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Oil-in-water emulsion as a modifier of water reflectance

ZBIGNIEW OTREMBA

Gdynia Maritime University, Morska 81-87, 81-225 Gdynia, Poland

The paper presents a component of the water reflectance in the visible region, stimulated by oil-in-water emulsion in the concentration of 1 ppm. A proxy for reflectance which is in use in oceanic optics has been studied. A significant change in reflectance for water contaminated by oil emulsion is revealed. In general, the reflectance generated by oil emulsion grows with light wavelength increase and in cases when small oil droplets dominate in oil-emulsion.

Keywords: water, reflectance, spectra, oil, emulsion.

1. Introduction

The dependence of water basins color on mineral and biological constituents is an evident phenomenon and thus it provokes interest in computable relationships between various natural water optical properties and the amount of suspended and dissolved substances. The color of a defined water basin manifests itself through measurable values such as spectra of irradiance reflectance R_E (ratio of upward irradiance and downward irradiance) or radiance reflectance R_L (ratio of upward vertical radiance and downward irradiance). So in order to establish the relationship between water-body constituents and the reflectance, an adequate proxy for reflectance as a mathematical function of inherent optical properties (IOPs) of those constituents has been investigated. It has been revealed that the irradiance reflectance R_E measured in the so-called “case-I” oceanic waters just beneath the sea-surface can be expressed by a ratio of backscattering and absorption coefficients bb/a multiplied by an empirical coefficient which depends on solar position (about 0.3). One of the earliest implementations of such a type was proposed by MOREL and PRIEUR in 1977 [1]. Earlier, GORDON *et al.* in 1975 [2] proposed the ratio $bb/(a + bb)$ as a value proportional to the radiance reflectance. This ratio is still in use for estimation of concentration of chlorophyll and dissolved organic matter. WOZNIAK and STRAMSKI in 2004 [3] used $bb/(a + bb)$ for modeling of the impact of mineral particles on chlorophyll estimation from remote sensing protocols.

T a b l e. Mean radiuses r_{mean} of oil droplets and parameters of size distribution (r_o and σ) of oil-in-water emulsion after various times of ageing.

Sample	Time of ageing [days]	r_{mean} [μm]	r_o [μm]	σ
a	0	1.18	0.250	1.02
b	1	0.84	0.200	0.98
c	2	0.66	0.180	0.93
d	7	0.42	0.125	0.90
e	14	0.25	0.080	0.87
f	21	0.17	0.065	0.80
g	35	0.12	0.050	0.75

As was mentioned, ocean reflectance can be related to the bb/a also (for example by GORDON *et al.* [4] or RISOVIĆ [5]) because bb in denominator, as a value considerably lower than a, can be neglected. The proportionality-coefficient between measurable reflectance and reflectance expressed by a combination of bb and a is determined experimentally and must be related to the defined water area. It is not necessary when the ratio of reflectances for two wavelengths – the so-called spectral band ratio – is applied (various spectral band ratios are implemented to protocols for remote estimation of the concentration of marine constituents, especially chlorophyll).

In this paper, the intrest is narrowed to analysis of the spectra of both ratios bb/a and $bb/(a + bb)$ for oil-in-water emulsion, taking into account the types of oil and the variability of oil droplet size distribution.

2. Material

Investigated oil-in-water emulsion consists of natural surface water (near-shore water sampled from the Gulf of Gdańsk, Poland) polluted by crude oil droplets of various diameters. Microscopic analyses of sizes of oil droplets in previously prepared emulsion were carried out after various time-periods of storing of emulsion in stabilized temperature. Details of procedure as well as oil droplets size distribution were presented in the earliest paper [6] (easy accessible on-line), where optical properties of oils used for emulsion preparation were also described. Only the parameters of oil size distribution for investigated samples are quoted in this paper in the Table. Labeling of samples (letters a–g) is further implemented in Figs. 1–4.

3. Methods

Spectra of both absorption and refraction coefficients of oil, as well as oil droplet size distribution were used to determine the volume scattering functions (VSFs, denoted as β) for various wavelengths. They are vertically symmetric (independent of azimuth angle), therefore knowing VSFs for various wavelengths, spectra of backscattering coefficients *bb* were derived as follows:

$$bb = \int_0^{2\pi} \int_{\frac{\pi}{2}}^{\pi} \beta(\theta, \varphi) \sin\theta \, d\theta d\varphi = 2\pi \int_{\frac{\pi}{2}}^{\pi} \beta(\theta, \varphi) \sin\theta \, d\theta$$

where θ is the scattering angle, φ is the azimuth angle.

In derivations of VSFs, the Mie scattering theory [7] was applied. Calculations for radii of oil droplets from 0.025 μm to 50 μm were carried out, with a step of 0.025 μm (2 000 radii). Size distributions were normalized to the oil volume concentration of 1 ppm.

To derive both ratios bb/a and $bb/(a + b)$, also spectra of absorption coefficient were needed. The spectra of absorption coefficient of oil-in-water emulsion have been already used for comparison of the shapes of absorption spectra of emulsion with absorption spectra of oil from which emulsion was made [6]. Those data were also used in this paper. They play a role of a gradual product ("half-finished products") for bb/a and $bb/(a + bb)$ analogously to the spectra of *bb* (which were derived for the purpose of this paper only).

4. Gradual products of proxies for reflectance

Both spectra of absorption coefficient *a* and spectra of backscattering coefficient *bb* of oil-in-water emulsion are treated as half-finished products of *a* proxy for reflectance. The graphic form of spectra of *a* are presented in the above mentioned paper [6], whereas spectra of *bb* are presented in this paper in Fig. 1. Backscattering coefficient has maximum value when emulsion is aged for a long time (sample *g*), that is when the advantage of the number of small droplets over the number of large oil droplets

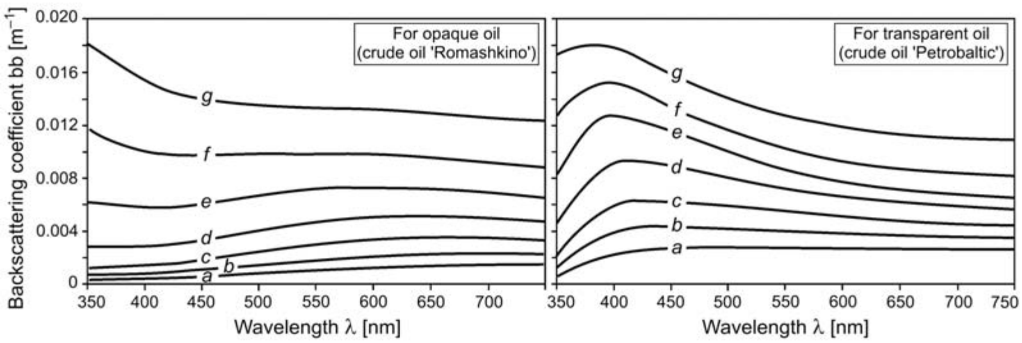

Fig. 1. Spectra of backscattering coefficient of oil-in-water emulsion and their dependence on size distribution of crude oil droplets. Letters *a*–*g* are explained in the Table.

increases. Maximum of *bb* reaches 0.018 m^{-1} independently of the kind of oil, whereas minimal values of *bb* (several ten-thousandths) are observed for fresh emulsion.

5. Results

The results obtained show the contribution of oil emulsion to ocean reflectance represented by two forms of proxy for reflectance which ratios are bb/a and $bb/(a + bb)$. This contribution of oil emulsion to shapes of spectra of both ratios can be similar or not – depending on the kind of oil. Namely, if transparency of oil is low (crude oil "Romashkino" well represents such oils), both ratios are similar (Fig. 2). On the contrary, when oil is relatively transparent (for example crude oil "Petrobaltic"),

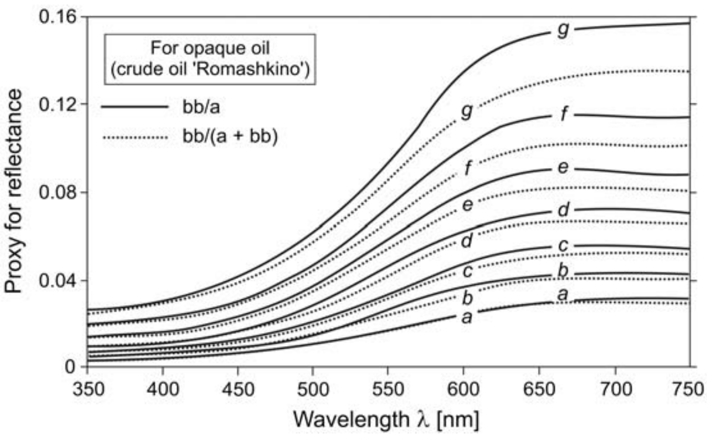

Fig. 2. Spectra of two versions of proxy for oil-in-seawater emulsion reflectance as the dependence on the size distribution of "Romashkino" crude oil droplets. Letters a–g are explained in the Table.

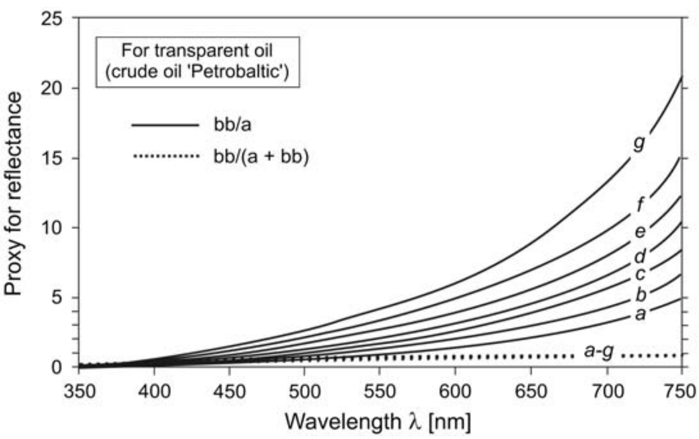

Fig. 3. Spectra of two versions of proxy for oil-in-seawater emulsion reflectance as the dependence on the size distribution of "Petrobaltic" crude oil droplets. Letters a–g are explained in the Table.

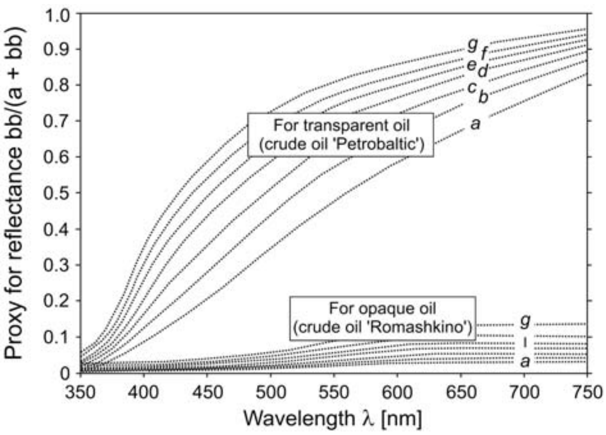

Fig. 4. Comparison of spectra of proxy for oil-in-seawater emulsion reflectance $bb/(a + bb)$ for two optically different types of oil. Plots are related to dotted lines placed in various scales in Figs. 2 and 3.

then spectra of bb/a and $bb/(a + bb)$ differ to some extent (Fig. 3). Both ratios bb/a and $bb/(a + bb)$ related to low-transparent oil are similar due to low value of bb in relation to a. However, for transparent oil bb in denominator begins to manifest itself strongly and $bb/(a + bb)$ approaches unity in long wavelength range (where transparency of oil is highest). At the same time reflectance represented by bb/a increases dramatically at long wavelengths even by several tens.

Generally, comparing curves of bb/a in Figs. 2 and 3, reflectance for "transparent oil" is several tens times greater than for "opaque oil". To indicate the scale of this fenomenon with reference to $bb/(a + bb)$ additional chart is made (Fig. 4) in which one can notice that $bb/(a + bb)$ for "transparent oil" is also greater than for "opaque oil" but on a smaller scale.

6. Discussion

Oil droplets can disturb various band ratio measurements for the defined water-body constituent concentration so that mineral particles may ruin remote measurements of chlorophyll concentration. Similar observations were made by WOZNIAK and STRAMSKI [3]. Fortunately oils do not occur in the marine environment on the same scale as mineral particles.

In the case when optical properties of seawater in a defined area are well known, then application of data presented in this paper facilitates the quantitative determination of deformations of spectra of reflectance caused by oil emulsion. On the other hand rapid disturbances in any remotely measured band ratio may indicate that pollution, for example oil-in-water emulsion, manifests its appearance. Additional specific remote methods or chemical analyses would have to be applied then. If oil emulsion is considered, spatial distribution of above water upward radiance can help detect specific kind of pollution, since introductory knowledge exists on oil emulsion impact on bidirectional reflectance distribution function [8]. Unfortunately, technical possibilities of measurements of bidirectional reflectance distribution function (BRDF) are limited and only rare cases of relations from measurements appear, *e.g.*, for above water measurements [9] or for below water measurements [10].

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