

Optical measurements in the tropical North Atlantic

Irradiance Absorption coefficient Chlorophyll Spectral irradiance meter Tropical North Atlantic

Éclairement Coefficient d'absorption Chlorophylle Spectral irradiance-mètre Atlantique tropical Nord

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ABSTRACT

Measurements of total and spectral irradiance have been performed in the eutrophic and oligotrophic waters of the Atlantic Ocean. A relationship between the shape of the irradiance profiles and the structure of the euphotic zone of the tropical ocean is demonstrated. From the scalar and vector spectral irradiance data, the absorption spectra were calculated. Apart from differences in the spectra at the stations located in waters with different concentration of suspended matter, variations in the spectra at different depths were also found where the two layer structure of the euphotic zone occurred. Preliminary results of laboratory analyses indicate relatively increased concentrations of the carotenoid pigments, with respect to the concentration of the chlorophyll pigments in the upper layer.

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RÉSUMÉ

Mesures optiques dans l'Atlantique tropical Nord.

Des mesures spectrales de l'éclairement sous-marin, effectuées dans l'Atlantique NE tropical, en zone eutrophique (Mauritanie) et en zone oligotrophique (Canaries) sont présentées. La forme des profils d'éclairement en fonction de la profondeur apparaît liée à la structure de la couche euphotique.

A partir des valeurs des éclairements vectoriels et scalaires, les coefficients d'absorption peuvent être calculés; les spectres d'absorption ainsi obtenus varient d'une station à l'autre avec la teneur en matières en suspension. Ils varient également, en une même station, avec la profondeur, en particulier lorsqu'une structure à deux couches existe dans la zone euphotique. Dans ce cas, la chromatographie montre que, pour la couche superficielle, la proportion des caroténoides par rapport à celle des pigments chlorophylliens est accrue. Le coefficient d'absorption, en tant qu'index de la concentration en chlorophylle, apparaît meilleur que le coefficient d'atténuation diffuse.

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INTRODUCTION

Generally, experimental and theoretical study of the optical processes in the ocean can be utilized for two purposes. Data on photosynthetic available radiation (PAR) are essential in the study of marine photosynthesis and primary productivity. On the other hand, apparent and inherent optical properties of the seawater supply important information about nature and concentration of the dissolved and suspended materials in the watercolumn. Various papers on these subjects were published recently, particularly with respect to remote sensing experiments (Smith, Baker, 1978*a*, *b*; Jerlov, 1978; Morel, Prieur, 1977; Morel, 1978; Højerslev, 1978; Tyler, 1979). Determination of either total or, preferably, spectral solar irradiance as function of depth can serve efficiently for both purposes mentioned above.

The measurements presented in this paper of photon scalar irradiance (spherically collected irradiance,

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Geographical position of stations in the tropical North Atlantic.

integrated between 350 and 700 nm), spectral irradiance and absorption coefficient in situ, were performed within the framework of research on the carbon cycle in the euphotic zone of a permanently stratified part of the Atlantic Ocean (Baars, Zijlstra, Tijssen, 1979) during October 1977 and November 1978 (Nectar R/V HMS Tydeman). The location of the stations where measurements were taken is displayed in Figure 1. Since the stations cover both eutrophic (eastern part) and oligotrophic (western part) regions of the Atlantic Ocean, substantial spatial differences of the observed optical quantities and of their correlations with other oceanographic parameters can be expected. Vertical stratification in particulate matter and a deep layer of maximal chlorophyll concentration (two-layer tropical structure of the euphotic zone) observed in the western part of the investigated area (Gieskes, Kraay, Tijssen, 1978) affect the attenuation of the irradiance in a more complex way than in well mixed coastal regions, where the irradiance attenuation coefficient is assumed to be constant over the whole of the euphotic zone (Smith, Baker, 1978 a).

Measurements of photon scalar irradiance and of spectral irradiance, as function of depth at the different stations, were performed. Special attention was paid to the irradiance attenuation and absorption spectra with respect to the structure of the watercolumn and to the distribution and composition of the suspended particulate matter.

Besides the irradiance measurements, continuous *in situ* chlorophyll fluorescence measurements were performed and utilized for rapid tracing and direct sampling of layers with different biogeneous particles' concentration.

INSTRUMENTS AND METHODS

A photon scalar irradiance meter (Spitzer, Wernand, 1979 a) was employed for the total irradiance measurements. Irradiance-depth profiles were obtained by recording simultaneously the output of an underwater unit in combination with a depth sensor and the output of an identical reference deck unit by means of an X-Y recorder in a lab on board.

Scalar and vector irradiance and absorption spectra were calculated from the outputs of a spectral irradiance meter (Spitzer, Wernand, 1979 b), which detects subsequently the incident irradiance at 11 wavelengths between 370

and 700 nm. In this wavelength region, the transmission of solar radiation undergoes its most substantial changes when suspended algal particles are present. Detecting scalar and vector irradiance gradients over a depth interval, the absorption coefficient can be determined by employing the integrated radiative transfer equation (see for instance Preisendorfer, 1976 a) :

$$a(\lambda, z) \mathbf{E}_0(\lambda, z) = -\frac{d\vec{\mathbf{E}}(\lambda, z)}{dz},$$

where a (λ , z) is the absorption coefficient at the wavelength λ , and depth z, $\vec{E}(\lambda, z)$ is the net downward (vector) irradiance, $E_0(\lambda, z)$ is the scalar irradiance. Net downward irradiance \vec{E} expresses the difference between the downward and upward irradiance.

A commercial instrument (Variosens) was employed for continuous chlorophyll fluorescence detection as function of the depth.

For direct data processing on board, an automatic data acquisition system HP 3052 A was used.

All measurements were performed around noon with solar elevation varying between 45° and 55° at each station. The influence of the ship (reflections, shadowing) and of the sea-state on the measurements was minimal at that time.

RESULTS

Relative photon scalar irradiance data for stations representing the investigated area is displayed in Figure 2. One can distinguish different slopes of the lines



Figure 2

Relative photon scalar irradiance (in percents of the surface value) as function of depth. Number at each line corresponds with the number of the station displayed in Figure 1. Depths of the upper boundary of the chlorophyll layer are indicated.

recorded in regions with different concentration of suspended material. A curvature of the profiles can be recognized where vertical stratification of the watercolumn (a layer of increased chlorophyll concentration) appeared, as confirmed by analysis of samples taken at different depths. This is shown in Figure 3, where the distribution of the chlorophyll together with the relative irradiance levels and attenuation depths are presented for the whole investigated area. Two layers can be recognized from the displayed data. Substantially increased concentration of chlorophyll characterizes the lower layer. The nearly monotone increase of the depths of the irradiance levels (Fig. 3b) from the East to West is disturbed only at the station 3, which was located in



Figure 3

Distribution of chlorophyll a (a), irradiance levels (b) and irradiance attenuation depths (c) at different stations of the investigated area. Chlorophyll concentration (in mg Chl a m^{-3}) and percents of relative irradiance are indicated, as well as the depth of the mixed layer (dashed line, a, b). The upper line in the diagram c corresponds to the attenuation depths found in the upper layer, the lower line corresponds to the attenuation depths found in the lower of the euphotic zone throughout the whole area. Secchi disc depths and the average particulate organic carbon (POC) concentration within the mixed layer (dashed line, c) are displayed too in the diagram c.



Figure 4

Scalar and downwelling vector spectral irradiance as detected in the eutrophic waters at the station 2 (a, b) and in the oligotrophic waters at the station 5 (c, d). Numbers at each line refer to the depth.

a transition region between the upwelling and the permanently stratified parts (Baars *et al.*, 1979). Both layers are also characterized by different irradiance attenuation depths (reciprocal value of the irradiance attenuation coefficient), throughout the whole area (Fig. 3c).

As one can expect (Morel, Prieur, 1977; Smith, Baker, 1978 b), significant differences were noticed also in the irradiance spectra in regions with different concentrations of biogeneous material. Figure 4 shows spectra of scalar and vector irradiance as determined at a station in the eastern part (eutrophic water) and at a station in the western part (oligotrophic water) of the investigated area. Not only the irradiance attenuation differs, but also the irradiance maxima are shifted from about 520 nm in the eutrophic (moderately green) waters, to about 490 nm in the oligotrophic (blue) waters (Morel, Smith, 1974).

These data can be presented also as function of depth, as shown in Figure 5. Again, curvature of the profiles indicates two-layer structure of the investigated part of the watercolumn, particularly the western part of the area.





Scalar and downwelling vector spectral irradiance as function of the depth. Graphs a, b, c and d, refer to the same stations as in Figure 4. Numbers at each line refer to the wavelength. Errors of the measurements are indicated.

From these data (Fig. 4, 5) the absorption coefficients were computed as presented in Figure 6 for the two representative stations. Positions of the maxima of the absorption spectra correspond with the positions of the known absorption maxima of major photosynthetic pigments (chlorophyll a around 430 and 680 nm, carotenoids around 480 nm). Absorption spectrum for pure water redrawn from Morel's data (Morel, Prieur, 1977), exhibits a bump at 520 nm. This slope structure between 500 and 520 nm is likely responsible for the feature, around 520 nm, revealed by the curves found at station 2.



Figure 6

Absorption coefficients computed from the spectral irradiance data presented in Figure 4. Dashed lines correspond to the measurements in the upwelling region at the station 2, full lines correspond to the measurements performed in the clear oceanic water at the station 5. The depths are indicated. Absorption coefficients for pure water given by Morel and Prieur (1977) are also presented (dashed line --). The values corresponding to the station 2 (eutrophic waters) and the values for pure water are divided by 10 to place these data in the scale of this figure.

Apart from the regional differences in absorption spectra as shown in Figure 6, considerable variations with depth, not only of the heights of the absorption peaks but also of the shape of the absorption spectra, were found. Decrease and shift of the absorption maxima towards the longer wavelengths (see Fig. 6, full lines) were observed in the upper part of the euphotic zone in the oligotrophic waters. Also, absorption spectra of acetone extracts of filtered matter collected in both layers exhibited substantial differences. The chlorophyll absorption peak (at about 435 nm) was lower in the upper layer, when besides chlorophyll absorption, carotenoids' absorption (peak at about 480 nm) appeared to be significant. Thin layer chromatography indicated increased concentration of the carotenoid pigment lutein in the upper layer of the euphotic zone (Gieskes, pers. comm.).

Figure 7 displays spectra obtained by both *in situ* and laboratory methods. Since the spectral resolution of the laboratory spectrophotometer is far better (1 nm) than the resolution of the spectral irradiance meter (20 nm), finer structure of the spectra (two bands between 450



Figure 7

Absorption spectra measured in situ (full lines) compared to the absorption spectra of the acetone extracts of the filtered matter (dashed lines). All spectra are reduced by subtraction of the absorption coefficient of pure oceanic water as found in the very clear waters of the central Atlantic Ocean (station 7). Depths and errors are indicated. Data at smaller depths refer to the measurements within the upper layer, data at greater depths refer to the measurements in the lower layer of the euphotic zone. and 500 nm) can be recognized. The observed spectral differences give an indication of the varying composition of the suspended biogeneous material at different depths, which could be a consequence of different algal population or of more rapid bleaching of chlorophylls than carotenoids in the surface waters (Kiefer *et al.*, 1979), or of adaptation of the algal pigments with respect to the well known radiation protective properties of the carotenoids. Increase of absorption at shorter wavelengths (below 400 nm) can be ascribed to the presence of particulate material other than algal cells and of dissolved organic matter (yellow substance).

DISCUSSION

In well mixed layers, assumption of a constant diffuse irradiance attenuation coefficient is often made (Smith, Baker, 1978 a). Departures from this approximation were observed in the upper layer of the watercolumn (Jerlov, 1977, see Fig. 2; Ivanoff, 1975), in clear waters at depths below 50 m (Jerlov, 1977, see Fig. 2), and where vertical stratification in turbidity appeared (Ivanoff, 1975). Strong absorption of longwave and shortwave radiation is responsible for this effect in the upper few meters under the surface (Jerlov, 1977). It is also evident that the attenuation of the irradiance is related to the concentration of the suspended particles. However, variations of the attenuation coefficient in deep clear waters as observed also during our investigations remained as yet unexplained (Jerlov, 1977). From the chlorophyll concentration measurements, performed simultaneously with our irradiance measurements, a deep maximum chlorophyll concentration layer was found (Gieskes et al., 1978, see Fig. 3). It appears that the depth of this chlorophyll layer in deep clear water correlates with the depth where curvature of the irradiance profiles is observed, as shown in Figure 8. This





Depth of the irradiance attenuation change as function of the depth of the sharp upper boundary of the chlorophyll layer. The term "depth of the irradiance attenuation change" stands for the depth of intersection point of the irradiance profiles' asymptotes. Data found in the North Atlantic (\bigcirc 's) are supplemented by data found in the Gulf of Guinea (\bigcirc 's). The solid line shows a fit to all data.

means that the depth of the chlorophyll layer can be simply evaluated also from the irradiance measurements. The two evidently different slopes of the irradiance profiles characterize the typical two-layer structure of the euphotic zone, as shown also in Figure 3. This typical tropical structure has been often a subject of investigations. It appears that the depth of the maximum chlorophyll concentration layer is not correlated to the depth of the mixed layer (see Fig. 3). It is correlated well to the depth of the nutricline (Gieskes *et al.*, 1978; Herbland, Voituriez, 1979).

When such a two-layer structure is present, the application of the Secchi disc depth measurements for characterizing the watercolumn is limited only to the upper part of the euphotic zone (see Fig. 3c), with relatively low concentrations of suspended particles. As expected (Smith, Baker, 1978*b*), a correlation can be seen in Figure 3c between the attenuation depth in the upper layer (and the Secchi disc depth) and the average particulate organic carbon (POC) concentration in the mixed layer (Postma, Rommets, 1979).

Due to the "absorption-like character" of the irradiance attenuation coefficient (Preisendorfer, 1976 *b*), relation between total diffuse irradiance (in quanta $s^{-1} \cdot m^{-2}$) attenuation coefficient and the concentration of chlorophyll *a* and "chlorophyll-like" pigments has been investigated previously (Smith, Baker, 1978 *a*). Several effects disturb the desired linear dependence between the two quantities:

a) the influence of the "nonlinear biological effects" has been extensively discussed by Smith and Baker (1978 a). Briefly, the amount of particulate organic carbon (POC), including also the photosynthetically nonactive particles, can affect substantially the irradiance attenuation coefficient since both phenomena, absorption and scattering are involved in the attenuation process;

b) the apparent optical properties, diffuse absorption and diffuse scattering coefficients (and therefore also the diffuse irradiance attenuation coefficient) have different physical meaning and definitions than the inherent optical properties, the absorption and scattering coefficients defined by the Lambert-Beer law and by the radiative transfer equation. The diffuse coefficients describe optical alterations along an infinitesimally thin absorbing and scattering layer, while the coefficient corresponding to the inherent properties refer to optical alterations along an infinitesimally short optical path length (parallel beam): see Preisendorfer (1976 c), Spitzer and Ten Bosch (1976). Preisendorfer (1976b) has derived a rule of thumb relating the diffuse attenuation coefficient to the absorption coefficient. Direct proportionality between both quantities can be postulated only in extreme cases. This means that one cannot simply expect a linear relationship between the diffuse irradiance attenuation coefficient and the concentration of the absorbing substance, like in the case when the Lambert-Beer law holds:

c) the absorbing pigments' molecules are present in the sea chiefly in particulate matter (algal cells and detrital particles). Moreover, distribution of these molecules within a cell is far from being homogeneous. This means that even within a particle, the Lambert-Beer law does not hold exactly with a consequence of possible nonlinear relationship between the optical absorption (including the inherent absorption) and the pigment concentration;





Irradiance attenuation coefficient (determined from the photon scalar irradiance measurements) as function of the chlorophyll a concentration (\bigcirc 's, data found in the North Atlantic, \bullet 's, data found in Gulf of Guinea, 1979). The solid line is a least squares fit presented by Smith and Baker (1978 a) $K_r^{-1} = 8.78 - 7.51 \log C_k$.

d) the total irradiance attenuation coefficient refers to the irradiance integrated over a certain wavelength region (350-700 nm). Diverse spectra may lead to the same integral which contributes to the nonlinear behaviour discussed.

The collected data on the irradiance attenuation coefficient (determined from the photon scalar irradiance measurements) as function of the chlorophyll a concentration are presented in Figure 9, together with nonlinear fit as calculated by Smith and Baker (1978 a) to a number of data collected previously.

A single straight line fit (linear correlation coefficient .96) was calculated to our data on the absorption coefficient at 430 nm (absorption band of major algal pigments), as function of the chlorophyll a concentration displayed in Figure 10. The presented data found in the North Atlantic Ocean are supplemented by the data found in the tropical East Atlantic (Golf of Guinea) to substantiate the line fit. Since the number of spectral measurements does not coincide with the number of total irradiance measurements, numbers of points in Figures 9 and 10 differ. Unfortunately, no data were collected in the concentration range 0.8-1.3 mg Chl a m⁻³, which makes the straight line fit in the Figure 10, being only an



Figure 10

Absorption coefficient at 430 nm as function of the chlorophyll a concentration (O's represent data collected in the North Atlantic Ocean, •'s represent data collected in the Gulf of Guinea). interpolation in this concentration range. The relationship between the absorption coefficient and the concentration of chlorophyll *a* is determined not only by the absorption of algal cells, but also by absorption of detritus and other suspended matter and of dissolved organic material. The amounts of these components are not necessarily co-varying with chlorophyll a content, and can introduce residual terms. The optical absorption (and scattering) of phytoplankton populations is strongly dependent on the growth rate and nutritional state of the population. Variations up to a factor 10 of the absorption coefficient per mg chlorophyll $a \text{ m}^{-3}$ have been found on various cultures (Kiefer et al., 1979; Bricaud, 1979). The value of the absorption coefficient per unit of chlorophyll a concentration found in the tropical North Atlantic is about factor 1.3 to 5 higher than values of laboratory measurements reviewed by Bricaud (1979), but it is comparable with the values of the absorption coefficients for aged batch cultures with relatively high content organic detritus of (Kiefer et al., 1979), abundant also in the ocean waters. Considerable amounts detrital particulate material (co-varying with chlorophyll a (Smith, Baker, 1978b; Morel, 1980)) were demonstrated by Gieskes et al. (1978, 1979) and by Postma and Rommets (1979). Thin layer chromatography measurements suggest that about 50 % of the absorption of total pigments in the oligotrophic waters can be ascribed to the "nonfunctional chlorophyll" (Gieskes et al., 1979). Since the absorption coefficient of pure water has not been subtracted from the absorption data, the point of intersection of the straight line fit with the zero concentration axis (0.019 m^{-1}) , determines the absorption coefficient for pure oceanic water at 435 nm. The value of this coefficient is in good agreement with the value 0.015 m⁻¹ presented previously (Morel, Prieur, 1977), considering the uncertainties in the extrapolation of the regression line due to the complex nature of the absorption and the uncertainties in the determination of the absorption coefficient for pure water. No substantial influence of the carotenoid pigments' absorption can be recognized in the data presented in Figure 10, since this absorption was significant only at very low concentrations of the suspended biogeneous particles (large relative errors of measurements). Tight covariation between the absorption coefficient at 678 nm (absorption band of chlorophyll pigments) and sum of the concentrations of chlorophyll and phaeopigments was found by Kiefer and SooHoo (1980), using a specially constructed laboratory spectrophotometer for measurements or samples of surface water of Baja California. Due to the low irradiance levels under water, particularly at larger depths, we did not obtain enough reliable data on the absorption *in situ* at the longer wavelengths to investigate similar correlation in the Atlantic Ocean.

From the spectral measurements, also the ratio between the total quanta and total energy within the spectral region of photosynthetic activity (Morel, Smith, 1974; Jerlov, 1978) was calculated. The values of this ratio varied between 2.3×10^{18} and 2.6×10^{18} quanta $s^{-1} W^{-1}$, which is in agreement with the values reported previously by Morel and Smith (1974).

An optical classification of the investigated region of the oligotrophic ocean according to Jerlov's (1977) classification (limited to the upper part of the euphotic zone) in terms of quanta irradiance would be:

Station	Watertype
3	IB
4	IB-IA
5	IA
6	IA-I
7	Ι

The classification has not been applied to the measurements performed at the station 2, since the content of the strongly attenuating upwelling waters rich on algal (by)products differs from the content of the strongly attenuating coastal waters (high-concentration of yellow substance) described by Jerlov.

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