coefficient in the natural gulf water at the volume concentration of 2 ppm. However, the value of the absorption coefficient in the suspension of the crude oil *Petrobaltic* is comparable to the value of the absorption coefficient of sea water when the oil concentration reaches c. 100 ppm.

The spectra of the absorption and scattering coefficients of the oil suspension have different shapes than the analogous spectra of the natural sea water. In the long wave part of the spectrum of light absorption coefficient for oil suspension the value of the absorption coefficient decreases, while in the case of natural sea water it increases (Fig. 6). For the medium and short waves the absorption coefficient spectra for the oil suspension and for natural sea water have similar shapes. In the spectrum of the scattering coefficient, the changes are the opposite.

The calculated spectra of the absorption and scattering coefficients for oil suspensions in the water will be used for modeling the underwater and above-water radiation fields, connected with the illumination of the water reservoir with natural solar radiation.

Acknowledgements

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