

Remote sensing
Fluorescence
Optical tracers
Spectral measurements
Two-flow model
Téledétection
Fluorescence
Traceurs optiques
Mesures spectrales
Modèle à deux flux

Multispectral remote sensing of fluorescent tracers: theory and experiments

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ABSTRACT

Remote measurements of the optical tracer distribution in the sea appear to be a promising method for the observation of coastal dynamics. A passive remote sensing method is described, as well as the region where this method is applied. A two-flow model describing the absorption, back-scattering and the fluorescence of the dye tracer in the seawater is developed. Specific approximations with respect to rhodamine B and "Case 1" waters are used to simplify the calculations. Measurements of the upwelling radiance at 575 nm (emission maximum) are more suitable than the measurements of the radiance at 550 nm (absorption maximum of rhodamine B) for the remote concentration determinations in the range 10^{-7} – 10^{-3} kg.m⁻³ of rhodamine B in the seawater. The vertical irradiance attenuation in the sea is generally higher when the concentration of the fluorescent dye increases. The environmental influences and errors due to the approximations applied are briefly discussed. Spectra of the upwelling radiance, downwelling irradiance and their ratio as recorded during the experiment are presented. Laboratory analyses of the sea-truth samples taken during the overflights were performed. Results of these analyses (concentrations of pigments, dry seston, yellow substance and rhodamine B), applied to a theoretical model developed, and compared with the optical measurements testify to the observed substantial inhomogeneous distribution of the dye in the seawater.

The remote sensing method proved to be suitable for detection even of low rhodamine B concentrations (10^{-6} kg.m⁻³), although more and improved *in situ* sampling procedures are necessary to establish the accuracy of the optical remote measurements.

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RÉSUMÉ

Téledétection multispectrale des traceurs fluorescents

L'observation à distance de la répartition des traceurs optiques dans la mer est une méthode d'avenir pour la dynamique côtière. On présente une méthode de téledétection passive et un modèle décrivant l'absorption, la rétrodiffusion et la fluorescence d'un traceur dans l'eau de mer. Des approximations sont appliquées au cas de la rhodamine B et aux eaux de type 1. Les mesures de luminance à 575 nm (émission maximale) sont préférable aux mesures de luminance à 550 nm (absorption maximale de la rhodamine B) pour déterminer des concentrations de rhodamine B de l'ordre de 10^{-7} à 10^{-3} kg.m⁻³. L'atténuation verticale de l'éclairement dans la mer augmente en général quand la concentration du pigment fluorescent diminue. On discute brièvement les effets de l'environnement et les erreurs dues aux approximations. Des spectres de luminance ascendante et d'éclairement descendant sont présentés, ainsi que les analyses de vérité-mer correspondantes. Les résultats des analyses en pigments, seston sec, substance jaune et rhodamine B, appliqués au modèle théorique et comparés aux mesures optiques, sont en accord avec la répartition des traceurs dans l'eau de mer. La téledétection à distance est une méthode qui peut déjà s'appliquer aux faibles concentrations de rhodamine B (10^{-6} kg.m⁻³), mais les prélèvements *in situ* restent indispensables pour déterminer la précision des mesures de téledétection optique.

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INTRODUCTION

The applications of passive and active remote sensing (RS) methods in oceanography have been extensively investigated in the past decade (see e. g. reviews by Sathyendranath, 1981 and by Viollier, 1980). In the optical observations, most effort has been concentrated on the investigation of correlations between the remotely sensed spectral data and the concentrations of diverse natural suspended and dissolved components of the watercolumn.

The study of watermass dynamics often involves use of artificial optical (dye) tracers (Pak, Plank, 1974; Weidemann, 1974). Of particular interest are the coastal areas, where vigorous transport and mixing processes are strongly influenced by atmospheric and tidal forces. Special attention has been recently paid to these processes in connection with the discharge of pollutants and oil spills. As emphasized previously (Hoge, Swift, 1981), classical *in situ* concentration measurements by ship-borne or towed instruments cannot provide a synoptic image of tracer distribution in real time, and suffer from various problems, e. g. disturbance of the environment (dye spot), drifting and spatial and temporal discontinuity of sampling. Synoptic data can be obtained by remote observations of tracer distribution as a function of time (Hoge, Swift, 1981; Gehlhaar *et al.*, 1981; Valerio, 1981). Optical RS may offer essential improvement of dispersion measurements. Several active (Franz *et al.*, 1982; Hoge, Swift, 1981; Gehlhaar *et al.*, 1981) and passive (Slater, 1980; Valerio, 1981) techniques for remote measurement of the distribution of the dye tracers have been developed.

The specific optical properties of fluorescent dyes serve for concentration determinations, both *in situ* and by remote measurements.

Aircraft photographic methods involve the registration of variations in colour (absorption) or in the solar-induced fluorescence of the dye (Weidemann, 1974; Valerio, 1981) on an appropriate wavelength band. Slater (1980) reviews a sensitive method, whereby the solar-stimulated luminescence of a dye is (remotely) observed on the wavelength of a selected Fraunhofer line in the solar spectrum by means of a Fabry-Perot system.

Active RS methods employ laser-induced tracer dye fluorescence and water Raman backscatter to determine dye concentrations from an aircraft (Franz *et al.*, 1982; Hoge, Swift, 1981; Gehlhaar *et al.*, 1981).

Passive (solar-induced) multispectral remote sensing can supply important information concerning not only the absorption and fluorescence (concentration) of the dye in the sea but also the concentrations of other natural suspended and dissolved materials, such as phytoplankton, non-chlorophyllous particles and "yellow substance" (component of the dissolved organic matter). These data are essential for classification of the watermass and for proper description of the detected upwelling radiance in relation to the concentration of the fluorescent substance. The treatment of the radiative

transfer and the experiments described in this paper involve the application of passive RS (optical signals induced by incident solar radiation), when multispectral measurements of upwelling radiance and downwelling irradiance in the visible wavelengths region (400-700 nm) can be employed, and when sea truth data (concentrations of algal pigments, total suspended matter, yellow substance and dye), measured simultaneously from a ship, are available. The treatment is focused on the specific properties of fluorescent dyes emitting radiation at longer wavelengths (rhodamine B) which have been selected as the most suitable tracers (Weidemann, 1974), and on the watermasses characteristic for the North Sea. The inherent and apparent optical properties of the seawater are determined by the properties of pure water, of particulate chlorophyllous and non-chlorophyllous material, of dissolved organic matter, and—in our case—of the dissolved dye. From the numerous previous observations in the regions and during the seasons concerned, it can be concluded that:

- 1) no stratification of the watercolumn (average depth 28 m) can be expected;
- 2) the phytoplankton pigments (chlorophyll *a* + pheophytin *a*); concentration can vary between 1 and 15 mg. m⁻³;
- 3) the concentration of the total suspended matter is less than 3 g. m⁻³;
- 4) the concentration of the fluorescent component of the dissolved organic matter (yellow substance) is generally low;
- 5) the waters may be described as so-called "Case 1" waters, where the optical properties are chiefly determined by planktonic algae and co-varying products (Morel, 1980).

The dye concentration to be remotely measured can vary from 10⁻² kg. m⁻³ (about 30 min. after release from the ship) to about 10⁻⁷ kg. m⁻³ which is the lower limit of the detection system as determined during laboratory experiments. The diameter of the dye spot can be then between 1 and 2 km (about 20 hours after release). Homogeneous vertical dye distribution can be expected within 1 to 3 hours after release.

The test area was located in the southern part of the North Sea, about 50 km from the coast. The weather and seastate conditions during the experiments were favourable (clear sky, low wind-speed). For the purposes of the experiment, 300 kg of the tracer dye rhodamine B were released from a vessel in a single operation.

THEORY

Background

The availability of numerous spectral irradiance measurements in and above the water, and consequently a better knowledge of irradiance than of radiance transfer in natural waters, make irradiance models for radiative transfer in the sea attractive. Moreover, since emitted fluorescence radiation can be assumed to be completely diffuse (isotropic angular distribution), the

application of a relatively simple two-flow model (up and down) is advantageous in cases where fluorescence dominates the other optical processes (Spitzer, Ten Bosch, 1976). This model has in the past been often applied for the description of optical processes in various scattering and absorbing media. An exhaustive treatment, including solutions for natural waters, is given by Preisendorfer (1976).

The attenuation of the upwelling irradiance E_u and of the downwelling irradiance E_d at a fixed wavelength can be described by the two differential equations:

$$-\frac{dE_u(z)}{dz} = -(a_u + b_{bu})E_u(z) + b_{bd}E_d(z) + \frac{1}{2}F(z), \quad (1)$$

$$\frac{dE_d(z)}{dz} = -(a_d + b_{bd})E_d(z) + b_{bu}E_u(z) + \frac{1}{2}F(z), \quad (2)$$

where z stands for the depth, other symbols stand for: $a_u = D_u a$, the absorption coefficient for upwelling irradiance; $a_d = D_d a$, the absorption coefficient for downwelling irradiance; b_{bu} , the backscattering coefficient for upwelling irradiance; b_{bd} , the backscattering coefficient for downwelling irradiance; a , the absorption coefficient for a collimated beam; D_u , the distribution function for upwelling irradiance; D_d , the distribution function for downwelling irradiance.

For exact definitions, see Preisendorfer (1976). $F(z)$ is the symmetrical fluorescence source function.

General solutions of the system (1), (2) (two-D model) are also given by Preisendorfer. However, the solution can be substantially simplified when known relationships between the coefficients, specific to the watertype and the wavelength region, can be introduced into the equations. Since we are dealing with "Case 1" waters (Morel, 1980), and dyes emitting fluorescence at longer wavelengths, it can be assumed (Morel, Prieur, 1977) that:

$$a_u \gg b_{bu},$$

$$a_d \gg b_{bd}.$$

Also, that:

$$E_d \gg E_u.$$

Moreover, the reabsorption effect (shoulder of the strong dye absorption band at the emission wavelengths), together with the fact that the value of the dye scattering coefficient is always negligible, reinforce the above inequalities.

The two-flow equations can be then written in the form:

$$-\frac{dE_u}{dz} = -a_u E_u + b_{bd} E_d + \frac{F}{2}, \quad (3)$$

$$\frac{dE_d}{dz} = -a_d E_d + \frac{F}{2}. \quad (4)$$

The fluorescence term at the emission wavelength λ_f can be expressed as an integral within the limits λ_1, λ_2 of the absorption (excitation) spectrum:

$$F(\lambda_f) = \int_{\lambda_1}^{\lambda_2} \varphi_f(\lambda) [E_d(\lambda) a_{Rd}(\lambda) + E_u(\lambda) a_{Ru}(\lambda)] d\lambda, \quad (5)$$

where $\varphi_f(\lambda)$ is the fluorescence yield (ratio of the emitted energy at the wavelength λ_f to the absorbed energy), $a_{Ru} = D_u a_R$, $a_{Rd} = D_d a_R$ are the absorption coefficients of the dye solution for the upwelling and downwelling irradiance respectively. Introducing the specific absorption coefficient of the dye a_R^* , the dye absorption coefficient for collimated light $a_R = C_R a_R^*$ where C_R is the dye concentration ($\text{kg} \cdot \text{m}^{-3}$). The fluorescence source function can be then written as:

$$F(\lambda_f) = C_R \int_{\lambda_1}^{\lambda_2} a_R^* \varphi_f (E_d D_d + E_u D_u) d\lambda, \quad (6)$$

which is equal to:

$$F(\lambda_f) = C_R \int_{\lambda_1}^{\lambda_2} a_R^* \varphi_f \dot{E} d\lambda, \quad (7)$$

where \dot{E} is the scalar irradiance.

Since we are dealing only with the backscattering coefficient for downwelling irradiance, the symbol b_{bd} will be replaced further by the symbol b_b .

Assuming an exponential (Lambert-Beer's) depth dependence of the \dot{E} and depth independence of the coefficients a_u, a_d, b_b and of the C_R (homogeneous watercolumn structure), solutions of the systems (3), (4), (5) are:

$$E_d = m_2 e^{-a_d z} + \frac{C_R}{2} \int_{\lambda_1}^{\lambda_2} a_R^* \dot{E}_0 \varphi_f \frac{e^{-K_0 z} - e^{-a_d z}}{a_d - K_0} d\lambda, \quad (8)$$

$$E_u = m_1 e^{a_u z} + \frac{m_2 b_b e^{-a_d z}}{a_u + a_d} + \frac{C_R}{2(a_u + a_d)} \int_{\lambda_1}^{\lambda_2} a_R^* \dot{E}_0 \varphi_f \times \frac{(a_u b_b + a_d b_b + a_u a_d - K_0 a_u + a_d^2) e^{-K_0 z} - (a_u b_b + K_0 b_b) e^{-a_d z}}{(a_u + K_0)(a_d - K_0)} d\lambda,$$

where m_1, m_2 are the constants of integration, \dot{E}_0 is the scalar irradiance at zero depth, K_0 is the irradiance attenuation coefficient, $K_0 = -d(\ln \dot{E})/dz$. It should be recalled that the coefficients a_u, a_d, b_b refer to a single (maximum) emission wavelength λ_f , while $a_R^*, K_0, \dot{E}_0, \varphi_f$ are generally spectral functions within the excitation wavelength interval (λ_1, λ_2) .

Going further into approximations,

$$E_u \approx m_1 e^{a_u z} + \frac{m_2 b_b e^{-a_d z}}{a_u + a_d} + \frac{C_R}{2(a_u + a_d)} \int_{\lambda_1}^{\lambda_2} a_R^* \dot{E}_0 \varphi_f \times \frac{(a_u a_d - K_0 a_u + a_d^2) e^{-K_0 z}}{(a_u + K_0)(a_d - K_0)} d\lambda. \quad (9a)$$

At zero depth, $E_d(0) = m_2 \approx E_{d0}$ neglecting the contribution due to the reflection of $E_u(0)$ at the water-air interface. E_{d0} is the (incident) downwelling irradiance just under the sea surface.

$$E_u(0) = E_{u0},$$

$$E_{u0} = m_1 + \frac{E_{d0} b_b}{a_u + a_d} + \frac{C_R}{2(a_u + a_d)} \times \int_{\lambda_1}^{\lambda_2} a_{\#}^* \dot{E}_0 \varphi_f \times \frac{a_d b_b + a_d a_u - K_0 a_u + a_d^2 - K_0 b_b}{(a_u + K_0)(a_d - K_0)} d\lambda, \quad (10)$$

or:

$$E_{u0} \approx m_1 + \frac{E_{d0} b_b}{a_u + a_d} + \frac{C_R}{2(a_u + a_d)} \times \int_{\lambda_1}^{\lambda_2} a_{\#}^* \dot{E}_0 \varphi_f \frac{a_d a_u - K_0 a_u + a_d^2}{(a_u + K_0)(a_d - K_0)} d\lambda. \quad (10a)$$

To determine the constant m_1 , a boundary condition for $E_u(z)$ must be introduced. The third term in the equation (9) describes the contribution to E_u due to fluorescence, the second term is a contribution due to the backscattering of E_d , the first term represents the contribution of the upwelling irradiance from below. Both irradiances E_u , E_d strongly (exponentially) decrease with depth even, as evaluated (see further), in the presence of the absorbing and fluorescent substance. It can be thus assumed that at a certain depth z_1 , $E_u(z_1) = 0$. The second and the third term in the equation (9) are then very small ($z_1 > 20$ m); the term $e^{a_u z}$ is large, which means that m_1 must be very small and negative. As evaluated for the dyes and the watermasses concerned, the magnitude of m_1 is always smaller than $10^{-6} \text{ W} \cdot \text{m}^{-2}$. At zero depth, m_1 is much smaller than the other two terms and may thus be neglected.

Calculations with respect to rhodamine B

When rhodamine B is used as the tracer $\lambda_1 = 220$ nm, $\lambda_2 = 600$ nm, $\lambda_{f \text{ max}} = 575$ nm.

The emission spectrum of a dye exhibits generally a nearly symmetric (gaussian) peak around its maximum at $\lambda_{f \text{ max}}$. The number of emitted quanta at the maximum is then within a few percent proportional to the total number of the emitted quanta. As determined in the laboratory experiments:

$$\varphi_{\text{max}} \approx A \varphi,$$

where φ is the total quantum yield (ratio of the total emitted quanta to the absorbed quanta), φ_{max} is the quantum yield at the maximum (575 nm) fluorescence, A is the proportionality constant in nm^{-1} . For rhodamine B, $A = 0.0235 \text{ nm}^{-1}$.

For practical reasons, further treatment can be restricted only to the wavelength of the maximum fluorescence emission. The index "max" will be thus omitted in the following expressions.

The $\varphi_f(\lambda)$ and φ can then be related as:

$$\varphi_f(\lambda) = \frac{\lambda A}{\lambda_f} \varphi,$$

where λ is the excitation wavelength. The quantum yield φ of rhodamine B is high, $\varphi = 0.9$ (Guilbaut, 1973), and is moreover independent of the excitation wavelength (Melhuish, 1962). The equation (10) becomes then:

$$E_{u0} = \frac{E_{d0} b_b}{a_u + a_d} + \frac{A \varphi C_R}{2(a_u + a_d) \lambda_f} \times \int_{\lambda_1}^{\lambda_2} a_{\#}^* \dot{E}_0 \lambda \frac{a_d b_b + a_d a_u - K_0 a_u + a_d^2 - K_0 b_b}{(a_u + K_0)(a_d - K_0)} d\lambda. \quad (11)$$

The scattering, absorption and attenuation coefficients are related to the components of the seawater, including the fluorescent tracer. $a_{\#}^*(\lambda)$ can be determined in the laboratory using standard methods and instruments. Though instruments and methods exist for the determination of the coefficients a , b_b , K_0 *in situ* (Prieur, Sathyendranath, 1981; Spitzer, Wernand, 1981), it is in practice unrealistic to measure accurately all these coefficients in the entire remotely sensed region in real time. These coefficients will be further evaluated with respect to the materials suspended and dissolved in the sea.

The total backscattering coefficient b_b is composed of contributions:

$$b_b = r_w b_w + r_c b_c + r_x b_x,$$

where the indices w , c , x refer to the scattering by water molecules, by chlorophyllous and by other particles respectively. r 's are the backscattering to scattering ratios. Previous extensive measurements and analyses give values: $r_w = 0.5$, $b_w = 0.00165 \text{ m}^{-1}$, $r_c = 0.005$, $r_x = 0.02$, $b_c = 0.11 C_c^{0.63} \text{ m}^{-1}$ at 575 nm (Morel, Prieur, 1977; Prieur, Sathyendranath, 1981; Prieur, 1981; Smith, Baker, 1981), where C_c is the concentration of chlorophyll a + pheophytin a pigments (in $\text{mg} \cdot \text{m}^{-3}$) determined in acetone extracts by standard methods. In "Case 1" waters, the concentration of total (dry) suspended matter (seston) C_p (in $\text{g} \cdot \text{m}^{-3}$) generally covaries with C_c :

$$C_p = 0.30 C_c^{0.62},$$

and:

$$b = b_w + b_c + b_x = 1 C_p (\text{m}^{-1}),$$

where b is the total scattering coefficient (Morel, 1981).

Hence:

$$b_b = 7.9 \times 10^{-4} - 1.65 \times 10^{-3} C_c^{0.63} + 0.02 C_p, \quad (13)$$

or, when C_p is not separately determined:

$$b_b = 7.9 \times 10^{-4} - 1.65 \times 10^{-3} C_c^{0.63} + 6 \times 10^{-3} C_c^{0.62}, \quad (14)$$

$$b_b \approx 7.9 \times 10^{-4} + 4.35 \times 10^{-3} C_c^{0.63}.$$

From the definitions $a_u = D_u a$, $a_d = D_d a$.

Analogously to b_b :

$$a = a_w + a_c + a_x + a_y + a_R,$$

referring to the absorption of water, phytoplankton, nonchlorophyllous particles, dissolved organic matter (index y) and of the dye.

At 575 nm, $a_w = 0.094 \text{ m}^{-1}$ (Smith, Baker, 1981). The distribution functions D_u , D_d exhibit little wavelength dependence and can be estimated as $D_u = 2.5$,

$$D_d = \frac{0.6}{\cos j} + 0.47,$$

where j is the sun zenith angle in water (Prieur, Sathyendranath, 1981). For overcast sky $D_d = 1.16$.

The a_y can be determined experimentally by absorption measurements on the filtered watersamples (Bricaud *et al.*, 1981). Generally, at 575 nm a_y is much smaller than the other terms in the equation (15).

$a_R = C_R a_R^*$ can be measured in the laboratory. At 575 nm, $a_R^* = 13580 \text{ m}^{-1}/(\text{kg} \cdot \text{m}^{-3})$.

In order to estimate $a_c + a_x$, two approaches may be employed.

1) The absorption coefficient a and the downwelling irradiance attenuation coefficient K_d can be related as:

$$a - a_R = \frac{K_d [1 - (E_u/E_d)] \cos j}{0.6 + [0.47 + 2.5 (E_u/E_d)] \cos j}$$

(Morel, Prieur, 1975; Prieur, Sathyendranath, 1981).

For low diffuse reflectance ($R = E_u/E_d$) values:

$$a - a_R \approx \frac{K_d \cos j}{0.6 + 0.47 \cos j} = \frac{K_d}{D_d},$$

which concurs with the approach $a_d \gg b_b$.

Going further into approximation, a "rule of thumb" $a - a_R \approx 0.75 K_d$ can be found (Preisendorfer, 1976).

Smith and Baker (1978) extensively investigated the (spectral) relationship between the K_d and the materials suspended and dissolved in seawater.

For $C_c > 1 \text{ mg} \cdot \text{m}^{-3}$ they found:

$$K_d = K_{dw} + K_{dc} + K_{dx} = K_{dw} + K_x + k_2 C_c,$$

where K_x represents the contribution to spectral attenuation attributable to the non-chlorophyllous material, k_2 is the specific attenuation coefficient due to the chlorophyll-like pigments. At 575 nm:

$$a = \frac{1}{D_d} (0.136 + 0.009 C_c) + a_y + 13580 C_R. \quad (16)$$

2) Another, more exact, approach involves the expression of the respective absorption coefficients by means of the specific absorption coefficients a_c^* , a_x^* (Prieur, Sathyendranath, 1981).

$$a = a_w + C_c a_c^* + C_x a_x^* + a_y + C_R a_R^*.$$

a_c^* , a_x^* can be determined by regression. Using a standard method for the pigment concentration measurement, Prieur and Sathyendranath (1981) found for $C_c > 1 \text{ mg} \cdot \text{m}^{-3}$ at 575 nm:

$$C_c a_c^* = 0.0155 + 0.00482 C_c.$$

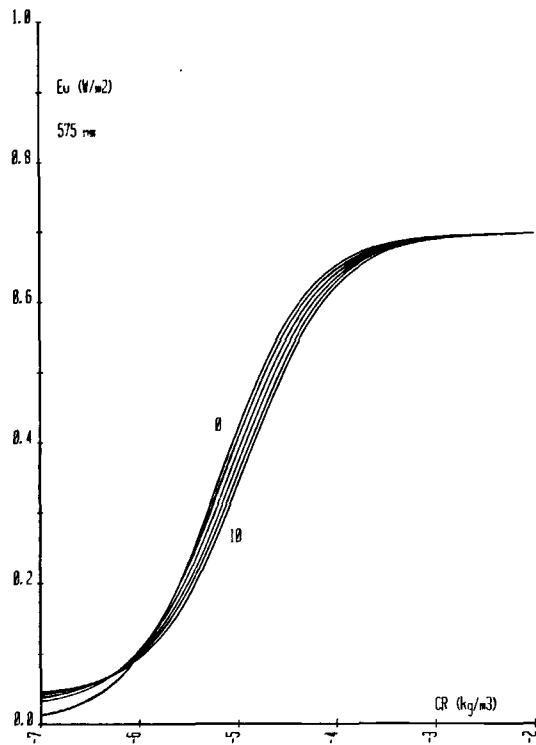


Figure 1

Upwelling irradiance $E_u(575)$ at zero depth and maximum emission wavelength, as a function of rhodamine B concentration C_R for various pigment concentrations C_c . The dye concentration scale is logarithmic, the numbers at the "tic marks" along the x-axis refer to powers of 10 (10^{-7} - $10^{-2} \text{ kg} \cdot \text{m}^{-3}$). Six lines are presented for the $C_c = 0, 2, 4, 6, 8$ and $10 \text{ mg} \cdot \text{m}^{-3}$. With increasing C_c , the E_u generally decreases. Limit values of the C_c are indicated at appropriate lines. Parameters used for calculations: sun zenith angle $j = 45^\circ$; distribution function $D_u = 2.5$.

If the total scattering coefficient measurements are applicable, an analogous formula was found for $C_p a_p^*$ (Prieur, Sathyendranath, 1981).

In the second approach, a can then be expressed as:

$$a = 0.109 + 0.00482 C_c + C_x a_x^* + a_y + 13580 C_R. \quad (17)$$

Compared to the formula (16), the approach (17) refines the absorption relationship with respect to the influence of nonchlorophyllous particles, although it requires additional knowledge (or regression analysis) of the parameter $C_x a_x^*$.

The coefficient $K_0(\lambda)$ and the incident irradiance $\dot{E}_0(\lambda)$ must be evaluated within the whole interval (λ_1, λ_2) i. e. between 220 nm and 600 nm. However, most marine-optical instruments and thus most of the collected spectral data do not include wavelengths shorter than 350 nm. Fortunately, since the absorption spectrum of rhodamine B is dominant between 490 and 580 nm and the \dot{E}_0 strongly decreases below 350 nm, the approximation $\lambda_1 = 350 \text{ nm}$ will not substantially influence the value of the integral in the equation (11).

In practice, the observations more often include the measurements of the downwelling irradiance E_{d0} than those of the scalar irradiance \dot{E}_0 . Since particularly at the longer wavelengths $E_{u0} \ll E_{d0}$, another approximation can be made: $\dot{E}_0 = D_u E_{u0} + D_d E_{d0} \approx D_d E_{d0}$.

Errors due to the above approximation must be considered. In our case, when no scattering coefficient data are available, the treatment will be further restricted to the first approach.

Figure 1 shows the increase of upwelling irradiance E_{u0} at the maximum fluorescence wavelength $\lambda_f = 575$ nm, as a function of the dye concentration C_R for various pigment concentrations C_c . For very high rhodamine B concentrations ($C_R > 10^{-3}$ kg.m $^{-3}$), E_{u0} appears to vary only little with C_R . Remote fluorescence measurements employing an active laser system (Franz *et al.*, 1982) reveal analogous saturation effects at rhodamine B concentrations higher than 10^{-4} kg.m $^{-3}$. This difference is possibly due to the different forms of excitation of fluorescence in each method. E_{u0} decreases when pigment concentration C_c increases, except for very low dye concentrations ($C_R < 10^{-6}$ kg.m $^{-3}$). At the lowest dye concentrations considered (10^{-7} kg.m $^{-3}$), the radiation backscattered by the waterbody dominates the emitted fluorescence radiation.

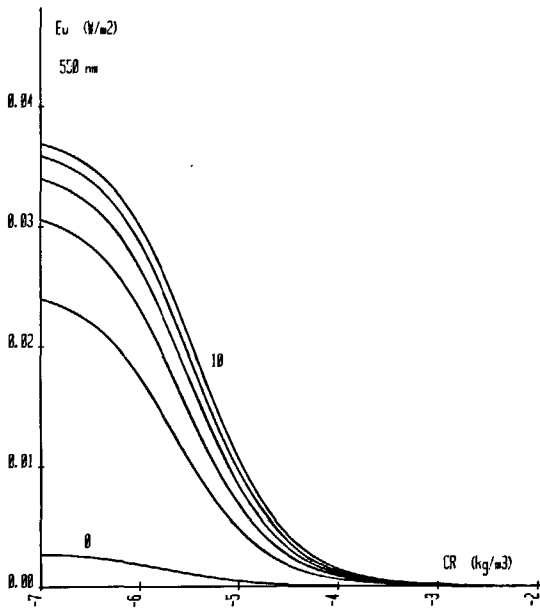


Figure 2
Upwelling irradiance $E_u(550)$ at maximum absorption wavelength and zero depth as a function of dye concentration C_R for various pigment concentrations C_c . Indications at the lines and along the axes, as well as the parameters used for calculations, are analogous to Figure 1.

Analogously, Figure 2 shows the decrease of E_{u0} at the maximum absorption (rhodamine B) wavelength $\lambda_a = 550$ nm, as a function of the dye concentration C_R for various pigment concentrations C_c . With decreasing pigment concentration C_c , and consequent decreasing (back) scattering and increasing optical pathlength, E_u also decreases. Obviously $E_u(550) < E_u(575)$; in addition, the usable rhodamine concentration range is narrower for absorption effects detection than for fluorescence, and is limited by the minimum detection limit (signal to noise ratio).

The depth dependence of both $E_u(z)$ and $E_d(z)$ at 575 nm is displayed in Figures 3, 4. It is evident that with increasing dye concentration C_R , the irradiance attenuation coefficient increases for both E_u and E_d . Worthy of note is the situation at small depths, where

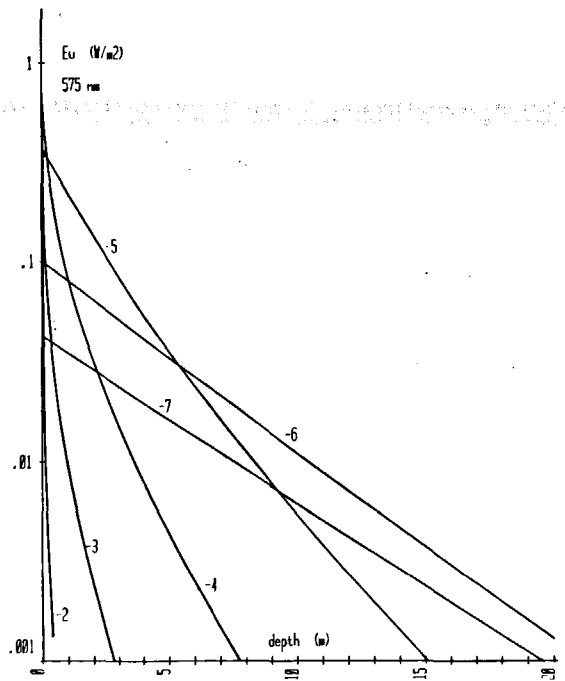


Figure 3
Upwelling irradiance $E_u(575)$ (log scale) at maximum emission wavelength as a function of depth for various rhodamine B concentrations indicated. Number at each line refers to the power of 10 ($10^{-7} \leq C_R \leq 10^{-2}$ kg.m $^{-3}$) of the dye concentration C_R . The pigment concentration $C_c = 5$ mg.m $^{-3}$ and other parameters identical with those in Figure 1, were used in calculations.

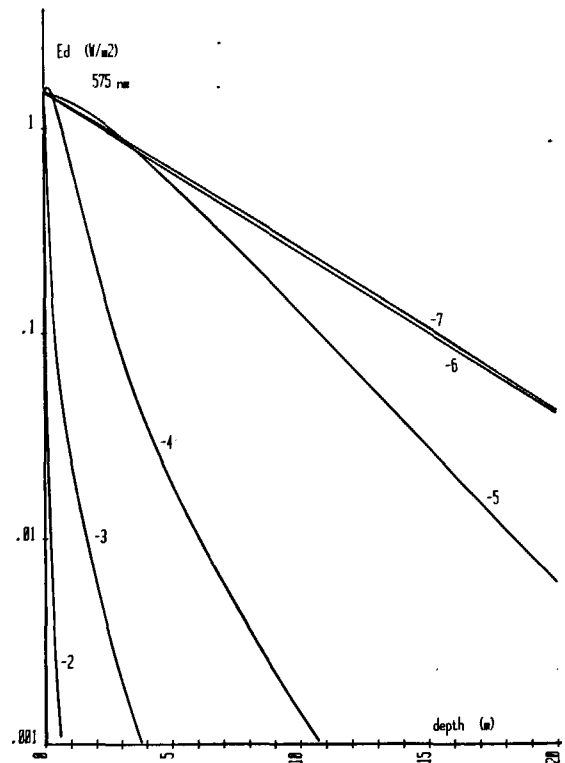


Figure 4
Downwelling irradiance $E_d(575)$ (log scale) as a function of depth for various dye concentrations indicated at each line analogously to Figure 3. The same parameters as in Figure 3 were used in calculations.

the E_u generally increases with increasing concentration while the E_d decreases, except in the case of intermediate C_R values. For instance, if $C_R = 10^{-4}$ kg.m $^{-3}$, E_d has a maximum at the depth of about 0.3 m. The estimate of absorption coefficients according to approach (1)

was applied for calculations presented by all the Figures 1-4. Irradiance attenuation coefficients tabulated by Smith and Baker (1978), incident irradiance data tabulated by Tyler and Smith (1970), (Crater Lake, clear sky) and the results of laboratory measurements of the absorption coefficient of rhodamine B solution in seawater were used for the calculations in Figures 1-4.

All the above considerations are based on knowledge of the "sea truth" data (a_y , C_c , C_p). This is not generally the case when remote observations of larger areas are performed. Concentrations must be then determined by means of appropriate algorithms, developed for the remote sensing of these substances using multispectral data. Various algorithms have been reviewed and discussed elsewhere (Sathyendranath, 1981; Viollier, 1980). However, at the wavelengths where the dissolved optical tracer absorbs or emits radiation, the applications of the algorithms must be reconsidered. An algorithm relating the chlorophyll fluorescence at 685 nm to the C_c (Neville, Gower, 1977, Spitzer *et al.*, 1982) is therefore most attractive for phytoplankton pigments concentration retrieval.

Remote sensors in aircrafts and satellites generally measure upwelling radiances. In case of completely diffuse upwelling irradiance, $E_{u0} = \pi L_{u0}$ where L_{u0} is the upwelling radiance at zero depth. The upwelling radiance just above the sea surface is $L'_{u0} = L_{u0}(1 - r_u)/n^2$, where r_u is the water-air Fresnel reflection coefficient, n is the refractive index of water. The above-water downwelling irradiance E'_{d0} is related to the in-water downwelling irradiance E_{d0} as $E'_{d0} = E_{d0}/(1 - \bar{r}_d)$, where \bar{r}_d is the averaged air-water Fresnel reflection coefficient. It has been estimated (*see e. g.* Morel, 1980) $(1 - r_u)/n^2 \approx 0.50$, $0.02 < \bar{r}_d < 0.10$, depending on the weather conditions and the sun elevation. The contribution of radiation specularly reflected on the sea surface and, at higher altitudes above the sea, of radiation scattered by the atmosphere into the sensor (path radiance), must be taken into account in the remotely measured signal (*see e. g.* Morel, 1980).

Discussion of the model

Fluorescence is often preferred to absorption coefficient measurements when dealing with low concentrations of the substances to be determined, although the emission might be substantially affected by environmental influences such as temperature, salinity or pH of the solvent. A thorough analysis of these effects is necessary. Various influences of the natural environment on the fluorescence of rhodamine B have been the subject of previous investigations, as reviewed by Weidemann (1974). These effects are not expected to play an important role in the remote observations described here. Uncertainties in the measurements can arise due to the adsorption effects of the dye by the particulate suspended material (Weidemann, 1974).

As mentioned above, the developed model describes optical effects in a vertically homogeneous and optically infinite medium (i. e. where the bottom reflection plays

no role). In the case of a stratified or shallow watermass, boundary conditions of the equations (8), (9) must be modified.

The used approximations $E_0 \approx D_d E_d$ (which follows from the initial approximation $a_d \gg b_b$) and $\lambda_1 = 350$ nm (instead of $\lambda_1 = 220$ nm) could lead to an underestimation of the fluorescence term in the equation (10). However, as calculated from available data, the error due to this underestimate is, in "Case 1" waters, always less than 5%.

The error due to the approximation $m_1 \approx 0$ is negligible in regions deeper than 20 m (*see also* Gordon, McCluney, 1975). A model principally identical with that developed in this paper, but with modified parameters specific to the fluorescent substance, can be applied for the description of the natural fluorescence of chlorophyll in seawater. This fluorescence emission with a maximum at 685 nm has been (remotely) observed in different watertypes, and might well serve for remote measurements of the pigment concentration in the sea (Neville, Gower, 1977; Doerffer, 1981; Spitzer *et al.*, 1982a).

EXPERIMENTS

Instruments and methods

The Coastal Optical Remote Sensing Airborne Radiometer (CORSAIR) developed in our laboratory was applied for the spectral measurements from the aircraft (Spitzer *et al.*, 1982b). The optical system includes: lightguide optics, monochromator, SIT detector, optical multichannel analyzer (OMA), CRT display and a desktop computer. 500 channels (400-725 nm, spectral resolution 2.5 nm) are scanned within 32 ms providing sufficient spatial resolution during overflights. In addition to upwelling radiance, downwelling irradiance and the background signal were periodically recorded, using a three-way switch at the entrance slit of the monochromator. Upwelling radiance was detected through an objective lens (28 mm focal length, field of view 12°), mounted at the bottom skin of the aircraft with a tilt angle of 15°. Downwelling irradiance was detected by a flat (cosine) opal-acrylic collector mounted in the roof skin of the aircraft. Both signals were transmitted through 5 mm diameter glass fiber lightguides to the switch at the monochromator. The OMA outputs can be followed on a CRT display. The entire measuring procedure is controlled by the computer.

The instrument was absolutely calibrated (error 5%) in the laboratory using standard radiation sources. Signal to noise ratio was 0.02. The whole setup can be assembled within 90 minutes in the aircraft (Piper-Seneca II).

3 hours after the dye release, airborne measurements were performed over a period of 2 hours.

The overflights were always performed with the lower (upwelling radiance) collector directed "away from the sun" in the sun-zenith plane, in order to prevent the contamination of the signal by the direct sun radiation

reflected on the sea surface (sun glitter). To minimize the influence of the atmospheric backscattering into the field of view (path radiance), the flight altitude was kept low, 150 m.

Each (ir)radiance measurement included four scans (130 ms).

The contribution of path radiance to the upwelling signal was evaluated from the measurements at increasing altitudes over a homogeneous site. During each overflight in the vicinity of the measuring vessel, surface samples of seawater were taken and later analyzed in the laboratory with respect to concentrations of algal pigments, total suspended matter (dry seston), yellow substance and rhodamine B. By means of real time registration on board the ship and in the aircraft, sampling was synchronized with the remote optical measurements.

Samples were analyzed with respect to the colour-determining components: chlorophyll *a* and pheophytin *a* pigment concentration (total biomass index) and total suspended matter content, using standard methods (Strickland, Parsons, 1968), yellow substance and rhodamine B concentration using both the fluorometrical method (Duursma, 1974) and absorption spectrophotometry (Bricaud *et al.*, 1981).

Results

During the measurements the total downwelling irradiance varied within 30%.

Figure 5 shows examples of the spectra measured from the aircraft for both a site with high rhodamine B concentration and a site with a zero dye concentration. The reflectance ($\pi L_u/E_d$) spectra of the seawater with no dye exhibit a maximum at about 560 nm. With

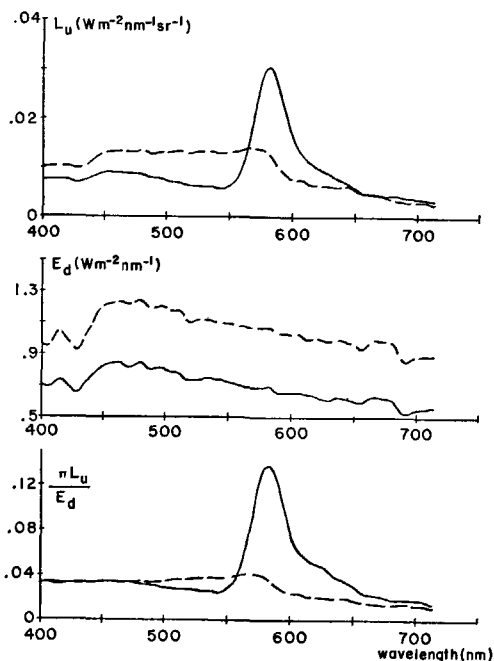


Figure 5

Spectra upwelling radiance L_u , downwelling irradiance E_d and reflectance $\pi L_u/E_d$. Full lines represent the measurements from the aircraft above a site with high concentration of rhodamine B ($2.8 \times 10^{-5} \text{ kg} \cdot \text{m}^{-3}$), dashed lines show the spectra measured above seawater with no dye contamination.

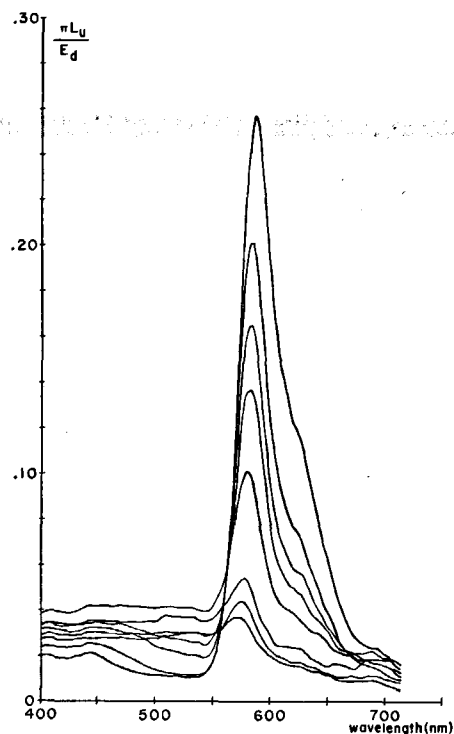


Figure 6

Variations of the spectral reflectance ($\pi L_u/E_d$) as detected above sites with increasing rhodamine B concentration. Corresponding to the lines, consecutive concentrations are 0.15×10^{-7} , 3.8×10^{-7} , 1.2×10^{-6} , 4.7×10^{-6} , 9.8×10^{-6} , $1.3 \times 10^{-5} \text{ kg} \cdot \text{m}^{-3}$.

increasing dye concentration, the emitted fluorescent radiation adds to the backscattered radiation. Consequently, the maximum reflectance increases and shifts towards the longer wavelengths, as shown in Figure 6. The reflectance spectra also exhibit a smaller maximum at the chlorophyll fluorescence wavelength 685 nm (Gower, 1980; Spitzer *et al.*, 1982 a).

The absorption effect of rhodamine B (maximum at 547 nm) can be recognized in Figures 5, 6. With increasing dye concentration, the reflectance at about 540 nm decreases, although, as predicted, the decrease is less significant than the reflectance increase at maximum fluorescence.

In addition to rhodamine B, a smaller amount of the fluorescent dye Uranin was released at a separate site. No *in situ* measurements were performed in this area. For illustration, the remotely measured spectra above the Uranin spot are presented in Figure 7.

Due to the spring algal bloom, an occurrence of horizontal phytoplankton patchiness was noticed both visually from the aircraft and in the results of the sample analyses. The chlorophyll *a*+pheophytin *a* concentration varied between 2 and 5 $\text{mg} \cdot \text{m}^{-3}$. The (dry) seston content varied between 1 and 3 $\text{g} \cdot \text{m}^{-3}$. The concentration of the dissolved organic matter was relatively low, the absorption coefficient of the filtered seawater (index of the yellow substance concentration) at 375 nm varied between 0.20 and 0.28 m^{-1} .

The concentration of rhodamine B varied during the experiment between 10^{-7} and $2.10^{-4} \text{ kg} \cdot \text{m}^{-3}$. Unexpectedly calm seastate and weather conditions caused substantially inhomogenous vertical and horizontal dye

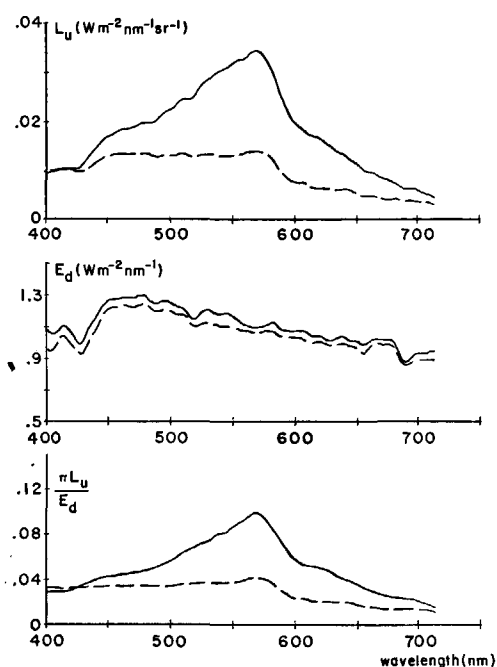


Figure 7

Spectra of upwelling radiance L_u , downwelling irradiance E_d , and reflectance $\pi L_u/E_d$. Analogously to Figure 5, full lines show the spectra measured above seawater with Uranin, dashed lines represent the spectra measured above the seawater without dye.

distribution, which thwarted proper *in situ* sampling, particularly during the first hours after release. Figure 8 shows a comparison between the values of the upwelling radiance L_u at the maximum fluorescence wavelength, as directly measured from the aircraft and the values, calculated from the two-flow model [equation (10)], using sea truth data (pigments and seston concentrations), together with the spectral values of the

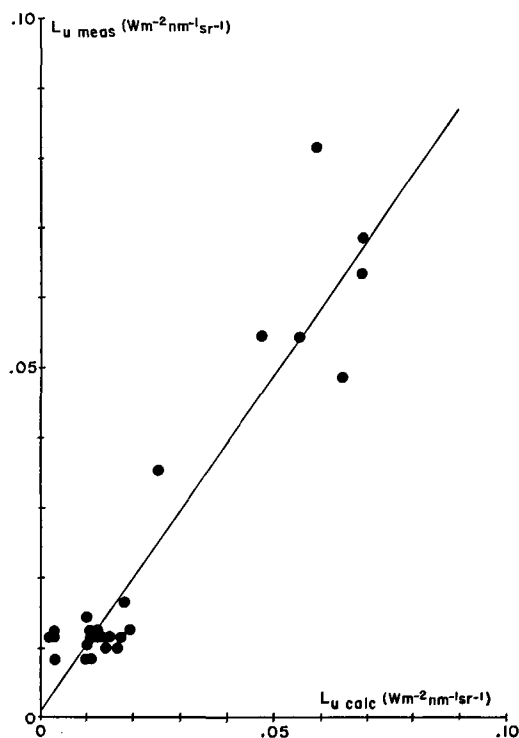


Figure 8
Measured values of the downwelling radiance L_u at the maximum emission wavelength, compared with values calculated from the two-flow model. Linear regression to these data is presented (28 points, $r=0.93$).

downwelling irradiance E_d , which were also directly measured. The inhomogeneous dye distribution mentioned above contributes substantially to the scatter of the points presented in Figure 8.

Discussion of the experiments

The results demonstrate the capability of the method described in this paper for the remote sensing of fluorescent dye distribution in the sea, though the accuracy of this method cannot be established from the present data. Imperfect discrete sampling from the vessel of the remotely sensed sites (diameter about 50 m), with patchy dye distribution and non-homogeneous vertical dye distribution (*see also Franz et al., 1982*), are responsible for the discrepancies between the measured and calculated values within a factor 2. To improve this, continuous *in situ* sampling, together with continuous remote optical measurements will be necessary. It should be mentioned that the atmospheric situation responsible for imperfect dispersion, and thus for inhomogeneous dye distribution, is rather unusual in the part of the North Sea where the tracer experiments were performed. Four hours after the release, the dye spot was about 1 000 m long and 200 m wide.

Our remote measurements appeared to be sensitive enough to detect concentrations of rhodamine B down to 10^{-6} $\text{kg}\cdot\text{m}^{-3}$. The influence of the path radiance (a fraction of the downwelling irradiance scattered by the atmosphere into the field of view of the sensor) can be neglected.

The contribution of sky glitter (radiation specularly reflected at the seasurface) was estimated to amount to 20-30% of the upwelling signal.

For the calculations of the upwelling radiance L_u from the two-flow model (in which the irradiances are treated), isotropic (diffuse) upwelling radiance distribution, including isotropic fluorescence radiance distribution (Spitzer, Ten Bosch, 1976), was assumed. This is not necessarily the case, particularly at low dye concentrations (Austin, 1980), which means that the slope of the regression line presented in Figure 8 (relation between the measured and calculated L_u values) might be less than 1. Furthermore, wave action can decrease the measured L_u values, resulting in the decrease of the slope (Gehlhaar, 1982).

To conclude, the multispectral remote sensing appears to be able to provide data on rhodamine B distribution in the sea even at low dye concentrations although a greater amount of thorough measurements, both optically from the aircraft and *in situ*, is necessary to determine the accuracy of the method.

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