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Phase functions of oil-in-water emulsions

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This paper presents the modelling of optical phase function (PF) of water polluted by dispersed oil. The shapes of PFs for various oil droplet size distributions and for two optically extremely different oil types are shown for various wavelengths from 350 to 750 nm. It is proved that changes of optical properties of oil (the complex refractive index) play minor role in PF shaping towards the impact of wavelength and size distribution. Water with oil emulsion has a PF significantly different from that of natural ocean water or harbour turbid water.

Keywords: ocean optics, phase function, oil, suspension.

1. Introduction

The entire set of inherent optical properties of natural water consists of the scattering coefficient, the absorption coefficient and the scattering phase function. The sum of absorption coefficient a and scattering coefficient b is called attenuation coefficient $c = a + b$. The attenuation coefficient c can be easily measured in water by so-called transparency meter. Parameter c controls in-water light fields, underwater visibility and some other biologically valid properties of aquatic environment in defined sea/lake/river areas. Unfortunately, precise determination of light transfer without knowledge of the components of c is impossible. Separate measurement of a and b directly in the bulk of water cannot be made with presently available techniques. The modelling of optical properties and analysis of spectral dependences of both scattering and absorption coefficients were carried out by OTREMBA and KRÓL [1], whereas in this paper, the modelling of phase function is shown.

Phase function describes angular dependences of light scattering. A fundamental function describing both phase function and scattering coefficient is the volume scattering function (VSF), defined as follows:

$$\beta(\theta) = \frac{\mathrm{d}I(\theta)}{E\,\mathrm{d}V} \quad [\mathrm{m}^{-1}\mathrm{sr}^{-1}] \tag{1}$$

where $\mathrm{d}I(\theta)$ is the infinitesimal radiant intensity deriving from an infinitesimal volume $\mathrm{d}V$, and E is the incident irradiance. Integral of VSF of full-solid-angle gives the scattering coefficient

$$b = \int_0^{2\pi} \int_0^{\pi} \beta(\theta) \sin(\theta) \mathrm{d}\theta \mathrm{d}\varphi \quad [\mathrm{m}^{-1}] \tag{2}$$

where θ and φ are spatial coordinates (nadir and azimuth, relatively).

The VSF for aquatic environment is assumed to be azimuthally symmetric, therefore integral (2) takes the more simple form

$$b = 2\pi \int_0^{\pi} \beta(\theta) \sin(\theta) \mathrm{d}\theta. \tag{3}$$

The VSF is often normalized by its angular integral to obtain the PF described as $p(\theta)$.

$$p(\theta) = \frac{\beta(\theta)}{2\pi \int_0^{\pi} \beta(\theta) \sin(\theta) \mathrm{d}\theta} = \frac{\beta(\theta)}{b} \quad [\mathrm{sr}^{-1}] \tag{4}$$

The integral of PF of full solid angle equals 1.

In this paper, the PFs considered are functions independent of concentration of oil in water. However, the concentration of oil is reflected in the value of the above mentioned scattering coefficient b.

2. Deriving of phase function

The procedure for deriving a phase function is based on rigorous scattering theory for a sphere of an arbitrary size [2]. This scattering theory was first described by MIE [3], so it is called the Mie theory. This theory is based on the set of Maxwell's equations together with the appropriate boundary conditions. The first numerical computations were carried out in the 1940s [4]. The first step towards facilitating the calculations was the possibility of using a look-up table of the Riccati–Bessel functions prepared using just invented electronic computational machine [5]. At present, a personal computer is fast enough for all computations of phase functions, even in the case of polydisperse emulsion. In our computational code, the input data are spectra of

components of complex coefficient of light refraction in oil, spectrum of refractive index in water and size distribution of oil droplets in oil emulsion.

3. Input data

A complex coefficient of light refraction in oil is expressed by the following equation:

$$m = n + ik \tag{5}$$

where: n – refractive index (real part of the complex coefficient of light refraction), k – non-dimentional absorption coefficient (imaginary part of a complex coefficient of light refraction).

The procedure for measuring the complex light refraction index m in oil was described by OTREMBA and KRÓL [1]. In this paper, data obtained for oil centrifuging from emulsions aged 1 day, 1 week and 2 weeks were used.

No radical changes in m are detected. Explicit differences appear only between fresh oil and oil centrifuged from emulsion. It was not possible to determine the value of m in oil in extremely overaged emulsion, such as 5 weeks old emulsion (that emulsion is very stable and concentration is very low). It was assumed that optical properties of such oil are similar to oil contained in moderately aged emulsions. Table 1 contains data concerning spectra of parameters n and k of the complex coefficient of light refraction in oil.

T a b l e 1. Components of a complex coefficient of light refraction in oils.

Wavelength [nm]	Crude oil "Romashkino"		Crude oil "Petrobaltic"	
	n	*k*	*n*	*k*
350	1.518	0.0154	1.490	0.00600
400	1.503	0.0125	1.486	0.00064
450	1.494	0.0089	1.482	0.00026
500	1.490	0.0060	1.479	0.00013
550	1.488	0.0040	1.477	0.00008
600	1.488	0.0030	1.476	0.00006
650	1.488	0.0028	1.476	0.00004
700	1.488	0.0030	1.477	0.00003
750	1.488	0.0030	1.496	0.00002

Determination of the most probable size distribution of oil droplets suspended in the water is necessary. Interaction of oil film with water movements evokes dispersion of oil and probably transportation in the bulk of water. There is no consistent and unequivocal theory, applicable in aquatic environment, that would concern the various kinds of oil emulsification. A tentative laboratory experiment shows the role of salinity,

T a b l e 2. Parameters of size distribution (Eq. (6)) of oil-in-water emulsions of various age.

Age of emulsion	r_o	σ
1 day	0.20	0.95
1 week	0.11	1.08
2 weeks	0.10	1.00
5 weeks	0.05	1.12

temperature and even light in this process. In the above mentioned experiment by OTREMBA and KRÓL [1], emulsions artificially prepared and aged/weathered one and two weeks were used as representative of typical oil suspensions in the sea water. Size distributions of oil droplets of such emulsion are mainly used in calculations presented in this paper as well, because more fresh emulsion is unstable due to flotation and coalescence processes of oil droplets of large diameters, whereas more aged emulsion has too small droplets to be registered by a microscopic method. Size distributions of very fresh and very old emulsions can be only roughly estimated.

Size distribution can be represented by the log-normal distribution

$$f(r) = C\exp\left[-\frac{\ln^2(r/r_o)}{2\sigma^2}\right] \tag{6}$$

where: r_o – mean droplet radius, σ – constant which characterizes distribution width, C – normalizing constant (depends on oil concentration).

Table 2 contains the parameters of size distribution of various oil-in-water emulsions used in phase function calculations.

4. Results and discussion

Results of calculations are presented in Fig. 1 as phase functions for various emulsions and various light wavelengths in a wide spectral range (from the close ultraviolet to the near-infrared). The parameters of size distribution of emulsion relate to moderate aged emulsions (1 week and 2 weeks).

The shapes of PFs in Fig. 1 depend on the wavelength, kind of oil and rate of emulsion ageing. A comparison of the calculated PFs with PFs typical of seawater is presented in Fig. 2**a**. One can notice that forward scattering strongly depends on the ageing rate or on the size distribution. Old emulsion is characterized by more forward scattering in comparison to the fresh emulsion. Nevertheless, forward scattering of any oil emulsion is smaller than in the case of seawater. However, the opposite happens when scattering at angles of several dozen degrees is considered. Assiging the role of the size distribution in backscattering is difficult. As one can see in Fig. 2**b** – which is

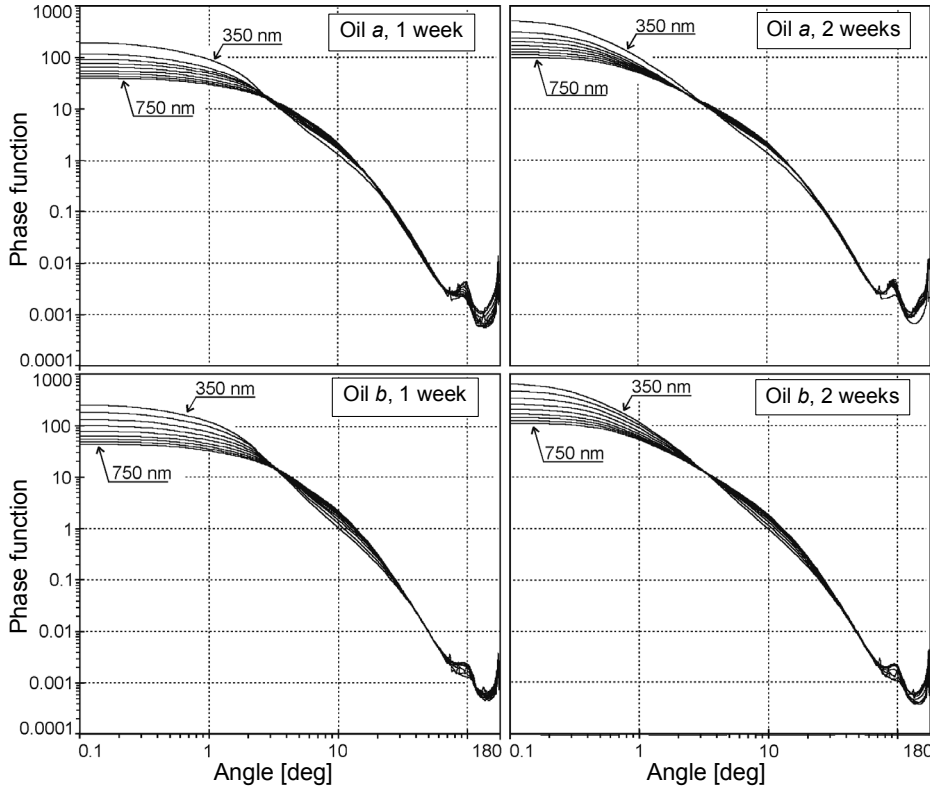

Fig. 1. Phase functions for two kinds of oil (*a* – Petrobaltic-type, *b* – Romashkino-type), and for two oil droplet size distributions (1 week – emulsion after 1 week of ageing, 2 weeks – emulsion after 2 weeks of ageing). Curves for wavelengths from 350 to 750 nm every 50 nm.

a fragment of Fig. 2**a** enlarged – different PFs tend to intersect. But backscattering (scattering towards 180°) decreases with the time of oil emulsion ageing. Additionally, it seems that backscattering in fresh oil emulsion is similar to backscattering in turbid harbour water. As the whole shape of phase function influences the in-water light transfer, it is difficult for the time being to fully determine how the contrast of oil "clouds" in the bulk of water is formed. But the results presented provide sufficient data for light transfer as well as reflectance modelling of the water areas polluted by oil.

5. Conclusions

Calculated light scattering phase functions (PFs) of oil-in-water emulsions presented in this paper, together with both light scattering and absorption coefficients (determined earlier [1]) give complete optical characterisation (so-called inherent optical properties – IOPs) of oil emulsion dispersed in the water. Nevertheless,

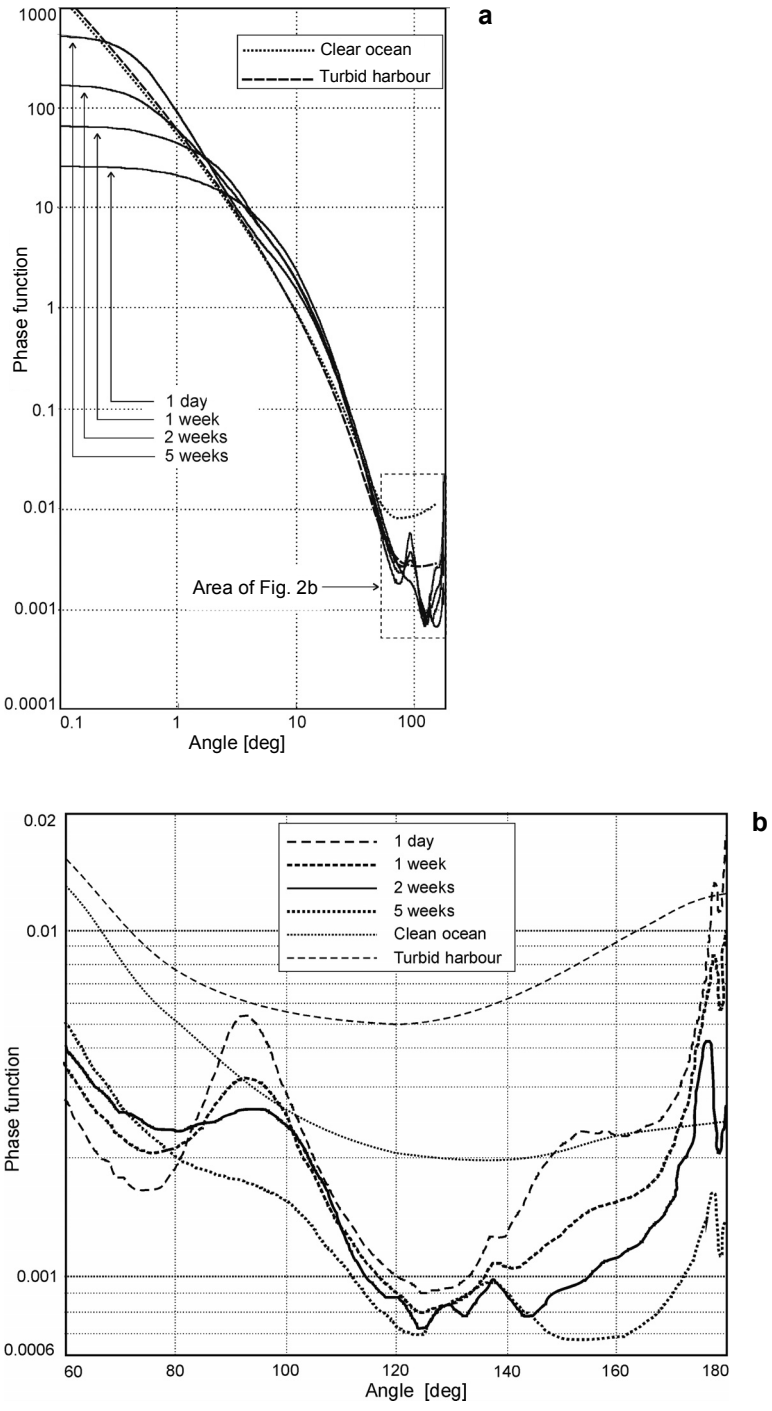

Fig. 2. Phase functions of oil-in-water emulsions for various times of ageing, phase function of clear ocean water and phase function of turbid harbour water (**a**), enlarged fragment of Fig. 2a (**b**).

visibility (possibility of detection) of such contamination depends on oil concentration as well as on light conditions, and finally on the state of water surface as a result of specified wind speed [6]. Determining the IOPs of oil-in-water emulsions gives the input data for modelling of light condition in water bodies contaminated by oil, as well as modelling the visibility of oil immersed in the bulk of water.

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