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MODEL OF SEAWATER POLLUTED BY OIL-IN-WATER EMULSION AS A RESPONSE TO THE INCREASING SHIPPING ACTIVITIES

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Abstract (150-250 words)

Intensive shipping affects marine environment in an extent degree, increasing seawater pollution by hazardous substances, including fuel oil and crude oil. Bilge water from ship power plants usually contains a mixture of dispersed oils, which form spherical droplets of diameter ranging from 0.01 to 10μm. Present methods for detection of dispersed oil require taking a water sample or putting a measuring device into seawater, which allows only to gather point data from limited locations. In order to meet the demand of remote monitoring of endangered zones, a study of optical properties of oil-in-water emulsions was conducted. Presented model of seawater polluted by oil-in-water emulsion can potentially enable remote optical detection of oil-in-water emulsion in visible bands. It is based on the fact that oil droplets become additional absorbents and attenuators in water body. Optical analyses consist of calculations of spectral absorption and scattering coefficients and scattering phase functions for oil emulsions on the basis of Lorentz-Mie theory including measurements of refractive index and determination of oil droplets size distribution. The radiative transfer theory is applied to simulate the contribution of oil emulsion to the remote sensing reflectance. Presented system for radiative transfer simulation is based on Monte Carlo code and it involves optical tracing of virtual photons.

Keywords: *oil pollution, oil-in-water emulsion, bilge water, remote sensing reflectance, seawater model*

1. Introduction

Pollution of marine waters with hazardous oil products has turned into a fundamental ecological problem in the last decades, since shipping technologies and industry became to develop rapidly. It has been therefore a subject of numerous research projects, including detection and identification of oil using optical methods [4,5,20,22]. The main source of seawater pollution are crude oils and petroleum products, in most cases descending from ship discharges and flowing in with the rivers. As an example, ship-related operational discharges of oil include the discharge of bilge water from machinery spaces, fuel oil sludge, and oily ballast water from fuel tanks. Most of oil pollution studies are focused on remote detection of extensive surface films with airborne and onboard satellite microwave radars and lidars. However, oil spill detection is focused on incidental accidents and does not deal with everyday pollution originating from shipping and maritime activities (e.g. routine shipboard operations such as cleaning of cargo tanks) and with the rivers from the land-based sources (e.g. agriculture and industrial activities, powerboat racing). The most significant amount of oil pollution enters the seas with river inflows containing industrial and agricultural runoff, or as a result of daily shipping activities and crude oil exploitation, or from natural seeps (GESAMP, 1993; GPA, 2002). Oil from this sources dissolves in a minor degree (0.2 – 0.7%) and is mostly found in the form of oil droplets dispersed in seawater (oil-in water emulsion). Oil emulsion amounts to over 80% of the total oil pollution in Baltic Sea estimated for 76 thousand tons per year (HELCOM, 1993). Among other sources, riverine input of oil products was estimated for 14-25 thousand tons yearly; sewage waters contribute for 4-14 thousand tons a year [4]. As the small-scale oil pollution is caused by human interference in marine environment, it should be also monitored on regular basis.

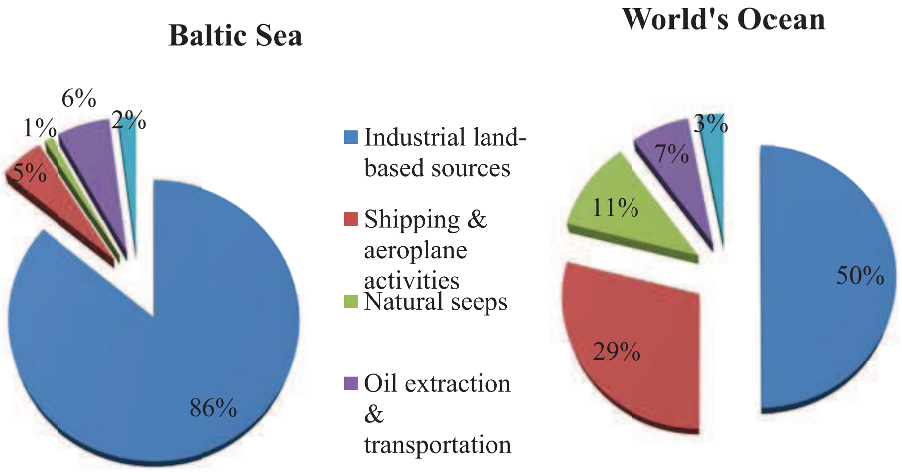

Fig. 1. Typical distribution of sources of oil pollution loads to the marine environment. (Source: Global Marine Oil Pollution Information Gateway, 2011)

There are currently no methods for remote detection of petroleum derivatives dispersed in seawater in the form of emulsion. Oil products can considerably modify optical properties of seawater surface layer, with accounts to the most exposed regions, like coastal zones, estuaries, marine transportation routes or oil fields. Oil droplets become additional light absorbents and scattering centres influencing the process of radiative transfer in seawater [11,14]. Their presence changes the inherent optical properties (IOPs) of seawater, and in consequence it influences the upwelling light stream (i.e. water-leaving radiance), which is the basis of algorithms for deriving ocean parameters from remote sensing, including satellite remote sensing. The range of changes of seawater apparent optical properties (AOPs) can be predicted by solving the radiative transfer equation (RTE) using numerical methods/models [8].

2. Optical properties of oil-in-water emulsions

The average concentration of dispersed oil droplets in seawater was estimated to the range from 10^9 m^{-3} in oceanic water to over 10^{13} m^{-3} in coastal waters, e.g. Pomeranian Bay (Baltic Sea) [3]. The most probable concentration of total hydrocarbons is 5-20 μg/kg (0.005 – 0.02 ppm) in the coastal part of the Gulf of Gdansk and 1-2 μg/kg (0.001 – 0.002 ppm) in the open Baltic Sea, but it can vary from immeasurable values to several ppm in the estuary and harbour zones [22]. According to the MARPOL convention, ship discharge waters may legally contain up to 15 ppm of oil. In some regions the limits are more restricted (e.g. up to 5 ppm in Canadian inland waters).

Preliminary analyzes on the possible influence of oil emulsion on upwelling light field showed that Lorentz-Mie theory can be applied to calculate inherent optical properties of oil-in-water emulsions [13]. Lorentz-Mie theory is a complete solution to Maxwell’s equation for scattering of electromagnetic waves by a homogeneous, spherical particle embedded in a nonabsorbing medium. It was also extended and applied for particles dispersed in absorbing media, such as seawater [1]. Oil dispersed in seawater was proved to form spherical droplets [6] and to fit the single scattering model [23]. According to Lorentz-Mie theory, the IOPs of oil-in-water emulsion can be computed on the basis of complex spectral refractive index of particles matter and particle droplets size distribution. Complex refractive indices of several oil products were given by Kaniewski et al. [5], by Otremba [12] in spectral (350-700 nm) and temperature (0-40°C) dependence, and by Rudz (Fig. 2).

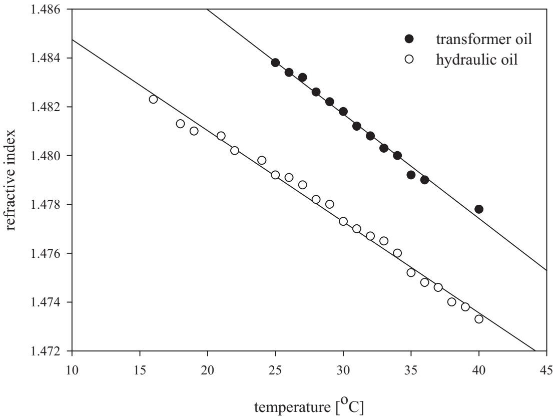

Fig. 2. Exemplary temperature dependence of refractive index for two types of oil

Exemplary oil droplets size distributions of two types of crude oil (*Petrobaltic* and *Romashkino*) were measured using an analogue microscope by Otremba and Krol [12,13]. They were also parameterized in relation to ageing time on water surface by a log-normal function. The study revealed that the majority of crude oil droplets dispersed in water had radius less than 2.5 µm. At the same time only a few droplets were larger than 5 µm in radius. It was shown that the maximum of size distribution function can shift from 0.4 µm to 0,05 µm in the period of two weeks causing a change in emulsion's optical properties. Lorentz-Mie theory was then applied to calculate light attenuation specific cross sections, spectral absorption and scattering coefficients [7]. Phase functions for oil-in-water emulsions of *Petrobaltic* and *Romashkino* crude oils were calculated by Otremba and Piskozub [15].

3. Radiative transfer model of seawater polluted by oil-in-water emulsion

Radiative transfer process in water body is described by equations linking the radiance, which was at first easier to measure, with inherent optical properties of seawater characterizing absorptive and scattering properties by its constituents (Eq. 1). Numerical radiative transfer simulations are used to predict the upwelling light stream using given seawater inherent optical properties. They compute the light propagation in seawater under specified conditions and allow evaluating the influence of each factor on remote sensing reflectance separately.

The model of marine environment consists of three elements:

(1) pure water – with spectral absorption coefficient given by Pope and Fry (1997) and spectral scattering coefficient given by Smith and Baker (1981);

(2) natural components of unpolluted seawater – with spectral absorption and attenuation coefficients measured in Baltic Sea using in-situ spectrophotometer AC-9 (WET Labs Inc.) during the ship cruises of Oceania r/v conducted by the Institute of Oceanology of Polish Academy of Sciences [21], and phase functions adapted from Petzold (1972), Mobley et al. [9] and Freda [2];

(3) oil droplets – with optical characteristics described above.

The time-independent Radiative Transfer Equation (RTE) for horizontally homogenous water, widely used in oceanography, is expressed by the following formula:

$$\cos\theta \frac{dL(z,\theta,\varphi,\lambda)}{dz} = -c(z,\lambda)L(z,\theta,\varphi,\lambda) + \int_{4\pi} L(z,\theta',\varphi',\lambda)\beta(z,\psi,\lambda)d\Omega' + S(z,\theta,\varphi,\lambda) \qquad (1)$$

where:

$c(z,\lambda)$ – total light beam attenuation coefficient equal to the sum of absorption coefficient and scattering coefficient: $c(z,\lambda) = a(z,\lambda) + b(z,\lambda)$,

$\beta(z,\psi,\lambda)$ – volume scattering function (describing angular distribution of scattering process),

ψ – scattering angle between the direction of incident light (θ,φ) and the direction of scattered light (θ',φ'),

$S(z, \theta,\varphi, \lambda)$ – source function describing emission and inelastic scattering into the beam (such as fluorescence or bioluminescence).

The above mentioned inherent optical properties of oil-in-water emulsions have been implemented into a system of radiative transfer simulation based on Monte Carlo code in order to estimate their influence on remote sensing reflectance [17,18]. Its general scheme is presented in the Fig. 3. The boundary conditions for radiative transfer simulations are the incident light zenith angle (modeling the sun height), statistics of sea surface waves parameterized by the wind speed (Cox and Munk distribution) and the sea bottom reflectance (which can be neglected by setting 1000 m depth). Simulations were conducted in the visible bands.

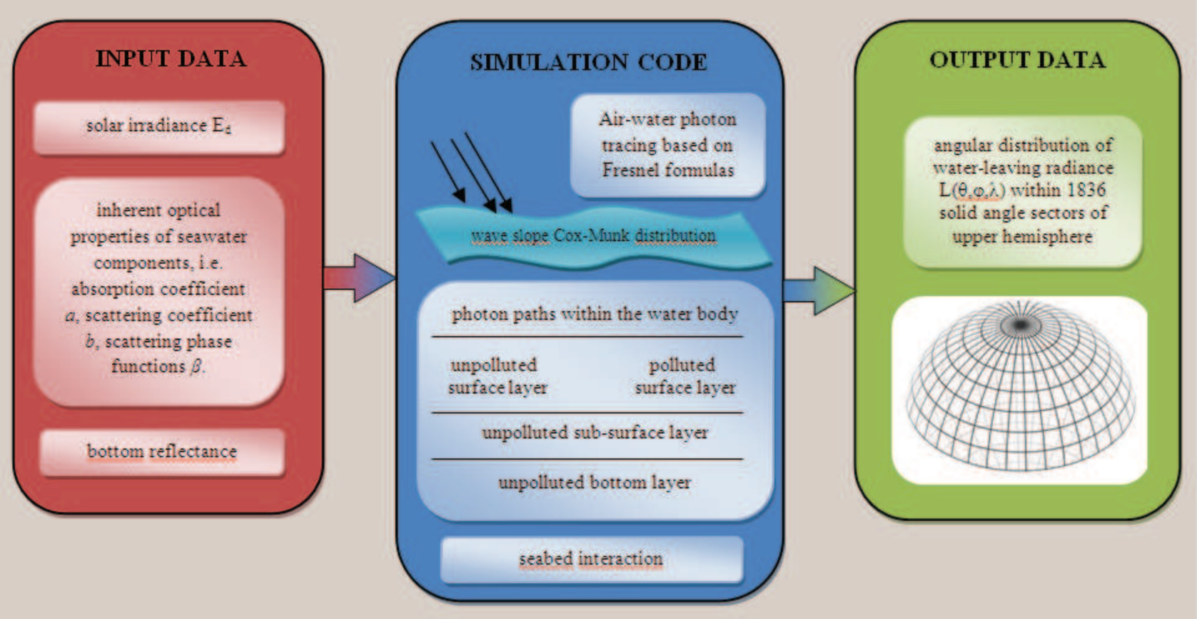

Fig. 3. General operational scheme of Monte Carlo radiative transfer simulation

Monte Carlo methods, developed during the second world war, are now widely used for radiative transfer modelling [8,10,11]. Monte Carlo methods effectively account for multiple scattering if the photon packets are followed until they contain a negligible amount of energy. In the presents study a model created by Piskozub (1992-2003) and developed by Otremba and Krol [12,13] and by Otremba and Rudz [16,19,20] was used. The Monte Carlo code involves optical tracing of photons within a given solid sector of upper hemisphere, on the basis of probability of visible light absorption and scattering by seawater constituents, including oil droplets. It allows conducting single-wavelength simulations limited to the wavelengths of which the seawater IOPs are known. It does not include inelastic scattering, which means that simulation results may differ from field measurements, especially in the spectral range of chlorophyll fluorescence (650-700 nm).

The code consists of a three-step interaction:

- Air – water interaction - probability of surface reflection is calculated from the refraction index of seawater according to Fresnel formulas.
- Absorption and elastic scattering within the water body. Probabilities are calculated respectively as follows:

$$p_a = 1 - e^{-a}, \qquad p_b = 1 - e^{-b} \tag{2}$$

- Interaction with the seabed (bottom reflectance coefficient).

4. Input data for radiative transfer simulation

Input data for Monte Carlo radiative transfer simulations are the inherent optical properties of all seawater components, i.e. spectral absorption coefficient a(λ), spectral scattering coefficient b(λ) and phase functions p(λ,θ) of the volume scattering function; and the boundary conditions, i.e. the zenith angle of incident light (modelling the sun height), statistics of sea surface waves parameterized by the wind speed (Cox and Munk distribution) and the sea bottom reflectance (neglected by setting 1000 m depth).

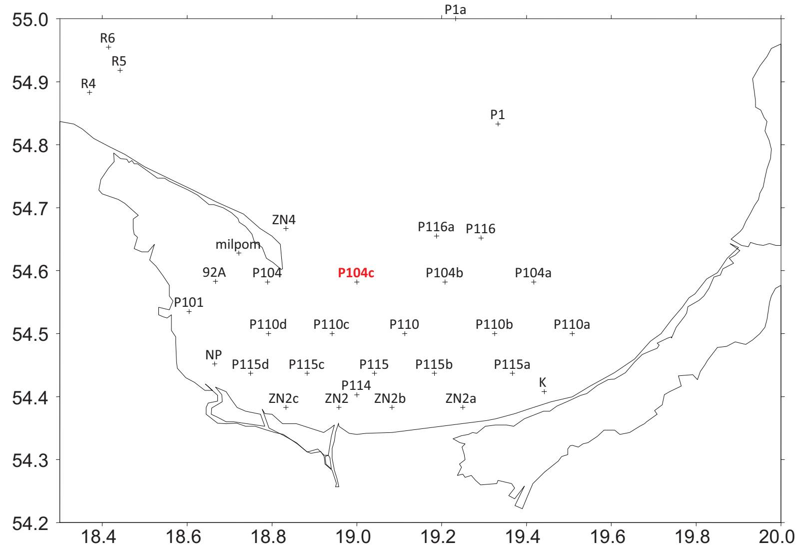

Fig. 4. Station P104c (54°35.0 N, 018°59.9 E) in the Gulf of Gdansk

The data for natural components of Baltic Sea were measured using *in-situ* spectrophotometer AC-9 (WET Labs Inc.) in the Gulf of Gdansk (station P104c) during the ship cruise of Oceania conducted by the Institute of Oceanology of Polish Academy of Sciences in April 2009 (Fig. 4). A three-layer seawater model were created in order to discretize continuous values for the purpose of radiative transfer numerical model. Only the surface layer (0-8 m) was then virtually polluted by 1 ppm of *Petrobaltic* and *Romashkino* crude oil separately (Fig. 3). Spectral dependences of absorption and scattering coefficients are shown in Fig. 5.

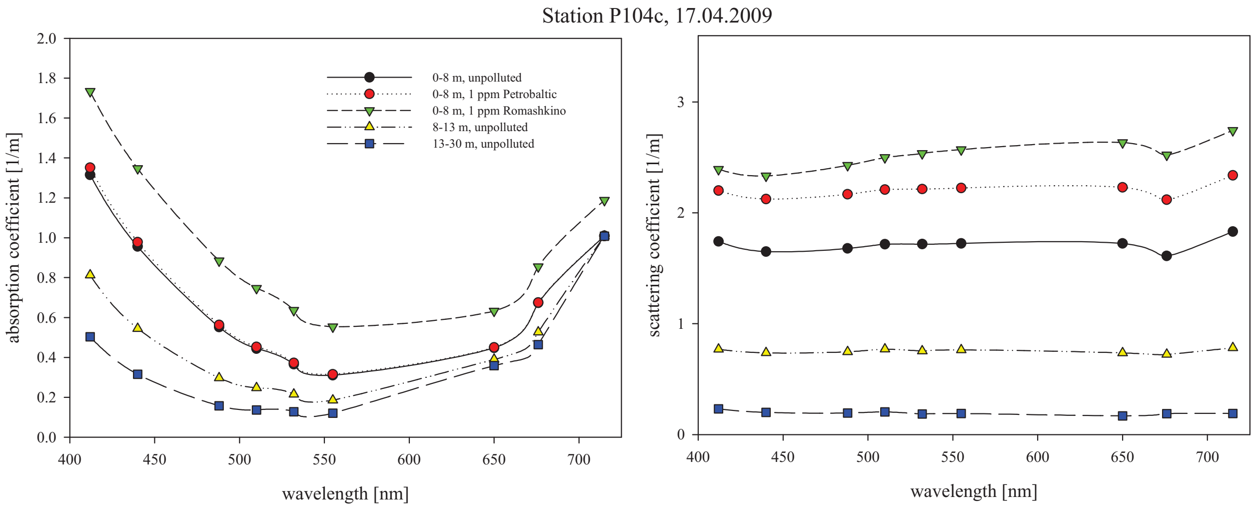

Fig. 5. Spectral distributions of absorption and scattering coefficients for a three-layer seawater model built on the basis of measurements in Baltic Sea at the stations 92A and P104c

5. Results and discussion

The water-leaving radiance L_w was calculated within the half angle of 7°, which corresponds to the Ramses Trios hyperspectral radiometers field of view. Remote sensing reflectance R_{rs} was calculated as the ratio of the water-leaving radiance to the downward sky irradiance E_d:

$$R_{rs} = \frac{L_w}{E_d}. \tag{3}$$

Simulations were conducted for a flat sea surface and for the sea surface characterized by the wind speed of 5 m/s. The wind speed measured at the station P104c was 6.7 m/s and the sun elevation was 44° (i.e. zenith angle set as a direction of incident photons). The output data is the spectral distributions of the upward radiance L(θ,φ,λ) within 1836 solid angle sectors.

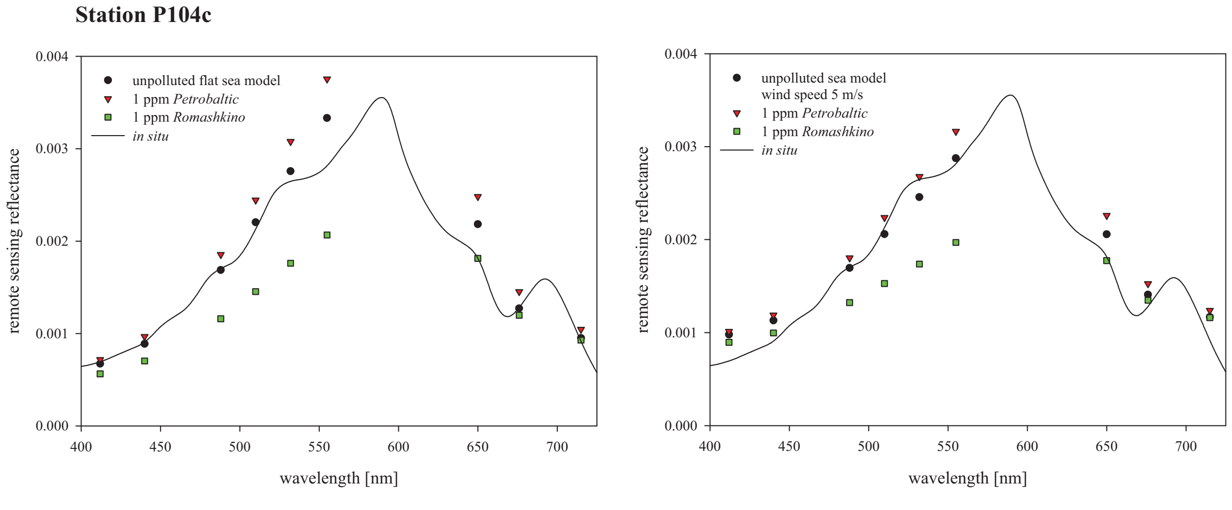

Fig. 6. Remote sensing reflectance from in situ measurements (solid line) in Baltic Sea and simulated results (points) for unpolluted seawater and for seawater polluted by 1 ppm of Petrobaltic and Romashkino crude oil emulsion, with the assumption of a flat sea surface (left graph) or for the sea surface parameterized by the wind speed of 5 m/s. (right graph).

The addition of *Petrobaltic* crude oil caused less than 2% increase of the total absorption coefficient of the surface seawater layer in the entire considered spectral range, and a significant increase (almost 30% for central wavelengths) of the total scattering coefficient. *Romashkino* emulsion significantly increased the total absorption coefficient for 60-74% and gave over 40% contribution to the scattering coefficient, in both cases slightly increasing with the wavelength (see Tab. 1).

Stronger absorption of *Romashkino* implies a decrease of the remote sensing reflectance. The impact of scattering coefficient depends on the angular distribution of the volume scattering function. High scattering in forward directions would drop the upward light stream and the advantage of backscattering would result in the increase of the water-leaving radiance. Addition of *Petrobaltic* emulsion barely affects seawater absorption coefficient, therefore the influence of scattering on remote sensing reflectance is more remarkable. Relatively high backscattering ratio can be explained by the domination of small oil droplets. The drop of R_{rs} caused by *Romashkino* emulsion together with its high absorption and high scattering coefficients suggest the stronger impact of absorption on the upwelling light stream. This could be a result of the advantage of forward scattering over backscattering caused usually by larger particles.

Tab. 1. Percentage increase of absorption and scattering coefficients in the surface 8 m layer caused by addition of 1 ppm of oil emulsion.

P104c	*Petrobaltic*		*Romashkino*	
wavelength [nm]	a [m^{-1}]	b [m^{-1}]	a [m^{-1}]	b [m^{-1}]
488	1.9	29.1	60.2	44.7
510	1.8	28.8	68.1	45.6
532	1.8	28.9	74.0	47.6

Tab. 2. Percentage increase or decrease (signed with "-") of remote sensing reflectance caused by addition of oil emulsion to the model of marine environment.

P104c	*Petrobaltic*		*Romashkino*		Model accuracy	
wavelength [nm]	Flat sea	5 m/s	Flat sea	5 m/s	Flat sea	5 m/s
488	9.9	6.4	-31.2	-22.0	-1.1	-0.6
510	11.0	8.7	-34.0	-25.8	1.2	-5.4
532	11.6	9.1	-36.1	-29.3	4.3	-7.1

Simulated R_{rs} for unpolluted seawater was compared with *in situ* measurements in the Baltic Sea. The best model accuracy was achieved for central wavelengths of 488, 510 and 532 nm and it was 1-7%. The results shown in the Fig. 6 reveal that in considered spectral range the light *Petrobaltic* crude oil caused 9-11% increase of R_{rs} while the heavy *Romashkino* reduced R_{rs} for 22-36% (Tab. 2).

6. Summary

Radiative transfer process is the physical basis for all ocean colour remote sensing and must be fully understood when evaluating the performance of any particular sensor and retrieved products. There is therefore a need of comprehensive datasets containing all the information necessary for a complete radiative transfer calculation, which is especially important in optically complex waters. Interpretation of reflectance spectra requires a simultaneous multi-parameter analysis of light propagation in seawater. The influence of each IOP parameter on remote sensing reflectance is non-linear and highly variable. However, it can be studied separately in terms of a numerical radiative transfer simulation. The introduced study begins a supplement of the missing knowledge about optical properties of oil-in-water emulsions and their contribution to the upwelling light field measured with remote sensing methods. The presence of high-absorptive and low-backscattering crude oil emulsions can be easily remarked on any marine water background, as they would cause a significant decrease of remote sensing reflectance. Those features usually imply large-sized droplets which scatter in forward directions. On the other hand, high backscatter fraction observed for small-sized particles should strengthen the water-leaving radiance, but that effect may be shadowed by high absorption. It seems that absorption spectrum of oil emulsion decides of its potential detectability in turbid waters. In clean ocean waters the backscatter fraction seems to be more significant. A separate study should be performed in order to determine the IOPs for more commonly used crude oils and their mixtures. Further study would also enable successive investigations on seawater affected by oil emulsion. As an example, the radiative transfer model can contribute to the improvement of satellite algorithms accuracy for determination of water parameters derived from the water-leaving radiance, regarding coastal zones, estuaries, main marine transportation routes and oil extraction areas. It will also improve the accuracy of shipboard and offshore measurements, which are used for calibration of satellite data and for other seawater optical observation and monitoring. It is also possible that it will enable the remote detection of oil-in-water emulsion.

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References

[1] Babin, M., Morel, A., Fell, V. F.-S. F., Stramski, D., *Light scattering properties of marine particles in coastal and open ocean waters as related to the particle mass concentration*, Limnology and Oceanography, 48 (2), pp. 843-859, 2003.

[2] Freda W., *Parameterization of light scattering phase function in the marine environment,* Ph. D. thesis (in Polish), Inst. Oceanol. PAS, Sopot 2011.

[3] Gurgul H., Staroń W., *The oil substances concentration of the River Świna*, Proc. 19th Conf. Of the Baltic Oceanographers, pp. 638-647, Sopot 1994.

[4] Hagerhaal B., *Where does the oil come from?* WWF Baltic Bulletin, pp. 2-9, 1995.

[5] Kaniewski, E., Otremba, Z., Stelmaszewski, A., Targowski, W., *Spectral relationships of the complex refractive index of selected kinds of oil*, Proc. XIX Conf. Baltic Oceanogr., pp. 158-165, Sopot 1994.

[6] Krol T., *A computed model of the Mie coefficients for spherical absorbing and scattering particles*, Stud. Mater. Oceanol. ((in Polish), 49, pp. 43-62, 1985.

[7] Król, T., Stelmaszewski, A., Freda, W., *Variability In the optical properties of a crude oil – seawater emulsion*, Oceanologia, 48 (S), pp. 203-211, 2006.

[8] Leathers, R. A., Downes, T. V., Davis, C. O., Mobley, C. D., *Monte Carlo Radiative Transfer. Simulations for Ocean Optics: A Practical Guide*, Naval Research Laboratory, Washington, DC, 2004.

[9] Mobley C. D., Sundman L. K., Boss E., *Phase function effects on oceanic light fields*, Appl. Opt. 41(6), pp. 1035–1050, 2002.

[10] Mobley, C. D., *Estimation of the remote-sensing reflectance from above-surface measurements*, Appl. Optics 38(36), pp. 7442-7455, 1999.

[11] Mobley, C. D., *Light and Water: Radiative Transfer in Natural Waters*, Academic Press, 1994.

[12] Otremba Z., Król T., *Modelling of the crude oil suspension impact on inherent optical parameters of the coastal seawater*, Pol. J. Environ. Stud., 11(4), pp. 407-411, 2002.

[13] Otremba, Z., Krol, T., *Light attenuation parameters of polydisperse oil-in-water emulsions*, Optica Applicata, XXXI (3), pp. 600-609, 2001.

[14] Otremba, Z., *Oil droplets as light absorbents in seawater*, Opt. Express 15 (14), pp. 8592-8597, 2007.

[15] Otremba, Z., Piskozub, J., *Phase functions of oil-in-water emulsions*, Optica Appl.. XXXIV (1), pp. 93-99, 2004.

[16] Otremba, Z., Rudz, K., *Ocean optics in application to remote detection of an oil-in-water emulsion originating from the engine room*, Journal of KONES Powertrain and Transport, 17 (3), Warsaw 2010.

[17] Rudz, K., Baszanowska, E., Rohde, P., Zielinski, O., *Fluorescence Methods and Monte Carlo Radiative Transfer Simulation Applied to Oil Detection in Baltic Sea*, Joint Proceedings, 24, pp. 52-59, Bremerhaven 2011.

[18] Rudź, K., Darecki, M., Toczek, H., *Modelling of seawater polluted by light and heavy crude oil droplets,* Journal of KONES Powertrain and Transport, 19 (2), pp. 473-480, Warsaw 2012.

[19] Rudź, K., *Emulsified Fuels of Machine Origin in Seawater – a Contribute to Remote Detection*, Journal of KONES Powertrain and Transport, 18 (3), pp. 375-382, Warsaw 2011.

[20] Rudz, K., *Skutki zrzutu olejowego w polu światła w morzu,* Zeszyty Naukowe Akademii Morskiej w Gdyni, nr 64, pp. 99-108, Gdynia 2010

[21] Sagan, S., *Rzeczywiste właściwości optyczne wód Bałtyku*, Polska Akademia Nauk, Rozprawy i monografie 21/2008.

[22] Stelmaszewski, A., *Determination Of Petroleum Pollutants In Coastal Waters Of The Gulf Of Gdańsk*, Oceanologia, 51(1), pp. 85–92, 2009.

[23] Stelmaszewski, A., Król, T., Toczek, H., *Light scattering in Baltic crude oil - seawater emulsion*, Oceanologia, 51(3), pp. 405-414, 2009.