Journal of KONES Powertrain and Transport, Vol. 19, No. 2 2012

MODELLING OF SEAWATER POLLUTED BY LIGHT AND HEAVY CRUDE OIL DROPLETS

Kamila Rudź

Gdynia Maritime University, Department of Physics
Morska Street 81-87, 81-225 Gdynia, Poland
tel.:+48 58 6901504, fax: +48 58 6901399
e-mail: kamilar@am.gdynia.pl

Mirosław Darecki

Institute of Oceanology, Polish Academy of Sciences
Powstańców Warszawy Street 55, 81-712 Sopot, Poland
tel.: +48 58 7311818, fax: +48 58 5512130
e-mail: darecki@iopan.gda.pl

Henryk Toczek

Gdynia Maritime University, Department of Physics
Morska Street 81-87, 81-225 Gdynia, Poland
tel.:+48 58 6901385, fax: +48 58 6901399
e-mail: hento@am.gdynia.pl

Abstract

Significant amounts of crude oil transported from offshore fields to the refineries using tankers or pipelines, demand increased control of seawater pollution. Tanker accidents resulting in oil spills drive much attention, as they influence local marine life and coastal industry. However, the most significant annual amount of crude oil enters the sea in the form of oil-in-water emulsion as a result of standard tanker operations, offshore oil extraction and daily work of refineries. Many branches of science are challenged to provide new methods for oil detection, less expensive, more sensitive and more accurate. Remote satellite or airborne detection of large oil spills is possible using joint techniques as microwave radars, ultraviolet laser fluorosensors and infrared radars. Some methods are capable to deal with oil streaks detection and estimation of oil thickness. Although there is currently, no method to detect small concentration of oil droplets dispersed in seawater. Oil droplets become additional absorbents and attenuators in water body. They significantly change seawater inherent optical properties, which imply the change of apparent optical properties, detectable using remote sensing techniques. To enable remote optical detection of oil-in-water emulsion, a study of optical properties of two types of crude oil was conducted. Radiative transfer theory was applied to quantify the contribution of oil emulsion to remote sensing reflectance (R_{rs}). Spectra of R_{rs} from in situ measurements in Baltic Sea were compared to R_{rs} spectra of seawater polluted by 1 ppm of crude oil emulsion, collected using radiative transfer simulation. The light crude oil caused a 9-10% increase of R_{rs} while the heavy one reduced R_{rs} up to 30% (model accuracy stayed within 5% for considered spectral range). Results are discussed concerning their application to shipboard and offshore oil content detection.

***Keywords**: oil pollution, remote sensing reflectance, Monte Carlo simulation, radiative transfer, oil-in-water emulsion*

1. Introduction

Oil pollution in the sea is not only a subject of scientific or political interest, but it is also an issue of great public concern. As a consequence of increasing global refinery products demand, the International Maritime Organization (IMO) has been working to prevent this kind of pollution in the frame of MARPOL (International Convention for the Prevention of Pollution from Ships), since the early seventies of 20th century. In 1974, the first Baltic Marine Environment Protection

Commission signed the Helsinki Convention to deal with growing pollution loads to the Baltic Sea, including oil pollution. Also, the European Union created a law on the disposal of waste oils (Council Directive 87/101/EWG) in order to limit their negative influence to the marine environment. Oil pollution is currently one of the major threats to the marine ecosystem as well as to the tourism and economical attractiveness of coastal zones. Oil loads to the world's ocean were estimated for over 3 million tons per year (IMO, 1983).

Oil products enter the marine environment from different sources (Fig. 1). In addition to oil spills at sea, the vast majority (approximately 60%) of oil input into the Baltic Sea comes from land-based sources via rivers or directly to the sea through run-off as well as discharges from municipal wastewater treatment plants and industries. The next significant source, reaching up to 30%, are normal shipping and airplane activities, like maintenance of ships, boats and jet engines. Natural seeps can contribute up to 11% in some regions. Oil from these 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). Usually less than 10% of oil pollution comes from oil transportation: tanker operations, accidents, illegal discharges (HELCOM, 2011).

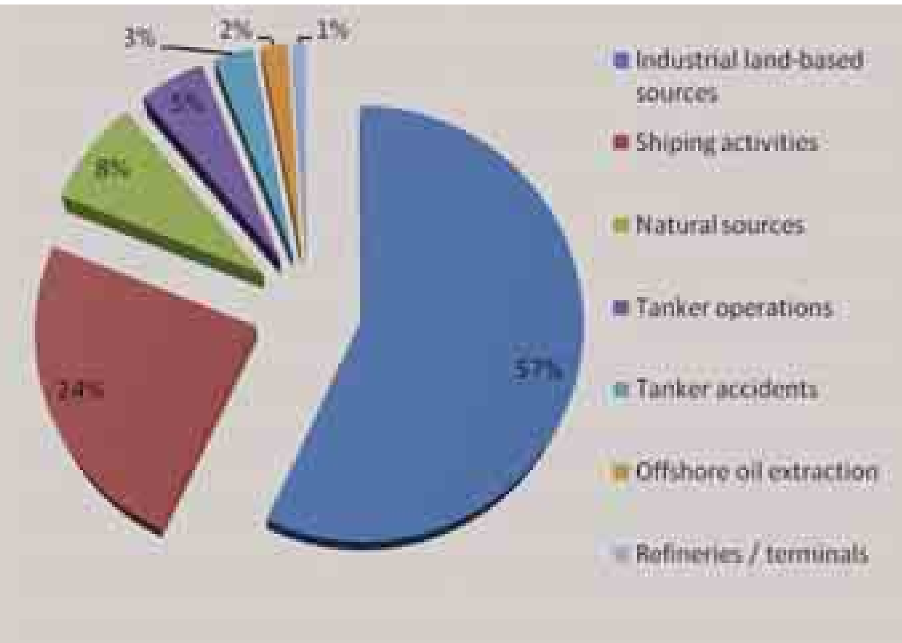

Fig. 1. Typical distribution of sources of oil pollution loads to the marine environment (Source: Global Marine Oil Pollution Information Gateway, 2011)

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 such basins like Pomeranian Bay. 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 [19]. 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). Oil droplets become additional light absorbents and scattering centres influencing the process of radiative transfer in seawater [12]. Their presence modifies the inherent optical properties of seawater, and in consequence it changes the upwelling light stream (water-leaving radiance), which builds algorithms for deriving ocean parameters from remote sensing (including satellite remote sensing).

Ocean colour - the spectral distribution of the water leaving radiance - is an important parameter carrying information about seawater constituents and processes within water body. Currently the satellite ocean colour data are widely used to monitor and understand the global and local climate change, to forecast and observe the accidents (such as harmful algal blooms, hurricanes or sand storms), and to gather useful information for offshore and coastal zone management [22, 23]. The accuracy and correct interpretation of ocean colour data and related parameters depend on suitable atmospheric correction, appropriate corrections for geometry of moving sun-sensor-ocean system, removal or reduction of noises (e.g. sea surface specular reflection) and, on the complete, accurate information on the interactions between seawater components and the light field [3, 9]. Satellite ocean colour data are verified and validated by sea-level data [23]. To meet the growing requirements of a good agreement between satellite and sub-satellite measurements (reaching 2%) it is necessary to apply local methods and models with accounts to all seawater constituents, such as mineral particles [24], CDOM [6], micro-bubbles [21], or oil droplets [12]. The knowledge about inherent optical properties of those additional components and the analysis of their influence on the upwelling light stream can contribute to the improvement of the accuracy of ocean colour algorithms for over 50% in case of mineral particles and up to 10% in case of air bubbles. Initial investigation shows that oil droplets can change the remote sensing reflectance for over 30% [18].

2. Method - radiative transfer in seawater polluted by oil-in-water emulsion

Initial analyzes on the possible influence of oil emulsion on upwelling light field were conducted in a narrow range. Otremba and Krol [11] showed that Lorentz-Mie theory could be applied to calculate inherent optical properties of oil-in-water emulsions. 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 tiny spherical droplets and to fit the single scattering model [20]. According to Lorentz-Mie theory, the IOPs of oil 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. [4] and by Otremba [15] in spectral (350-700 nm) and temperature (0-40°C) dependence. Exemplary oil droplets size distributions of two types of crude oil (*Petrobaltic* and *Romashkino*) were measured using an analogue microscope by Otremba and Krol [11]. 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 distribution function could 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 [13].

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. 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 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]. Monte Carlo methods, developed during the second world war, are now widely used for radiative transfer modelling purposes [8, 10], particularly in solution of time-dependent radiative transfer equation or 3D problems, such as modelling the influence of sensors' geometry on measured parameters [5], corrections for self-shadowing of sensors and measurement platforms [16], or analysis of light propagation in turbulent media [2]. 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 [11] and by Otremba and Rudz [14] 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).

3. Input data for radiative transfer simulation

Input data for both types of radiative transfer simulations are the inherent optical properties of all seawater components and the boundary conditions. The IOPs are spectral absorption coefficient a(λ), spectral scattering coefficient b(λ) and phase functions p(λ,θ) of the volume scattering function. The boundary conditions are the incident light zenith angle (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). The model of marine environment is constructed of pure water, natural components of unpolluted seawater and of oil droplets. The inherent optical properties of pure water were given by Petzold (1972) – phase functions, Smith and Baker (1981) – spectral scattering coefficients, Pope and Fry (1997) - spectral absorption coefficients [10].

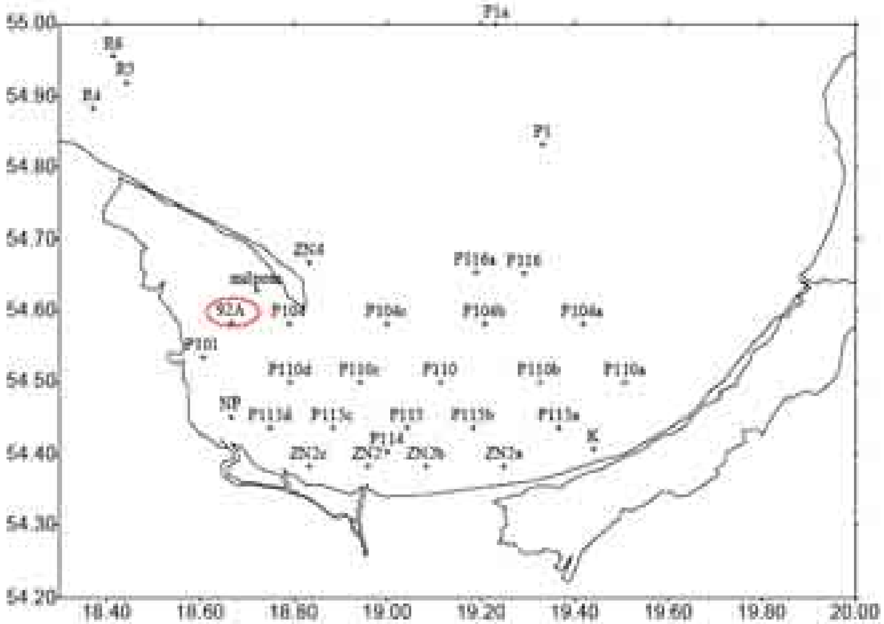

Fig. 2. Station 92A (54° 34,8920 N, 18° 39,7331 E) in the Gulf of Puck

The data for natural components of Baltic Sea were measured using *in-situ* spectrophotometer AC-9 (WET Labs Inc.) at the entry to the Gulf of Puck (station 92A, Fig. 2) during the ship cruise of Oceania conducted by the Institute of Oceanology of Polish Academy of Sciences in April 2009 (Fig. 3). The input data for oil-in-water emulsions were taken from previous studies [7, 13]. A three-layer seawater model was 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.

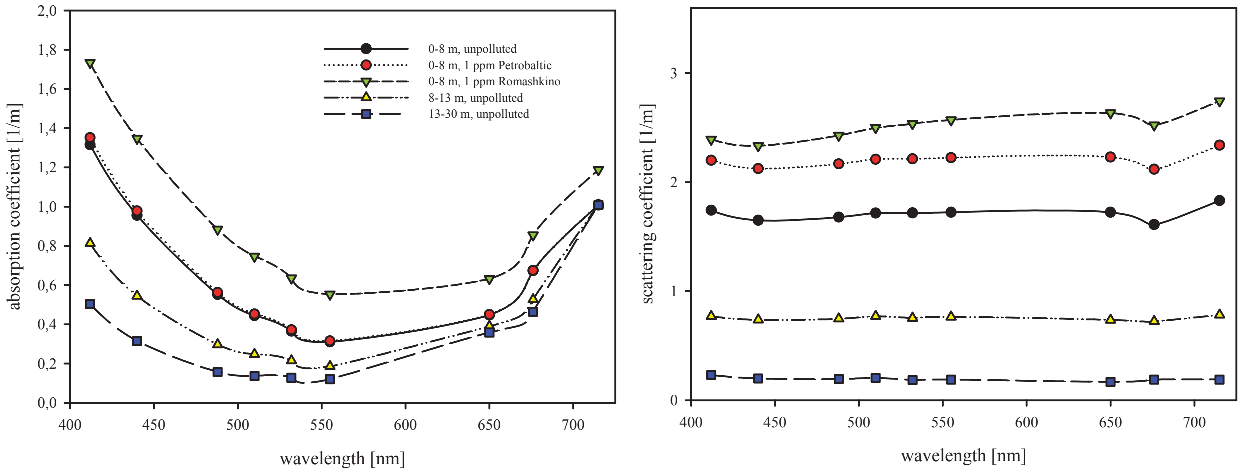

Fig. 3. Spectral distributions of absorption and scattering coefficients for a three-layer seawater model built on the basis of measurements in Baltic Sea at the station 92A

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 92A was 13.2 m/s, which exceed the range of application of the Cox-Munk slope distribution. The real sun elevation of 61˚ (zenith angle) was set as a direction of incident photons.

4. Results and discussion

Radiative transfer simulation output data were the spectral distributions of the upward radiance L(θ,φ,λ) within 1836 solid angle sectors. 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:

$$R_{rs} = \frac{L_w}{E_d}. \tag{1}$$

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 constant increase (approximately 27%) of the total scattering coefficient. *Romashkino* emulsion doubled the total absorption coefficient and gave over 40% contribution, slightly increasing with the wavelength, to the scattering coefficient of the surface layer of the seawater model (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.

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

	Petrobaltic		*Romashkino*	
wavelength [nm]	a [m^{-1}]	b [m^{-1}]	a [m^{-1}]	b [m^{-1}]
488	1.7	27.1	54.5	41.7
510	1.6	26.9	62.0	42.8
532	1.6	27.2	67.5	45.0

Addition of *Petrobaltic* emulsion barely affects seawater absorption coefficient, therefore the influence of scattering on remote sensing reflectance is more remarkable.

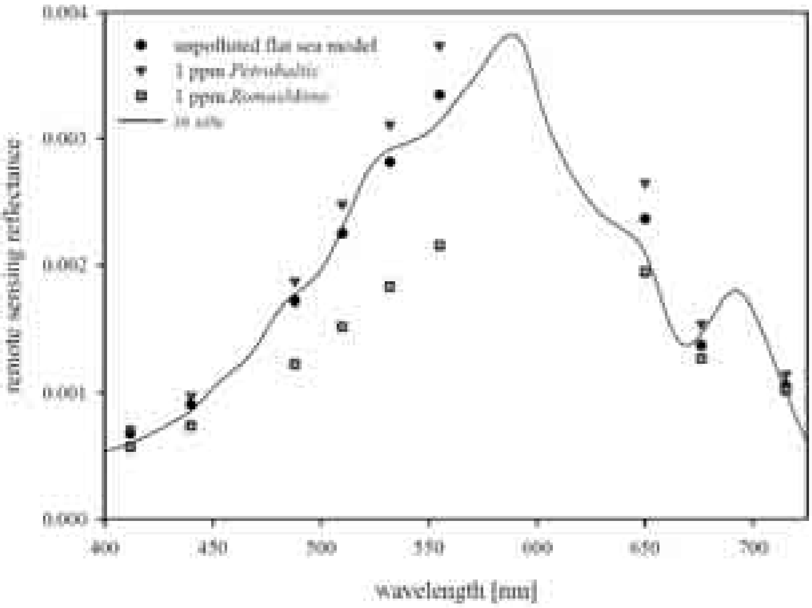

Fig. 4. Remote sensing reflectance from in situ measurements (solid line) in Baltic Sea (station 92A) and simulated results (points) for unpolluted seawater and for seawater polluted by 1 ppm of Petrobaltic and Romashkino crude oil emulsion, with the assumption of a flat sea surface

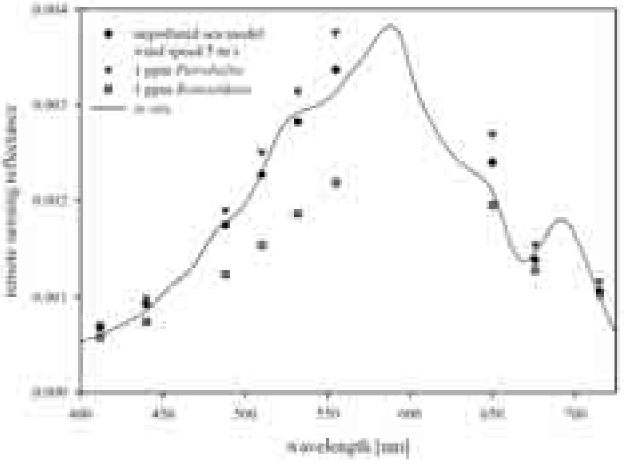

Fig. 5. Remote sensing reflectance from in situ measurements (solid line) in Baltic Sea (station 92A) and simulated results (points) for unpolluted seawater and for seawater polluted by 1 ppm of Petrobaltic and Romashkino crude oil emulsion, for the sea surface parameterized by the wind speed of 5 m/s

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.

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 2-4%. The results shown on the Fig. 4 and 5 reveal that in considered spectral range the light *Petrobaltic* crude oil caused 9-10% increase of R_{rs} while the heavy *Romashkino* reduced R_{rs} for 29-35% (Tab. 2).

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

	Petrobaltic		*Romashkino*		Model accuracy	
wavelength [nm]	Flat sea	5 m/s	Flat sea	5 m/s	Flat sea	5 m/s
488	9.1	8.9	-28.7	-29.3	3.1	1.9
510	10.3	10.4	-32.3	-32.0	4.1	3.4
532	10.6	11.3	-34.9	-34.2	3.1	2.8

The influence of wind speed on remote sensing reflectance is not remarkable in comparison with the impact of oil emulsion. It does not seem to affect the model accuracy.

5. Summary

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 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 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.

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] Bogucki, D. J., Piskozub, J., Carr, M.-E., Spiers, G. D., *Monte Carlo simulation of propagation of a short light beam through turbulent oceanic flow*, Opt. Express 15 (21), pp. 13988-13996, 2007.

[3] Gernez, P., Stramski, D., Darecki, M., *Vertical changes in the probability distribution of downward irradiance within the near-surface ocean under sunny conditions*, J. Geophys. Res.-Oceans, 2011.

[4] 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., 1994.

[5] Kirk, J. T. O., *Monte Carlo modeling of the performance of a reflective tube absorption meter*, Appl. Opt. 31, pp. 6463–6468, 1992.

[6] Kowalczuk, P., Stedmon, C. A., Markager, S., *Modeling absorption by CDOM in the Baltic Sea from season, salinity and chlorophyll*, J. Mar. Chem. 101 (1), pp. 1-11, 2006.

[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] Lysiak-Pastuszak, E., Bartoszewicz, M., Bradtke, K., Darecki, M. et al., *A study of episodic*

events in the Baltic Sea - combined in situ and satellite observations, Oceanologia, 2012.

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

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

[12] Otremba, Z., *Oil Droplets As Light Absorbents In Seawater*, Opt. Express 15 (14), pp. 8592-8597, 2007.

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

[14] 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.

[15] Otremba, Z., *The impact on the reflectance in VIS of a type of crude oil film floating on the water surface*, Opt. Express, 7, pp. 129-134, 2000.

[16] Piskozub, J., *Effect of 3-D instrument casing shape on the self-shading of in-water upwelling irradiance*, Opt. Express, 12 (14), pp. 3144-3148, 2004.

[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, Bremerhaven 2011.

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

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

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

[21] Terril, E. J., Melville, W. K., Stramski, D., *Bubble entrainment by breaking waves and their influence on optical scattering in the upper ocean*, J. Geophys. Res., 106 (C8), pp. 16815-16823, 2001.

[22] Wozniak, B., Bradtke, K., Darecki, M. et al., *SatBaltyk - A Baltic environmental satellite remote sensing system - an ongoing project in Poland. Part 1: Assumptions, scope and operating range*, Oceanologia, 2011.

[23] Wozniak, B., Bradtke, K., Darecki, M. et al., *SatBaltyk - A Baltic environmental satellite remote sensing system - an ongoing project in Poland. Part 2: Practical applicability and preliminary results*, Oceanologia, 2011.

[24] Wozniak, S. B., Stramski, D., *Modeling The Optical Properties Of Mineral Particles Suspended In Seawater And Their Influence On Ocean Reflectance And Chlorophyll Estimation From Remote Sensing Algorithms*, Appl. Opt., 43 (17), pp. 3489-3503, 2004.