The effect of pollutants of crude oil origin on the diffusive reflectance of the ocean*

Krzysztof Małachowski
Institute of Oceanology,
Polish Academy of Sciences,
Sopot

Jadwiga Mrozek-Lejman
University of Szczecin
Szczecin

Abstract

The contrast between clean and volumetrically contaminated ocean has been numerically determined for the natural red light of $\lambda = 630$ nm on the basis of laboratory measurements of optical parameters of emulsions and solutions of crude oil in sea water. Strongly absorbing crude oil emulsions decrease the quantity of light reflected by the ocean, whereas the crude oil solutions increase the value of diffuse reflection of radiance through the increase of the quantity of back-scattered light.

1. Introduction

Among various types of substances polluting seas and oceans, crude oil and the products of its refining constitute particularly noxious type of contaminants. On one hand, this is due to a variety of forms of hydrocarbons of petroleum origin in marine environment and, on the other hand, to their diversified effect on physical and chemical properties of water and the organisms living there.

The first visible effect of oil spill to the sea is formation of an oil patch. Under the influence of hydrometeorological factors the patch spreads, forming a thin layer tightly covering the water surface (Mironov, 1972). The layer formed (oil film) affects in a manner harmful to biological life the processes of exchange of (Nelson--Smith, 1970, 1972):

— oxygen and carbon dioxide between the sea and atmosphere,

---

* The investigations were carried out under the research programme MR.I.15, coordinated by the Institute of Oceanology of the Polish Academy of Sciences.

—energy, momentum and mass,
—energy of electromagnetic radiation.

Light petroleum fractions containing molecules with up to 8 carbon atoms quickly evaporate from the oil film to the atmosphere (Nelson-Smith, 1970). The remaining fractions of crude oil occur primarily in the following forms (FAO, 1977): pitch lumps (aggregates), oil in-water-emulsion, water-in-oil emulsion, solutions in sea water, oil adsorbed on organic and mineral suspensions.

Among the listed forms, particular stability is exhibited by finely dispersed emulsions and dissolved fractions of crude oil which—filling the entire volume of a basin (in seas with depth to 500 m)—change the density stratification and the composition of hydrosphere (Zhurbas, 1978). This affects the conditions of sunlight propagation in a water column, the processes of waving exchange of energy and gases. All these processes play an essential role in biological aspect of water environment and all disturbances in their course can lead to upsetting biological balance. In addition, emulsions and dissolved oil fractions directly influence biocenosis. Toxic and carcinogenic effect of some hydrocarbons can, in extreme cases, lead to total degradation of marine environment (FAO, 1977; Larson et al., 1977).

The above facts substantiate a need for experimental and theoretical investigations, the results of which could be utilized for the development of rapid (remote) methods of identification and recording of these pollutants.

2. Purpose of work, assumptions concerning model

The calculations performed aim at investigation of the effect of oil derivatives dissolved and emulsified in sea water mass on the diffusive reflectance of natural red light. Comparing the quantity of light reflected in the presence of pollutants with the value obtained for the clean ocean, the contrast is calculated the values of which can be employed for considering the possibility of development of passive remote methods of detecting such contaminants.

The following assumptions about a model, used to calculate the contrast, have been made:
—the ocean is optically homogeneous and infinitely deep,
—its surface is flat,
—in the case when the oil pollutants have been accounted for it was assumed that they are distributed uniformly in the entire water mass,
—no contaminants are present on the surface.

The atmosphere was not directly modelled, taking a set distribution of light incident on the ocean surface in the form-directed source (sun) + isotropic distribution (simplified model of atmospheric radiance) and assuming various fractions of the two components. All calculations were carried out for one wavelength of light $\lambda = 630$ nm. The calculations were performed:
(i) taking into account all orders of photon scattering,
(ii) for the so-called quasi-single scattering approximation (Gordon, 1973) in order to test the applicability of this approximation.

The assumptions of the above model will now be discussed:

— the assumption of optical homogeneity does not seem to be an oversimplification of the problem, since for our purposes, ie calculation of the diffusively reflected radiance, the distribution of optical parameters in the near surface layer of optical thickness of the order of $\tau = 2$ is essential; in order to demonstrate this, additional calculations were carried out for a non-homogeneous model,

— the assumption of a flat surface of the ocean (which was a necessity for the selected method of calculations) limits our conclusions to an undisturbed surface, ie the wind velocity $v \leqslant 5 \text{ m} \cdot \text{s}^{-1}$.

The radiance field can be calculated for a given distribution of incident light by setting two parameters—the scattering function β and the attenuation coefficient c (neglecting the effects associated with polarization of light). The values of these parameters for the clean ocean β_0, c_0 were taken from literature. The models of polluted ocean were obtained by adding to the parameters characterizing clean ocean the respective optical parameters β_p, c_p of oil pollutants, which were measured in a laboratory:

$$\beta_t = \beta_0 + \beta_p,$$

$$c_t = c_0 + c_p,$$

(1)

where β_t and c_t are the scattering function and the attenuation coefficient, respectively.

3. Preparation of solutions and emulsions of crude oil in sea water

Optical parameters of oil pollutants were determined in a laboratory, preparing colloidal solutions of crude oil in artificial sea water. Crude oil (Soviet oil from the Gdańsk Refinery) was introduced into artificial sea water in the 1 : 80 volumetric ratio and emulsified using an electric stirrer and an ultrasonic vibrator operating at the frequency $f = 22$ kHz. After stirring time $t_m = 15$ or 60 min, a portion of the emulsion formed was filtered through a sintered glass filter R4 (pore diameter $d = 5$– –15 μm). The filtering process aimed at separation of dissolved and colloidal phases.

The measurements of scattering function for samples prepared in such a manner were carried out instantly using the apparatus described elsewhere (Woliński, 1972) and repeated after storing the samples in closed glass bottles at $T = 291$ K for a period of 7 or 14 days. Some of the samples were stored in darkness and the remaining samples were illuminated by light from fluorescent tubes of the intensity $I = 31 \text{ W} \cdot \text{m}^{-2}$. A more complete description of sample preparation and the measurements is given in the papers cited (Małachowski, Mrozek-Lejman, 1984; Mrozek-Lejman et al., 1986).

According to the method of sample preparation, the differences between them consist in:

— filtering or not filtering,

—stirring time $t_m = 15$ or 60 minutes,
—storing for 0, 7 or 14 days,
—darkening or illumination during the storing period.
Symbolic designations of the samples are defined under Table 1.

4. Data handling

The values of scattering function obtained from the measurements in a reduced form for the angle $\theta = \dfrac{\pi}{2}$, ie normalized as follows: $\beta_p\left(\dfrac{\pi}{2}\right) = 1$, were approximated by third-degree curves:

$$\beta_p(\mu) = P_0 + P_1\mu^1 + P_2\mu^2 + P_3\mu^3, \tag{2}$$

where:
$\beta_p(\mu)$ —scattering function of pollutants,
P_1, P_2, P_3 —coefficients selected in such a manner so as to minimize the sum of squares of deviations of $\beta_p(\mu)$ from the experimental values ($P_0 = 1$ by assumption),
μ —cosine of the scattering angle.
The values of coefficients P_1, P_2, P_3, a factor R, by which equation (2) must be multiplied in order to obtain the true scattering function $\beta_p(\mu)$ and the scattering coefficients b_p for the samples calculated by integrating this function are listed in Table 1.

Table 1. P_i coefficients $i = 1, 2, 3$ of the polynomial approximating reduced scattering functions of pollutants of crude oil origin

Sample	P_1	P_2	P_3	$R \cdot 10^3$	$b_p 10^2 \cdot [\mathrm{m}^{-1}]$	$a_p[\mathrm{m}^{-1}]$
E15	0.157	1.55	0.761	3.05	5.81	75.5
E15N14	0.376	1.71	0.677	2.43	4.80	5.0
S15	−0.0765	1.07	0.171	1.10	1.87	0
S15Z7	0.0777	1.11	0.132	1.00	1.73	0
S15N7	0.137	1.24	0.275	0.99	1.76	0
S15Z14	0.182	1.15	0.152	0.943	1.64	0
S15N14	0.189	1.28	0.297	0.920	1.65	0
S60	0.0511	1.27	0.451	0.710	1.27	0
S60Z7	0.167	1.28	0.440	0.575	1.03	0
S60N7	0.350	1.36	0.430	0.602	1.10	0
S60Z14	0.227	1.36	0.517	0.522	0.953	0
S60N14	0.398	1.41	0.471	0.529	0.977	0

$P_0 = 1$ for all samples; R—factor providing for transition from the reduced form to the absolute scattering function; b_p, a_p—coefficients of scattering and absorption.
Sample designation: E—emulsion (unfiltered sample); S—filtered sample; 15—stirring time $t_m = 15$ min; 60—stirring time $t_m = 60$ min; N—illuminated sample; Z—sample stored in darkness; 7—storage period $t_p = 7$ days; 14—storage period $t_p = 14$ days; E15, S15, S60—samples for which the measurements were performed immediately after stirring

A graphical illustration of two reduced scattering functions for selected samples is shown in Figure 1.

The values of oceanic scattering function were taken from the paper of Petzold (1977); it contains the results of precise measurements of the scattering function in the region of southern coast of California: 33°30′ N and 118°23′ W. The oceanic
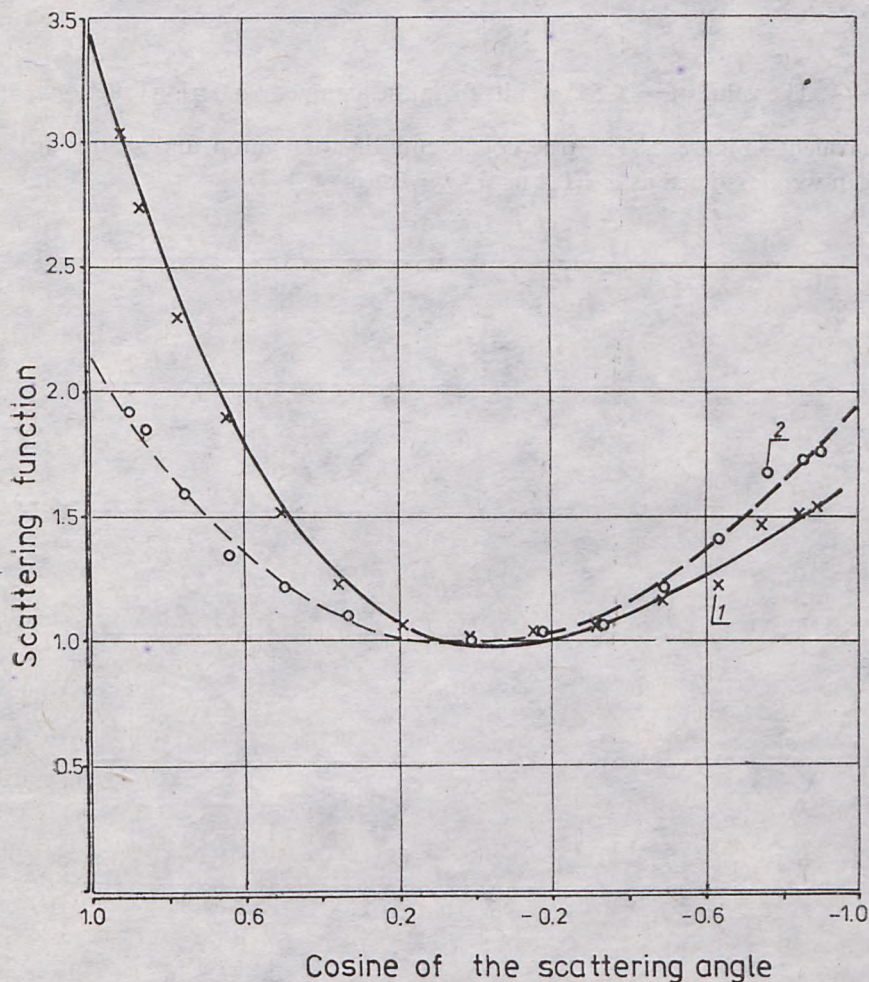

Fig. 1. Reduced scattering functions for the samples E15
(*1* — experimental points, continuous curve — approximation) and S15 (*2* — experimental points, dashed curve — approximation with a polynomial, according to Gordon, 1973)

scattering function is characterized by a very strong maximum for the zero direction of scattering, as a result of which a so-called transport approximation was employed (Potter, 1970). This consists in using for calculations a function of the same shape but with lower maximum instead of the true scattering function. Physically, this corresponds to treatment of photons scattered at small angles as the photons moving

without scattering and, consequently, requires the introduction of equivalent coefficients of scattering and attenuation b_0' and c_0'. If b_0 and b_0' are the scattering coefficients corresponding to true and equivalent scattering functions, respectively, then:

$$c_0' = c_0 - \gamma b_0,$$

$$b_0' = b_0(1 - \gamma),$$

$$(3)$$

where $\gamma = 1 - \dfrac{b_0'}{b_0}$. The value of $\gamma = 0.542$ results from the assumed scattering functions, true and equivalent—Figure 2. The true coefficients of attenuation and scattering for clean ocean were assumed as $c_0 = 0.4 \ \mathrm{m}^{-1}$, $b_0 = 0.2 \ \mathrm{m}^{-1}$.
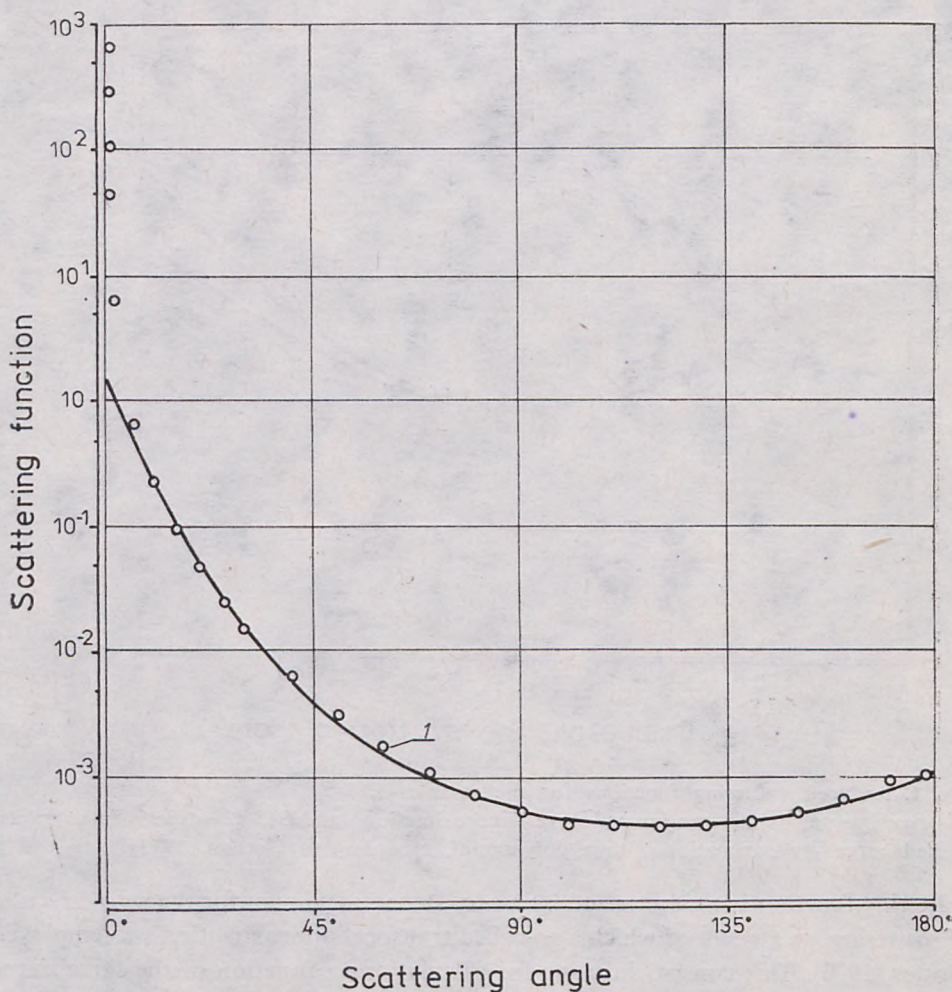

Fig. 2. Scattering function for clean ocean
1—experimental points after Petzold, 1977, solid curve—analytic equivalent function (4)

The common logarithm of the equivalent scattering function was approximated by a fourth-degree polynomial:

$$\log_{10} \beta_0'(\alpha) = \sum_{i=0}^{4} P_i \cdot \alpha^i, \tag{4}$$

where:

α — scattering angle (in degrees),

P_i — constant parameters with the following values: $P_0 = 0.2004$, $P_1 = -9.086 \cdot 10^{-2}$, $P_2 = 9.006 \cdot 10^{-4}$, $P_3 = -4.311 \cdot 10^{-6}$, $P_4 = 8.719 \cdot 10^{-9}$.

The plots of true oceanic scattering function and function (4) are presented in Figure 2. Basing on the results of Potter (1970) it can be judged that the error resulting from the transport approximation for azimuthally averaged, diffusively reflected radiation can be neglected.

5. Method of calculation of light field

For the calculation of stationary light field in a model consisting of flat-parallel layers, the matrix operator method (Plass *et al.*, 1973) is very convenient due to such advantages as: accounting for all orders of photon scattering; 'composing' of the model from an arbitrary number of layers of different properties, and obtaining the results in one series of calculations for many locations of the light source. The method also has the advantage that the calculations are carried out equally for any value of albedo of single scattering, ω_0. In general case this is advantageous but, since in our model ω_0 is always rather small, it was found purposeful to modify the classical method in a manner enabling reduction of computation time by several times with other advantages of the method remaining unchanged. A detailed description of this modification can be found in the paper (Małachowski, in press). The calculations according to the modified method are carried out using the following procedure:

— an iterative procedure is employed to calculate the reflectance matrix **R** for an infinite homogeneous medium according to the algorithm given in the paper (Małachowski, in press) (at this point ω_0 cannot be close to zero),

— a certain exponential matrix $\exp(\mathbf{K}\tau)$ is calculated for a given optical depth τ by means of the operator **R** and matrices containing time parameters of the modelled medium,

— the reflection and transmission matrices for the layer of medium of the depth τ can be expressed explicitly in terms of **R** and $\exp(\mathbf{K}\tau)$,

— for given reflection and transmission matrices for the layers of desired thickness, a non-homogeneous medium is modelled according to usual formulas of the matrix operator method.

The reduction of time of calculations in the method presented above is a result of simplicity of calculation (in the process of doubling the optical thickness of a medium) of the exponential operator $\exp(\mathbf{K}\tau)$:

$$\exp(\mathbf{K}2\tau) = \exp(\mathbf{K}\tau)\exp(\mathbf{K}\tau), \tag{5}$$

whereas in the classical method the sought reflectance operators $r(\eta)$ and $t(\eta)$ are calculated directly but using a larger number of operations

$$r(2\tau)=r(\tau)+t(\tau)r(\tau)[E-r(\tau)^2]^{-1}t(\tau),$$

$$t(2\tau)=t(\tau)[E-r(\tau)^2]^{-1}t(\tau).$$

(6)

As a result, a total number of operations is smaller in the proposed method.

The calculations were also carried out using a simple approximation of quasi--single scattering (Gordon, 1973). Formally, the approximation amounts to the use of expressions for single scattering with a substitution in these expressions of the attenuation coefficient c by $a+b_b$, where a is the absorption coefficient and b_b is the back-scattering coefficient.

6. The results of calculations

The calculations of contrast were performed for the clean ocean characterized by the phase function $P'_0(\mu)=\dfrac{\beta'_0(\mu)}{\zeta_1\beta'_0(\mu)\,d\mu}$, where the oceanic scattering function is described by equation (4), the values of c'_0 and b'_0 being defined by relationships (3)
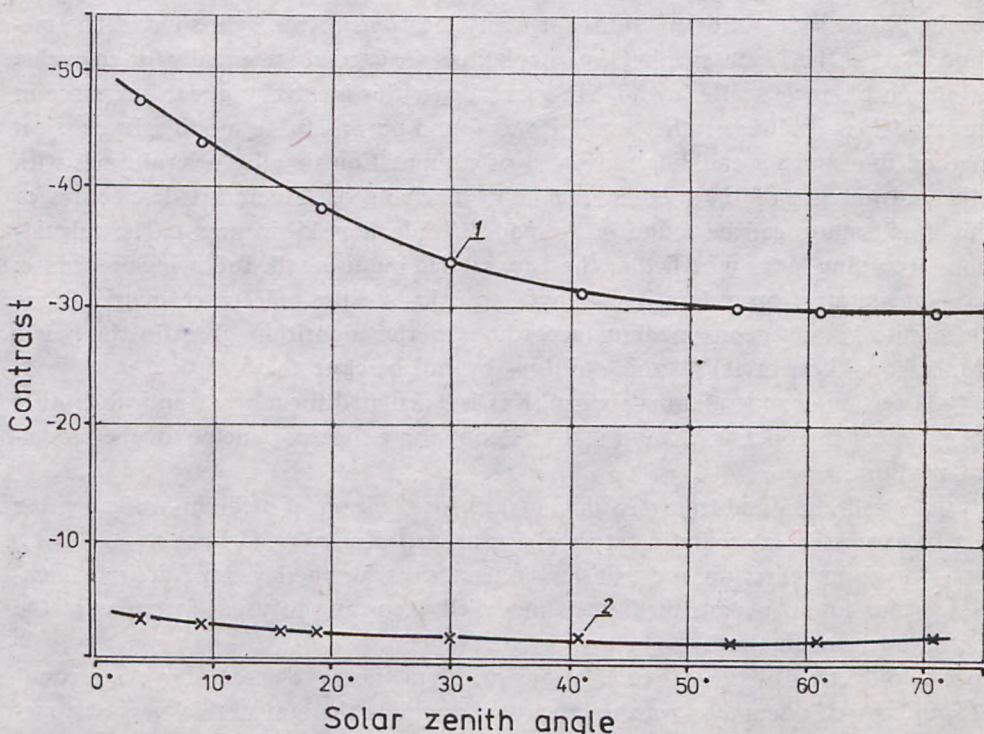

Fig. 3. Contrast according to def. (10) between the ocean contaminated as the samples E15−1 and E15N14−2, and clean ocean as a function of solar zenith angle, $S_0=0$
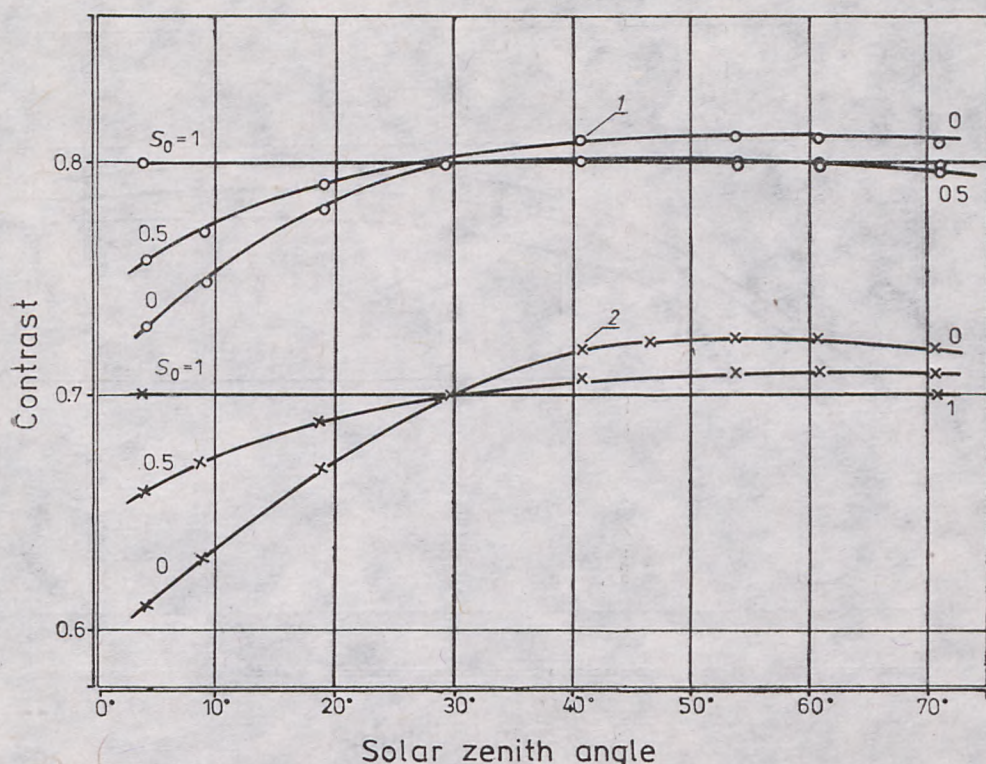
Fig. 4. Contrast between the ocean contaminated as the samples S15−*1* and S60−*2* and clean ocean as a function of solar zenith angle. The figure illustrates the effect of stirring time on contrast. Parameter S_0 is the ratio of illumination by the sky to total illumination

Table 2. Contrast between the ocean uniformly polluted such as the sample S15 and the ocean similarly polluted but only in the near surface layer of $\tau = 0.5$, 1.0 and 2.0.

Solar zenith angle [°]	Contrast		
	$\tau = 0.5$, $z = 1.6$ m	$\tau = 1 \cdot 0$, $z = 3.2$ m	$\tau = 2.0$, $z = 6.4$ m
4	0.36	0.18	0.04
9	0.37	0.18	0.04
19	0.38	0.18	0.04
30	0.39	0.18	0.04
41	0.38	0.18	0.04
54	0.37	0.17	0.03
61	0.36	0.16	0.03
71	0.35	0.15	0.03

and for the polluted ocean, for which the phase function was expressed in the following form:

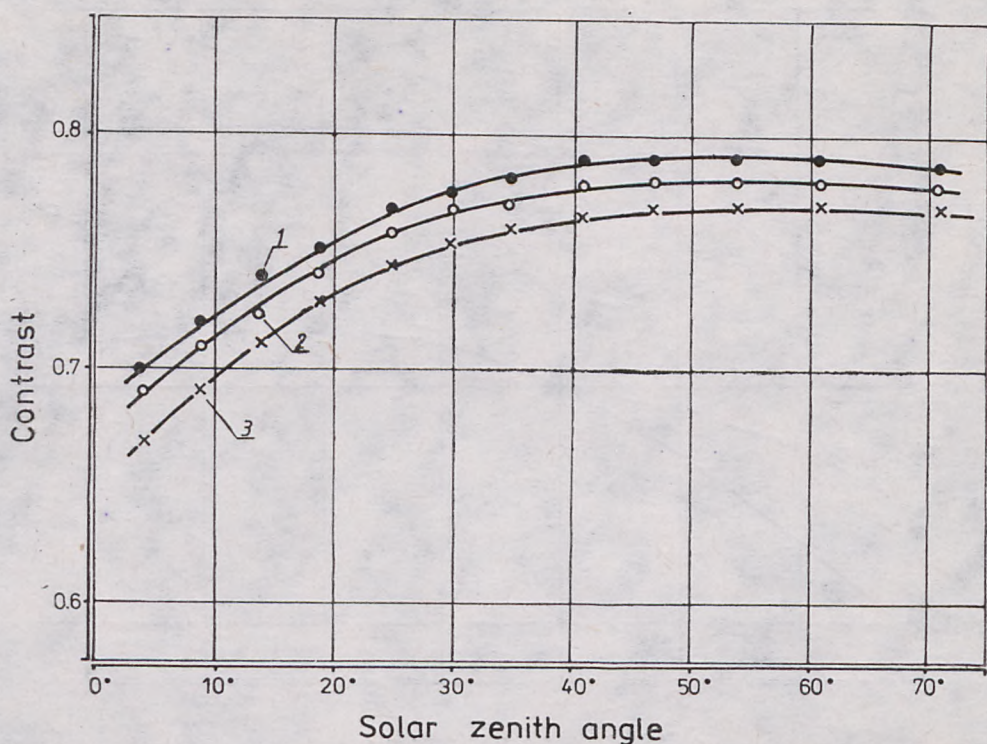$$P_s(\mu) = \frac{[b_0' P_0'(\mu) + b_p P_p(\mu)]}{b_0' + b_p}. \tag{7}$$

Fig. 5. Dependence of the contrast between the ocean polluted as the samples S15Z7 – *1*, S15N7 – *2* and S15Z14 (S15N14) – *3* and unpolluted ocean on the solar zenith angle, $S_0 = 0$. (The contrast values for the samples S15Z14 and S15N14 are almost identical)

The attenuation and scattering coefficients were calculated as sums of the respective coefficients for clean ocean and pollutants:

$$c_t = c_0' + c_p, \tag{8}$$

$$b_t = b_0' + b_p, \tag{9}$$

where c_p, b_p and $P_p(\mu)$ denote the attenuation coefficient, scattering coefficient, and the phase function for crude oil pollutants, obtained from the laboratory measurements.

The contrast was defined by an equation:

$$K = \frac{L_t - L_0}{L_t}, \tag{10}$$

where: L_t – vertical, diffusively reflected radiance for the polluted ocean; L_0 – the same radiance for the clean ocean.

Such defined contrasts were calculated for twelve positions of a source of directed light (sun), at various fractions of directed and isotropic (sky) sources. The ratio S_0 of the vector of illumination coming from the sky to the total illumination was
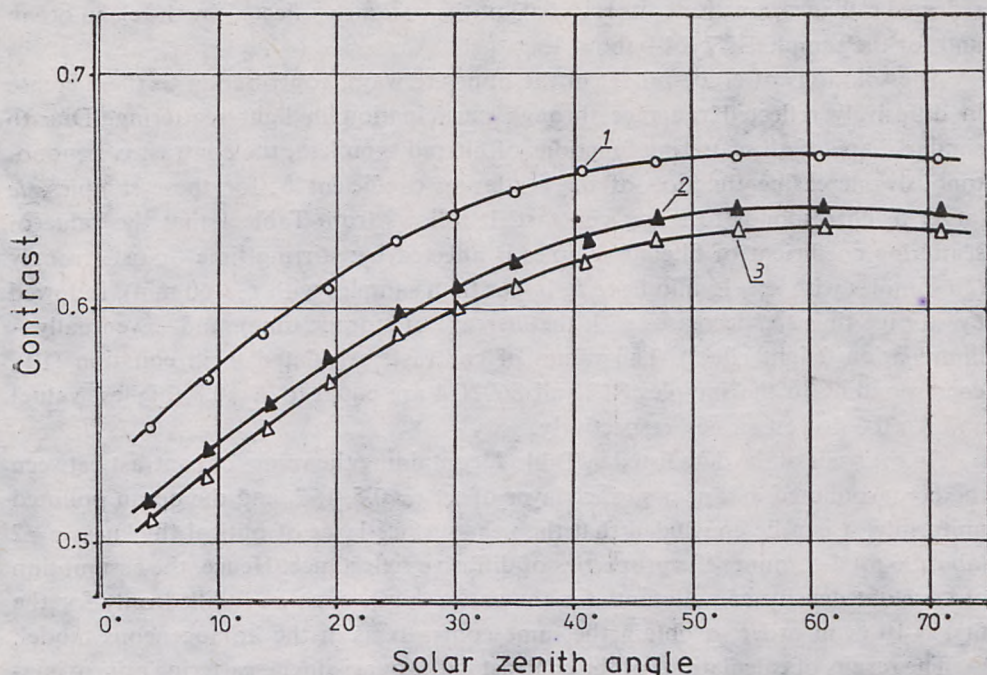
Fig. 6. Dependence of the contrast between the ocean polluted as the samples S60Z7 (S60N7) — *1*, S60Z14 − *2*, S60N14 − *3* and unpolluted ocean on the solar zenith angle, $S_0 = 0$. (The contrast values for the samples S60Z7 and S60N7 are almost identical)

taken as a measure of this fraction − $S_0 = 0$, 0.5, and 1 ($S_0 = 0$ corresponds to a source of light solely in the directed form and $S_0 = 1$ − to an isotropic source). The results of calculations are shown in Figures 3, 4, 5, and 6.

In order to investigate the influence of optical non-homogeneity of the ocean on the reflected radiance, exemplary calculations were carried out for a two-layer model consisting of a polluted near surface layer of optical thickness $\tau = 0.5$, 1, 2, and a semi-infinite layer of the clean ocean. For a model defined in this manner the contrast with the uniformly polluted ocean was calculated (Table 2).

7. Discussion of the results

The calculated values of contrast for the model described are presented in Figures 3, 4, 5, and 6. There is a qualitative difference between the influence of emulsions (Fig. 3) and solutions (Figs. 4, 5, 6) of crude oil on the diffusively reflected light.

Contaminants affect diffusively reflected light in two ways: back-scattering on contaminants brings about the increase of quantity of reflected light, absorption − the decrease. Since emulsions absorb light very strongly (for the sample E15 $a_p = 75.5 \text{ m}^{-1}$, for the sample E15N14 $a_p = 5 \text{ m}^{-1}$), these pollutants strongly decrease diffusively reflected light. For the ocean with the pollutants such as in the sample E15, vertically

reflected radiance constitutes only *ca* 0.03 of the radiance reflected by the clean ocean and for the sample E15N14—about $\frac{1}{3}$.

The solutions of crude oil act in the opposite ways, contributing to the increase in diffusively reflected radiance through participation in light scattering. Due to similar shape of all scattering functions of filtered samples*, the contrast is a monotonously increasing function of the scattering coefficient b_p for these samples, *ie* larger b_p corresponds to larger contrast. It follows from Table 1 that the value of scattering coefficient of filtered samples is affected by: stirring time—most strongly (all samples with $t_m = 15$ min have b_p larger than samples with $t_m = 60$ min), followed by storage time (b_p decreases with the increase of storage time), and—eventually—illumination (slight effect). The values of contrast, calculated from equation (10), corresponding to the samples S15 and S60N14 are equal to $K \approx 0.8$ (highest value) and $K \approx 0.6$ (lowest value), respectively.

On the basis of the data listed in Table 2, containing the values of contrast between the ocean polluted in a near surface layer of set $\tau = 0.5$, 1, 2, and the ocean polluted uniformly, it can be concluded that the near surface layer of optical thickness $\tau = 2$ (about 6 m) determines the properties of diffusive reflectance. Hence, the assumption of constant density of pollutants for the entire depth must be fulfilled only for the first 6–10 m in order to obtain the same contrasts as in the homogeneous model.

The results of calculations of the contrast in the quasi-single scattering approximation suggest the suitability of this simple approximation owing to its quite satisfactory accuracy—the difference between the results of exact calculations and the quasi-single scattering approximation is equal to *ca* 1–7%.

8. Conclusions

Model calculations performed, although assuming considerable simplifications of real conditions, allow to recognize the problem of the effect of volume crude oil pollution on the diffusively reflected light. The contaminants affect the diffusive reflectance in a different manner, depending on their composition—crude oil emulsions cause strong attenuation of the reflected light, whereas the solutions act in the opposite way. Crude oil is characterized by substantial scatter of optical parameters (see Zolotariev *et al.*, 1977) which, in conjunction with the above statement concerning various influences of pollutants of crude oil origin on the reflected light, creates difficulties in identification of these pollutants by the measurement of contrast in the visible light region.

For the solar zenith angle equal to *ca* 30° the contrast is almost independent of the diffusivity (Fig. 4). Therefore, it is recommended to carry out the measurement at this position of the sun.

---

* Indicatrices of dissolved hydrocarbons are similar to each other compared to completely different in shape oceanic scattering function; on the basis of small differences in shape of the scattering function of pollutants conclusions concerning the size distribution of crude oil droplets in colloidal solutions can be drawn (see Mrozek-Lejman *et al.*, in press).

References

1. FAO (GESAMP), 1977, *Impact of oil on the marine environment*, Rep. a Stud., 6.
2. Gordon H. R., 1973, *Simple calculation of the diffusive reflectance of the ocean*, Appl. Opt., 12, p. 2803.
3. Larson R. A., Hunt L. L., Blankenship D. W., 1977, *Formation of toxic products from fuel oil photooxidation*, Environ. Sci. Tech., 11, p. 492.
4. Małachowski K., Mrozek-Lejman J., 1984, *Wpływ rozpuszczonych i zemulgowanych składników ropy na pole światła w Morzu Bałtyckim*, Stud. i Mater. Oceanol. KBM PAN, 45, p. 49.
5. Małachowski K., *Modification of the matrix operator method for solving the equation of radiative transfer*, J. Quant. Spectrosc. Radiat. Transfer (in press).
6. Mironov O., 1972, *Biologicheskie resursy moria i nieftianyie zagraznienie*, Moskwa.
7. Mrozek-Lejman J., Zieliński A., Król T., Witkowski K., *Rozpraszanie światła w układach koloidalnych ropa naftowa-woda morska*, Oceanologia (in press).
8. Nelson-Smith, 1970, *The problem of oil pollution of the sea*, London, New York.
9. Nelson-Smith, 1972, *Oil pollution and marine ecology*, London.
10. Petzold T. J., 1977, *Volume scattering functions for selected ocean waters*. [In:] *Light in the sea*, Ed. J. Tayler, Dowden, Hutchinson and Ross Inc., Stroudsburg, PA, 152–174.
11. Plass G. N., Kattawar G. W., Catchings F. E., 1973, *Matrix operator theory of radiative transfer*, Appl. Opt., 12, p. 314.
12. Potter J. F., 1970, *The delta approximation in radiative transfer theory*, J. Atm. Sci., 27, 943–949.
13. Woliński L. M., 1972, *Rozpraszanie światła i związane z nim badanie własności fizyko-chemicznych cząsteczek*, Wyd. Uniw. Gdańskiego.
14. Zhurbas W. M., 1978, *Osnownyie mekhanizmy rasprostranienia niefti v morie*, Mekh. zhidkosti i gaza, 12.
15. Zolotariev V. M., Kitushyna J. A., Sutovskij S. M., 1977, *Opticheskie kharakteristiki nieftei v diapazonie 0.4–15 μm*, Okieanologia, 6, p. 1113.