EMULSIFIED FUELS OF MACHINE ORIGIN IN SEAWATER – A CONTRIBUTE TO REMOTE DETECTION

Kamila Rudz

Gdynia Maritime University, Department of Physics
Morska Street 81-87, 81-225 Gdynia, Poland
tel.+48 58 6901284, fax: +48 58 6901399
e-mail: kamilar@am.gdynia.pl

Abstract

Development of industry and trade in the last few decades caused a huge increase in the pollution of the world's oceans. Substantial contributors to marine pollution come with the rivers from land-based sources including the by-products of industry, run-off from agriculture activities such as biocides as well as effluents from urban areas. Moreover, a significant amount of marine pollution is caused by shipping and maritime activities. The operation of ship plants gives a real possibility for engine oils and fuels to reach the marine environment. Discharge waters contain a certain amount of petroleum derivatives in the form of dispersed droplets (oil-in-water emulsion). The presence of oil emulsion cause measurable changes in the optical properties of seawater. It is conceptually possible to detect these changes using a standard radiance or irradiance reflectance meter. Hence, a set of radiative transfer simulation has been carried out. This paper presents a computed photon trace simulation based on the Monte Carlo code, applied to the marine environment. The results are presented as reflectance spectra for the models of Baltic Sea and ocean water both pure and polluted by oil emulsion. It is shown that even small amounts of petroleum pollution rise the values of irradiance reflectance and cause a spectral shift by certain conditions. A possibility for remote evaluation of oil pollution is discussed as well as the perspective for improving the interpretation of shipboard and offshore light field analyses.

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

1. Introduction - optics of seawater

Pollution of marine waters with oil emulsion has turned into a fundamental ecological problem within the last few decades, since ship 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 [1, 3, 6]. The main source of seawater pollution are crude oils and petroleum products, in most cases descending from ship discharges or underwater oil pipeline leakages 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 oil surface films with airborne and onboard satellite microwave radars (scatterometers, Synthetic Aperture Radars). Oil spill detection is based on smoothing of wind-generated capillary waves by oil film [3]. It is successfully applied in medium wind speed conditions in open ocean and coastal waters, as long as the dimension of oil slick is higher than sensor's resolution. Oil spill detection is focused on incidental accidents and does not deal with everyday pollution coming from shipping and maritime activities (e.g. routine shipboard operations such as the cleaning of cargo tanks) and with the rivers from the land-based sources (e.g. agriculture activities, powerboat racing). As the small-scale oil pollution is caused by human interference in marine environment, it should be also monitored on regular basis. There are currently no methods for remote detection of engine oil dispersed in seawater in the form of emulsion. However, it is conceptually possible to extract the information about the concentration and the sort of oil pollutant from the water-leaving light field analyses.

The sunlight entering the sea surface is a stream of photons. Photons are on the one hand described as electromagnetic wave packets carrying energy and on the other hand as particles carrying linear momentum and angular momentum. From oceanographic point of view the electromagnetic interaction between photons and seawater is sufficient to predict light propagation in water body [5]. The fundamental quantity of light in radiometric terms is *radiance* – a measure of the energy of light. The radiance L is measured operationally as a function of time, location, direction and wavelength and usually expressed in [W m^{-2} sr^{-1} nm^{-1}]:

$$L\left(x,y,z,t,\varphi,\theta,\lambda\right)=\frac{\Delta Q}{\Delta t\ \Delta A\ \Delta\Omega\ \Delta\lambda}, \tag{1}$$

where:
ΔQ - amount of light energy,
Δt - unit of detection time,
ΔA - unit area detecting light energy,
$\Delta\Omega = \sin\theta\, d\theta\, d\varphi$ - solid angle unit (due to detector viewing),
θ, φ - respectively zenith and azimuth angle of light beam propagation,
$\Delta\lambda$ - spectral resolution of measurement,
x,y,z - Cartesian coordinates.

The incident solar radiance is lost due to absorption and scattering out of the beam and gains due to elastic scattering into the beam from all other directions as well as due to emission or inelastic scattering. Conservation of energy expressed by the balance of radiance in seawater is described by Radiative Transfer Equation (RTE). The time-independent RTE for horizontally homogenous water, widely used in oceanography, is expressed by the following formula [5]:

$$\cos\theta\frac{dL\left(z,\theta,\varphi,\lambda\right)}{dz}=-c\left(z,\lambda\right)L\left(z,\theta,\varphi,\lambda\right)+\int_{4\pi}L\left(z,\theta',\varphi',\lambda\right)\beta\left(z,\psi,\lambda\right)d\Omega'+S\left(z,\theta,\varphi,\lambda\right), \tag{2}$$

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).

Inherent optical properties of seawater (IOPs), as absorption coefficient and volume scattering function, are medium-dependent. It means they do not depend on the light field in the water, but only on the concentration, size distribution, and compositions of the particulate and dissolved material in the water. Whereas apparent optical properties (AOPs) strongly depend on IOPs and should weakly depend on the lightening and wind conditions. Therefore IOPs can be measured *in situ* or in the laboratory, while AOPs can only be measured *in situ* by remote sensors. Radiometers are designed to measure radiance and irradiance of water body. As a measure of downwelling light field, the most commonly used radiometric variable is spectral plane irradiance [5]:

$$E_d\left(x,y,z,t,\lambda\right)=\int_{\varphi=0}^{2\pi}\int_{\theta=0}^{\frac{\pi}{2}}L\left(x,y,z,t,\theta,\varphi,\lambda\right)\left|\cos\theta\right|\sin\theta\, d\theta\, d\varphi \ \equiv\ \frac{\Delta Q}{\Delta t\,\Delta A\,\Delta\lambda}. \tag{3}$$

The upwelling light field measured above sea surface consists of surface reflection (depending on sun elevation and surface waves) and water-leaving light (carrying information about IOPs). In order to minimize the contribution of surface reflection, radiance detectors are set in a nadir viewing position ($\theta=0$). The ratio of measured in this way water-leaving radiance L_w to downwelling sky irradiance E_d is called *remote sensing reflectance* [4, 5]:

$$R_{rs}=\frac{L_w}{E_d}. \tag{4}$$

2. Method – radiative transfer simulation

It is technically too difficult and time consuming to measure the total radiance distribution $L(x,y,z,t,\varphi,\theta,\lambda)$. Moreover, it is impossible to set desired environmental conditions *in situ*, therefore several types of numerical methods solving RTE have been developed [2, 5].Radiative transfer simulations allow computing the light propagation in seawater under specified conditions and to evaluate the influence of each factor on remote sensing reflectance separately. Numerical models simplify RTE by discretizing continuous radiance function of depth, direction and wavelength in order to receive a finite number of quantities to be computed. The angular distribution of radiance is widely computed using Monte Carlo code for photon trace simulation, which calculates the number of water-leaving virtual photons entering a given solid angle sector [2].

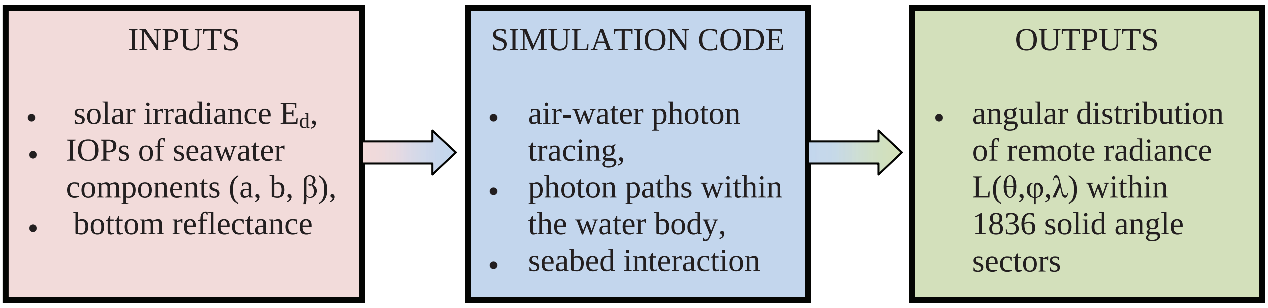

Fig. 1. General operational scheme of Monte Carlo radiative transfer simulation

Input data. Incident solar irradiance was computed as $2 \cdot 10^9$ photons entering plane sea surface at the zenith angle of 60° (equivalently 30° of sun elevation above the horizon). Computing a huge number of photons minimizes statistical errors. Simulations were performed for two models of marine waters: Baltic Sea and open ocean. Seawater absorption and scattering coefficients come from in situ measurements (chosen from literature) [5,8,9] (Fig. 2). Volume scattering function is computed in the form of phase function:

$$\tilde{\beta}(\psi) = \frac{\beta(\psi)}{b(\lambda)}. \tag{5}$$

For unpolluted seawater interpolated Petzold's phase functions were applied [5]. Both types of marine water bodies were virtually polluted by two types of oil emulsion in concentration of 1 ppm. The transparent Petrobaltic crude oil was obtained from southern Baltic (Polish Economic Zone) and the opaque Romashkino crude oil was delivered from reservoir in the Tatarstan (Russia). Oil droplets dispersed in seawater take spherical shapes due to hydrophobic interaction and surface tension. Spherical shapes allowed applying Mie Scattering Theory to calculate absorption coefficient, scattering coefficient and scattering phase functions on the basis of index of refraction and size distribution. Those parameters were measured in the laboratory of Department of Physics in Gdynia Maritime University [6,7,10]. Absorption and scattering coefficients for unpolluted and polluter water bodies are shown on the Fig 2.

Simulation code**.** 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:

$$p_a = 1 - e^{-a}, \quad p_b = 1 - e^{-b}. \tag{6}$$

- Interaction with the seabed. In order to eliminate bottom reflection, an infinite depth was set.

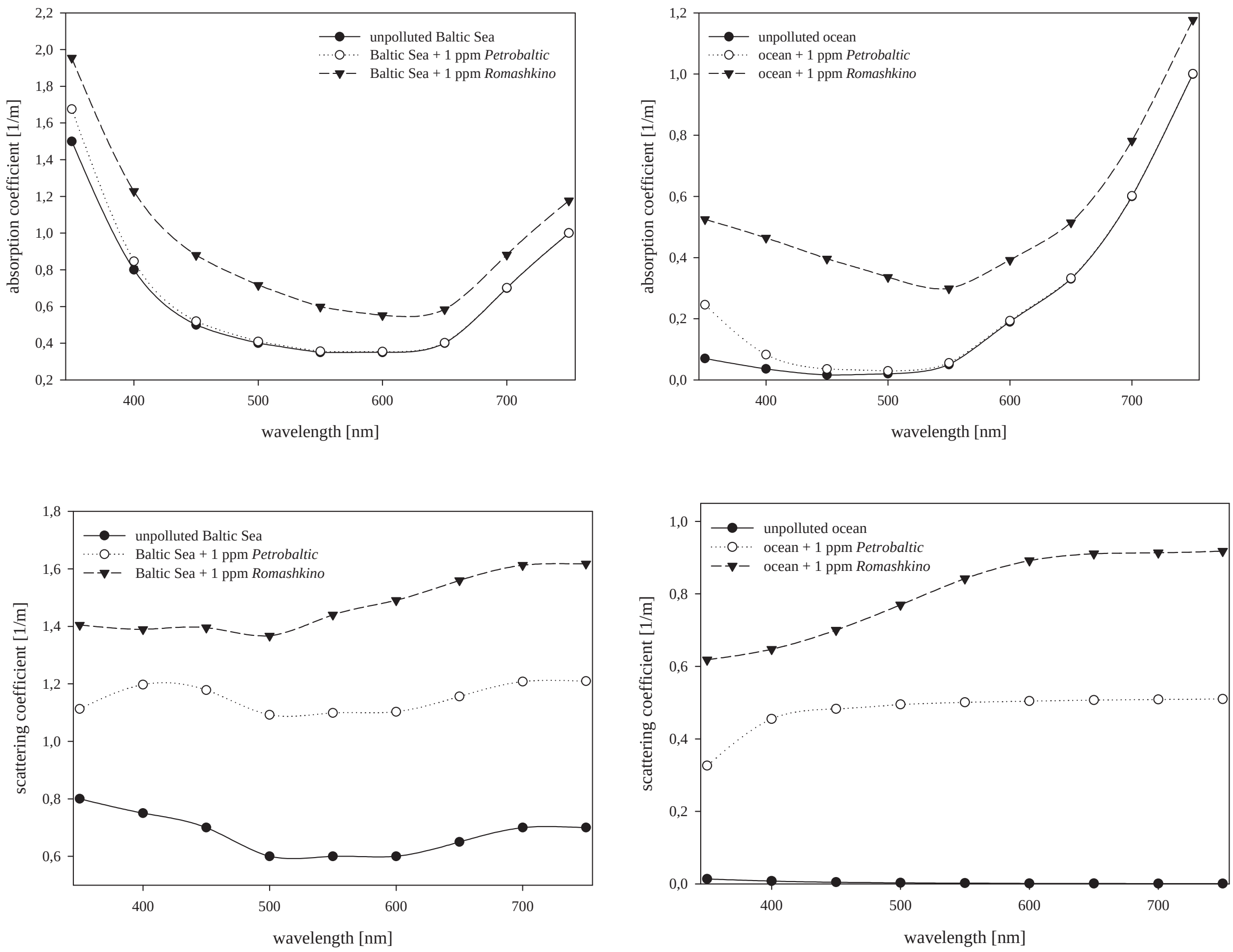

Fig. 2. Simulation inputs: absorption and scattering coefficients for exemplary unpolluted and polluted marine environments

3. Results and discussion

Output data is the angular distribution of remote radiance L(θ,φ,λ) within 1836 solid angle sectors. Water-leaving radiance L_w was calculated within the half angle of 4.9° (which corresponds to the solid angle sector of 0.023 sr) and afterwards remote sensing reflectance was calculated from the equation (4).

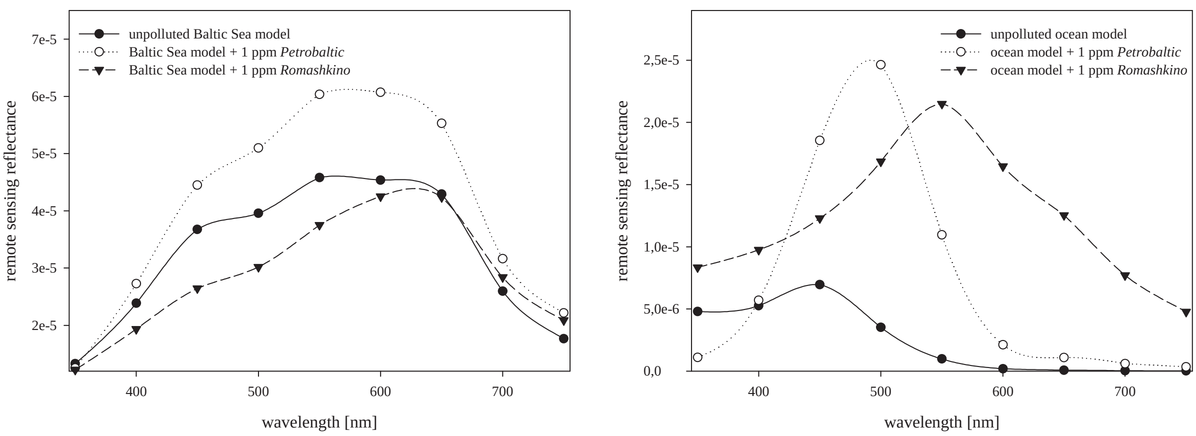

Fig. 3. Examples of remote sensing reflectance spectra (magnitudes are comparable)

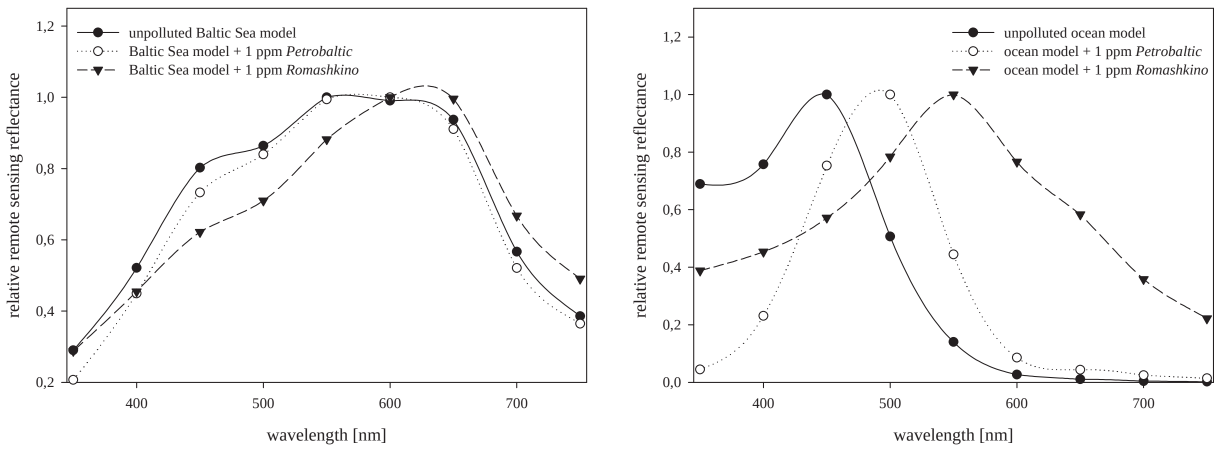

Fig. 4. Examples of relative remote sensing reflectance spectra (shapes are comparable)

It is shown on the Fig. 3 and 4 that oil substances significantly modify reflectance spectra and it is crucial to compare both, their magnitudes and shapes in order to interpret them correctly, as they carry different information about seawater IOPs. Simultaneous analysis of simulation inputs (Fig. 2) and outputs (Fig. 3) reveals that reflectance spectra are more sensitive to changes of absorption coefficient than to scattering coefficient. In fact, the total scattering coefficient describes the probability of scattering in any direction on the path of 1 m, therefore only the backscatter fraction is responsible for increasing reflectance values. The process of absorption is more simple: the higher it is, the less number of photons is able to leave the bulk of water. The maxima of remote sensing reflectance correspond to the minima of absorption for all types of analyzed marine environments. Spectral dependence of absorption coefficient is responsible for maximum shift of reflectance. It is seen clearly in open ocean and slightly worse in Baltic, because of more extended minimum of absorption in the turbid waters. Addition of *Petrobaltic* emulsion barely affects seawater absorption coefficient, therefore the influence of scattering on remote sensing reflectance is remarkable. The transparent and less dense *Petrobaltic* emulsion forms smaller droplets than *Romashkino*, and in consequence has a higher backscatter fraction. Although *Romashkino* has much higher scattering coefficient, it causes a drop of reflectance in Baltic and at the same time significant increase in ocean water. This is because relatively high absorption of Romashkino shadows the effect of scattering. The effect of shadowing depends on seawater backscatter fraction, which is higher for turbid water bodies containing large amounts of small particles (such as chlorophyll, minerals, suspended organic matter).

4. Summary – perspectives

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. Thus, it is possible to find a unique sensor configuration which would give ability to detect oil emulsion under specified environmental conditions. The presence of high-absorptive and low-backscattering crude oil emulsions can be easily remarked on any marine water background, as they 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. A separate study should be performed in order to determine IOPs for more commonly used crude oils and their mixtures.

In order to apply radiative transfer simulation for shipboard or offshore located radiometers an a proper atmospheric correction would be necessary [4]. Clear atmosphere affects the reflectance significantly only at high sun elevation angles (corresponding to the sunset or sunrise). In the case of total overcast the radiance distribution becomes direction-independent, and reflectance values depend only on a parameter which describes clouds' optical depth. Otherwise, in order to eliminate the atmosphere effect, Monte Carlo code may be used to compute underwater radiance distribution as well.

New possibilities of IOPs' *in situ* measurements will still deliver new input data to perform new simulations of local range. The impact of other pollution substances in various concentrations can be determined if their optical properties are known. Development of small and large angle scattering measurement methods will improve the credibility of the results. It is planned to create a database of spectral library of remote sensing reflectance, which in combination with *in situ* measurements will became an instrument for estimating the quantity of crude oil emulsions suspended in seawater, for better protection and monitoring of marine environment.

References

[1] Karpicz, R., Dementjev, A., Kuprionis, Z., Pakalnis, S., Westphal, R., Reuter, R., Gulbinas, V., *Oil spill fluorosensing lidar for inclined onshore or shipboard operation*, Applied Optics, Vol. 45, Is. 25, pp. 6620-6625, 2006.

[2] 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.

[3] Migliaccio, M., Gambardella, A., Tranfaglia, M., *SAR Polarimetry to Observe Oil Spills*, IEEE Trans. Geosci. Remote. Sens., vol 43, no. 2, pp. 506-511, 2007.

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

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

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

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

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

[9] Smith, R. C., Baker, K. S., *Optical properties of the clearest natural waters (200–800 nm)*, Applied Optics, Vol. 20, Issue 2, pp. 177-184, 1981.

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