Spectral irradiance
Passive fluorescence
Chlorophyll
Sargasso Sea
Éclairement spectral
Fluorescence passive
Chlorophylle
Mer des Sargasses

Optical measurements in the Sargasso Sea: solar stimulated chlorophyll fluorescence

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ABSTRACT

Measurements of total and spectral quantum irradiance were performed at a single location in the Sargasso Sea over a number of days. The spectro-optical characteristics of the water mass were consistent with a relatively high concentration of biogenic material for an oligotrophic ocean station. *In situ*, spectral, diffuse attenuation coefficients correlated well with the spectral characteristics of the absorption spectra of particles caught on GF/F filters. The fluorescence signature of chlorophyll *a*, stimulated by the sun, could be detected in all upward irradiance profiles down to depths of 80 m, that is to approximately the 1% of surface light level at 440 nm. Depth variations in the passive chlorophyll fluorescence also correlated with those in both the artificially-stimulated *in vivo* fluorescence and the fluorescence of acetone extracts of filtered samples. The rapid decay with depth of the emission (red) radiation allowed estimates to be made of the fluorescence efficiency at discrete depths throughout the water column. The depth-averaged quantum efficiency of fluorescence was in good agreement with theoretical and laboratory estimates.

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RÉSUMÉ

Mesures optiques pratiquées dans la mer des Sargasses : fluorescence chlorophyllienne stimulée par le soleil

Différentes mesures de l'éclairement total et spectral ont été effectuées en un même endroit de la mer des Sargasses au cours d'un certain nombre de jours. Les caractéristiques spectro-optiques de la masse d'eau correspondaient à une concentration relativement élevée de matière biogénique pour une station océanique oligotrophe. Les coefficients d'atténuation diffuse, spectrale et *in situ* se corrélaient bien aux caractéristiques spectrales du spectre d'absorption des particules retenues au moyen de filtres GF/F. La signature de fluorescence de la chlorophylle *a*, stimulée par le soleil, a pu être détectée dans tous les profils d'éclairement ascendant jusqu'à des profondeurs de 80 m, c'est-à-dire jusqu'au niveau où il ne reste qu'environ un pour cent de la lumière de surface à 440 nm. Les variations de profondeur dans la fluorescence chlorophyllienne passive se corrélaient aussi à celles qu'on trouve tant dans la fluorescence stimulée artificiellement *in vivo* que dans la fluorescence d'extraits d'acétone provenant d'échantillons filtrés. La décomposition rapide avec la profondeur de la radiation (rouge) d'émission a permis de faire des estimations de l'efficacité de la fluorescence à des profondeurs discrètes sur toute la longueur de la colonne d'eau. L'efficacité quantitative à profondeur moyenne de la fluorescence correspondait assez bien aux estimations théoriques et expérimentales (en laboratoire).

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INTRODUCTION

The underwater light field has traditionally been used as a tool to provide information such as turbidity, water type, photic depth and biological content of the ocean. Jerlov (1968) first used monochromatic and spectral information to categorise the world's oceans. More recently, Smith and Baker (1978) and Morel and Prieur (1977) used spectral information to determine the quantity and type of material present in the ocean. Open ocean areas such as the Sargasso Sea have often been considered to be amongst the world's optically clearest waters (Jerlov, 1968) which in turn indicates a low level of biomass. One of the more common estimates of biomass is an optical determination, by *in vivo* fluorescence, of the quantity of chlorophyll *a* pigment in marine organisms. The ability of chlorophyll *a* to fluoresce under controlled optical stimulation was recognised by Yentsch and Menzel (1963) and Holm-Hansen *et al.* (1965) as the basis for a laboratory method of determining chlorophyll content from acetone extracts of sea water samples as well as laboratory cultures. Lorenzen (1966) used a continuous flow through fluorometer to measure the fluorescence of seawater in the field. This application of fluorescence measurements to fieldwork problems has been used extensively over the years for a wide variety of problems such as mapping horizontal variations of chlorophyll concentration (*e. g.* Armstrong *et al.*, 1967), vertical profiling (*e. g.* Strickland, 1968) and short term temporal changes in phytoplankton concentration (*e. g.* Platt, 1972). Continuous fluorometric measurements in the field with the aid of commercial submersible fluorometers are now in common use. The absolute calibration of *in vivo* fluorescence measured by such techniques however still remains undefined (Kiefer, 1973). In the field the picture is also complicated by the fact that *in vivo* fluorescence also occurs for phaeophytin as well as chlorophyll *a* (Kiefer, 1973). During recent years attention has turned to the existence of passive (solar stimulated) chlorophyll *a* fluorescence and hence to the information the natural underwater light field contains about this photoactive component of marine material. Fluorescence has also received additional attention due to its potential to be monitored by remote sensing techniques (Neville, Gower, 1977). Such techniques, however, register the surface fluorescence signature emanating from the top few metres (4-5 m, Neville, Gower, 1977) and give no information concerning bio-optical processes deeper in the water column.

Theoretical considerations of the existence of high apparent surface reflectance at the chlorophyll *a* emission wavelength have been given both in terms of fluorescence (Gordon, 1979; Kattawar, Vastano, 1982) and anomalous dispersion (Gordon, 1974; Mueller, 1973). *In situ* optical data illustrating passive fluorescence are relatively few and has been recorded for relatively high concentrations of chlorophyll *a* (> 5 mg m^{-3}), Morel and Prieur (1977), Neville and Gower (1977) and Topliss (1982). Observations of the fluorescence peak have been noted in low (< 1 mg m^{-3}) chlorophyll *a* concentration surface water by Clarke *et al.* (1980). Most of the data presented in the literature, however, deal with the surface layer or an assumed vertically homogeneous water mass.

This paper examines a method by which the underwater light field can provide further or complementary information about the biogenic material present in the ocean. Both absorption in the blue/green portion of the spectrum and passive fluorescence in the red portion of the spectrum are shown to be useful indicators of the nature and concentration of phytoplankton in the ocean. This study also extends the observation of surface passive fluorescence to full depth profiles with comparisons between passive fluorescence profiles and the more commonly used artifically stimulated fluorescence profiles.

METHODS AND MEASUREMENTS

A single station in the Sargasso Sea (Fig. 1) was occupied for biological sampling for 11 days from April 9th to April 20th, 1983. Initial rough weather prevented optical measurements being made on transit and at the start of the long station. Moderately rough seas persisted during the remainder of the cruise period so that optical data could be collected only below the top 5-10 m, out of the influence of surface waves. Atmospheric conditions varied from heavily overcast to bright with clouds; no completely clear sky conditions were encountered.

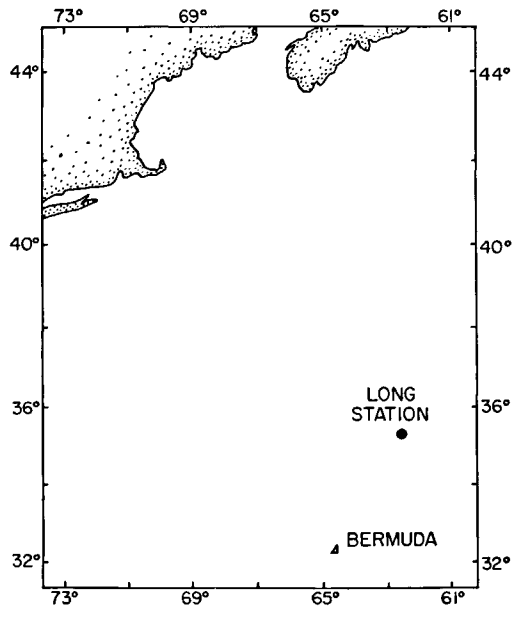

Figure 1
Geographical location of station maintained for eleven days in the Sargasso Sea. Location was selected with the aid of satellite imagery to be free of large scale thermal movement.

Optical measurements of surface, and subsurface downward and upward irradiance were made with a Techtum quantum irradiance meter capable of scanning from 400 to 750 nm. Figures 2 *a* and 2 *b* illustrate the main features of the underwater quantum irradiance spectrum for the long station. Maximum penetration

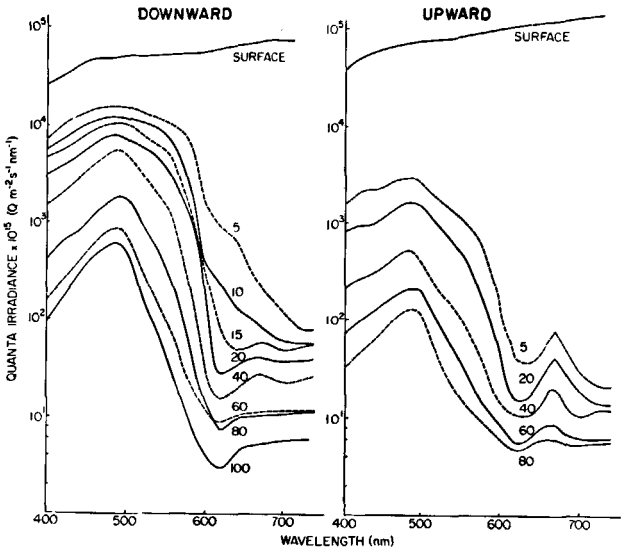

Figure 2

Example of downward and upward spectral quantum irradiance profiles obtained at long station. Numbers at each line refer to depth in metres [in both examples the surface spectra are measurements of shipboard (above-surface) downward irradiance].

of quanta occurred at 480 nm with indication, at some depths, of enhanced irradiance at 680 nm in the downward spectrum but consistent evidence of enhanced 680 nm irradiance at all depths in the upward spectrum. The feature at 680 nm was observed in all upward profiles throughout the cruise period. In Figures 2 *a* and 2 *b* the apparent wavelength independence of irradiance beyond about 700 nm is an artifact of the recording system. The spectral upward signal was only a few percent of the downward signal, such that at wavelengths greater than 600 nm the background upward light field below 10 m was very weak (approximately 0.06% of surface light for 650 nm at 20 m). The very low level of natural background light made it easy to distinguish the enhanced 680 nm feature from any fluctuations in background caused by changes in surface intensity and sea state. Additional, single wavelength measurements of downward quantum irradiance were made together with total quantum (400-700 nm) profiles using a LICOR system measuring the ratio of surface to underwater total quantum intensity.

Those biological variables measured that were directly relevant to this study included vertical profiles of *in vivo* fluorescence made with an Aquatracka ® submersible fluorometer and chlorophyll *a* and phaeophytin concentrations at discrete depths measured on samples filtered through Whatman GF/F filters and analysed according to Strickland and Parsons (1968). Detailed examination was made of the picoplankton contribution to total phytoplankton biomas and productivity estimates (Irwin *et al.*, 1984) as well as the spectral dependence of photosynthetic efficiency (Lewis *et al.*, 1984). The concentrations of pigmented material was typically between 0.5 and 1.0 mg m^{-3} with, on average, 35% being due to the picoplankton (< 1 μm) contribution. Phaeopigment contribution to the pigments was high, between 40% and 60% by weight. Photosynthetic rates, measured by the *in situ* method, were also comparatively high, typically 100-330 mg C m^{-2} per day.

SPECTRAL ATTENUATION MODELS

The vertical attenuation coefficient for downward irradiance, K_T, can be decomposed to show the explicit contribution of chlorophyll-like pigments (C_p in mg m^{-3}) by very simple linear models as governed by Lambert-Beer's law such that

$$K_T = K_w + K_{TP}.C_p, \qquad (1)$$

where K_w is the attenuation due to pure water and K_{TP} the specific attenuation coefficient per unit concentration of total pigmented material. This derivation ignores any contribution to attenuation caused by dissolved material or yellow substance (Højerslev, 1982) which is assumed to be negligible. The linear partitioning of optical properties is valid for such quantities as the absorption coefficient but is only an approximation in the case of the irradiance attenuation coefficient (Morel, Bricaud, 1981) with resulting uncertainty in specific coefficients for individual components of a water mass. Inherent and apparent optical properties have also been related to the sum of spectral contributions from total suspended minerals, dissolved organic material and suspended organic material through the work of Gordon (1973), Jain and Miller (1977), Prieur and Sathyendranath (1981) and Bukata *et al.* (1981). Smith and Baker (1978) utilised a spectral approach to quantify the spectral dependence of chlorophyll-like pigments and presented two wavelength dependent models: a) for very low concentrations of pigments (< 1 mg m^{-3}) where the ratio of living to total carbon is low; and b) for high pigment concentration waters (> 1 mg m^{-3}) where the ratio of living to total carbon approaches one. The division into two biological groups was based on the results of Hobson *et al.* (1973). The spectral values of coefficients for the two models given below are tabulated in Smith and Baker (1978):

$$K_T(\lambda) - K_w(\lambda) = K_1(\lambda).C_p \qquad (2a)$$

$$C_p < 1$$

$$K_T(\lambda) - K_w(\lambda) = K_{x2}(\lambda) + K_2(\lambda).C_p \qquad (2b)$$

$$C_p > 1$$

In the case of equations (2 *a*), $K_1(\lambda)$ represents the spectral attenuation due to chlorophyll and all covarying detrital material. Case (*a*) was considered to occur typically for low chlorophyll concentrations with the result that $K_1(\lambda) \gg K_2(\lambda)$ since it contained a contribution from material other than, but not statistically separable form C_p. In case (*b*), for higher pigment values, non-covarying detrital material is accounted for by $K_{x2}(\lambda)$ so that $K_2(\lambda)$ is interpreted as the specific attenuation coefficient due to the average ensemble of ocean phytoplankton.

COMPARISON WITH EXPERIMENTAL RESULTS

The exponential decay constant for light was calculated at 20 nm intervals from the scanning quantum irradiance records. The resulting values of K_T were very low, typically 0.053 m^{-1} at 500 nm and values for $\lambda > 600$ nm were difficult to estimate, being subject to large errors, as in Smith and Baker (1978) with occurences of $K_T < K_w$ as experienced also by Spitzer *et al.* (1982). The accurate estimation of the vertical attenuation coefficient for pure water, however, remains a research topic in itself (Jerlov, 1968). The spectral attenuation coefficients for chlorophyll-like pigments were obtained by applying a spectral form of equation (1)

$$K_T(\lambda) = K_w(\lambda) + K_{TP}(\lambda).C_p. \quad (3)$$

The resulting K_{TP} (λ) values, for $\lambda < 600$ nm, are shown in Figure 3 *a* together with values of K_2 (λ) from Smith and Baker (1978). Good agreement could also be obtained between K_{TP} (λ) and the spectral absorption properties of the filterable component of natural seawater estimated by Lewis *et al.* (1984). The term K_{TP} (λ) is obtained as an average of the top 10-50 m of the water column and on average slightly under-and-over-estimates the discrete depth samples from 10 m and 50 m respectively as shown in Figures 3 *b* and 3 *c*.

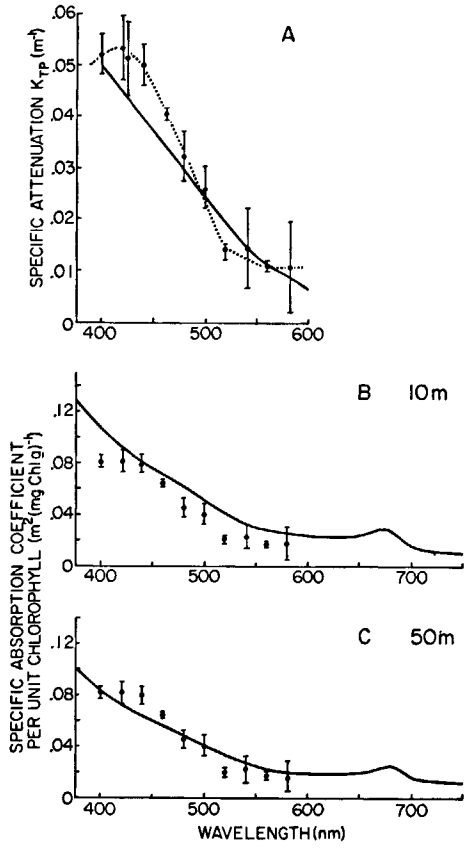

Figure 3

Spectral dependence of a) specific attenuation coefficient of total pigments as measured at the long station and as calculated by Smith and Baker, 1978 (solid line); b) absorption spectra of the filtered material (solid line) obtained from 10 m together with long station specific attenuation of chlorophyll averaged over 10-50 m; c) absorption spectra of filtered material (solid line) obtained from 50 m and specific attenuation of chlorophyll averaged over 10-50 m.

The data obtained from the Sargasso Sea gave values of $C_p < 1$ mg m^{-3} and so we might have expected the spectral K values to be modelled by an equation similar in form to that given by equation (2 *a*). This was indeed the case, with the best statistical fit being obtained by equation 3 which has no additional terms like the K_{x2} (λ) of equation (2 *b*). However, although the form of equation 3 matches that of equation 2 *a* the magnitude of the term K_{TP} (λ) is in close agreement with the term K_2 (λ) from equation 2 *b* (as shown in Figure 3 *a*) and not with K_1 (λ). Equations (3) and (2 *b*) would be in total agreement (form and magnitude) only under the condition that K_{x2} (λ) = 0.

FLUORESCENCE SIGNATURE THEORY

The theoretical basis behind the existence of enhanced radiation at about 680 nm has been given both in terms of anamolous dispersion and fluorescence emission. Fluorescence emission is currently the favoured theoretical explanation. Gordon (1979) incorporated fluorescence into the radiative transfer equations by considering fluorescence as inelastic scattering and formulating the problem in a manner analogous to elastic scattering.

Fluorescence involves the absorption of photons of energy at one wavelength, λ_E, followed by the emission of photons at a longer wavelength, λ_F. The fluorescence quantum efficiency, η, is defined as the ratio of the rate at which photons are emitted over a given emission wavelength interval, $\Delta\lambda_F$, to the rate at which photons are absorbed within a given excitation wavelength interval, $\Delta\lambda_E$. Consideration of the full wavelength radiation field however (both downward and upward spectral quantum irradiance) is difficult at $\lambda > 600$ nm where measurements are often unreliable. Since the upward fluorescence signature is strong and easy to identify, a very simplified, one dimensional, theory can be used by "lifting" the fluorescence peak from the remaining spectrum, as done by Neville and Gower (1977) with atmospheric measurements of oceanic fluorescence. The upward quantum irradiance due to fluorescence alone, $H^*_{qu}(z,\lambda_F)$ is obtained by subtracting the background irradiance, or baseline signal from the upward spectrum. The fluorescence signal is assumed to be symmetrical and to have a gaussian emission spectrum. The recorded signal includes contributions from fluorescent sources at various depths exponentially weighted by the attenuation of light at the fluorescence wavelength. To compare signal strengths from different depths and locations this fluorescence signal has to be suitably normalised. The total fluorescence signal, $F_q(z)$, adapted from Gordon (1979) is hence given by:

$$F_q(z) = \int_{\lambda_{F1}}^{\lambda_{F2}} \frac{2\,H^*_{qu}(z,\lambda_F)}{\int_0^{1/K_T} \exp[-K_T(\lambda_F)\,z]\,dz} \times \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left[\frac{-(\lambda_F-\lambda_{OF})^2}{2\sigma^2}\right] d\lambda_F. \quad (4)$$

A further approximation is to use the centre wavelength, λ_{OF}, of fluorescence and ignore small changes in $K_T(\lambda)$ over the fluorescence wavelengths, such that

$$F_q(Z) \simeq 2\ \gamma H^*_{qu}(z,\lambda_F)\ K_T(\lambda_{OF}), \qquad (5)$$

where γ is a constant containing the gaussian terms. The values of K_T for $\lambda > 600$ nm were not available from this study and specific coefficients were taken from Smith and Baker (1978) using the form of equation (3).

The energy absorbed by the fluorescing material is governed at each depth by the quantity of chlorophyll-like pigment, $C_p(z)$, the absorption coefficient, $\alpha(\lambda)$, of the material and the available energy (in quanta). An average surface loss taken from Jerlov (1968) was also assumed to represent an average in the wavelength domain and was subtracted from the above-surface spectral quantum irradiance $H_q(0,\lambda)$ before calculating the energy available for absorption. Fluorescence emission and absorption are related *via* fluorescence efficiency $\eta(z)$, (Gordon, 1979), so that

$$\times \int_{\lambda_{E1}}^{\lambda_{E2}} a(\lambda_E)\, H_q(0, \lambda_E)\, e^{-K_T(\lambda_E) z} f(\lambda_E, \lambda_F)\, d\lambda_E, \qquad (6)$$

where

$$f(\lambda_E, \lambda_F) = \frac{K_T(\lambda_F)}{K_T(\lambda_E)}\left(1 - \frac{K_T(\lambda_F)}{K_T(\lambda_E)} \mathrm{Ln}\left[1 + \frac{K_T(\lambda_E)}{K_T(\lambda_F)}\right]\right)$$

from Gordon (1979) is a factor to compensate for the fact that the excitation and emission radiations do not penetrate equally well through sea water.

The contribution to absorption from upward irradiance is assumed negligible as is any contribution from self induced fluorescence (Kattawar, Vastano, 1982). The values for absorption coefficients used were those of the specific absorption coefficients of phytoplankton (not *in vivo* chlorophyll) as given by Morel and Prieur (1977). Although this makes no use of the spectral attenuation measured *in situ* in the Sargasso it allows comparison to be made with previous work. As in Gordon (1979), the quantum efficiency, $\eta(z)$, is taken as independent of wavelength for wavelengths less than the fluorescence emission. The lower bound of the integration was taken as 400 nm to match the available measurements and it is assumed that contributions from below 400 nm are negligible within the accuracy of the field measurements.

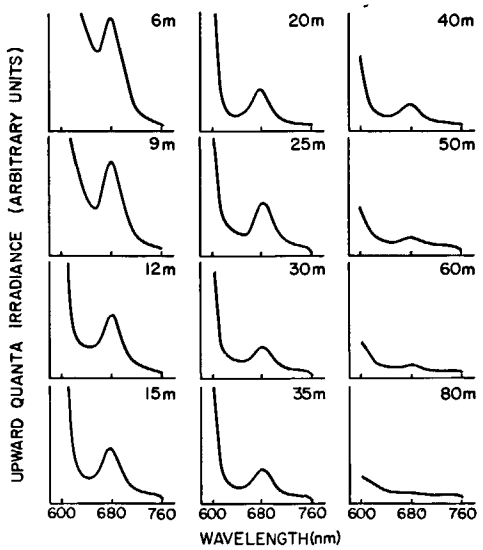

Figure 4

Depth attenuation of the chlorophyll a fluorescence peak as observed in the upward quantum spectral irradiance (insets do not all have the same vertical origin).

FLUORESCENCE RESULTS

The enhanced feature in upward quanta irradiance around 680 nm is given in detail for all depths, for a single profile, in Figure 4. The feature has an approximate gaussian shape with a half-band width, after correction for the gaussian response of the instrument, of 24 nm $\pm$ 3 nm. The peak wavelength is 681 nm $\pm$6 nm and the peak height decays almost exponentially with depth. These characteristics allow us to associate the enhanced feature with the fluorescence properties of chlorophyll *a*. The absolute size of the fluorescence peak varies during the day with the intensity of solar radiation (H_q in equation 6) available to excite fluorescence. Figure 5 illustrates the response of the fluorescence peak height throughout the water column to different levels of surface intensity and also reveals some residual structure caused by depth changes in the concentration of pigments ($C_p(z)$ in equation 6). For a

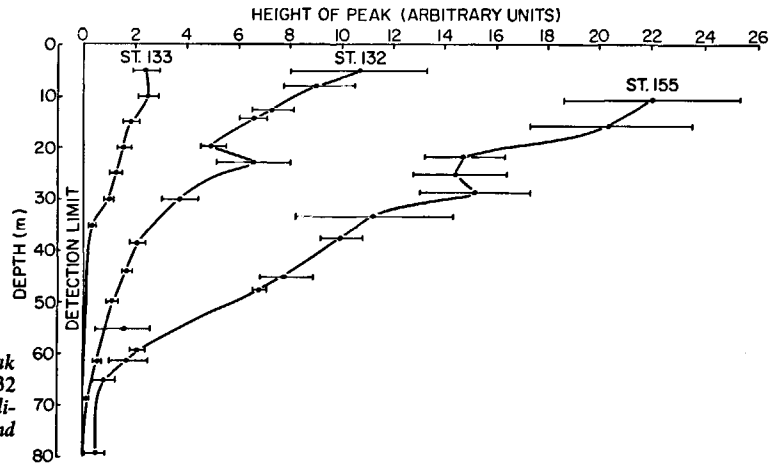

Figure 5

Variation of the height of the chlorophyll a fluorescence peak with depth and with surface illumination. Profile for, ST132 corresponds to a mid-morning profile under dull, cloudy conditions, for ST155 early afternoon on a bright, cloudy day and ST135 late, afternoon on dull, overcast day.

Table
Optical characteristics of the Sargasso Sea station.

Station	K_{FL}(1)	K_{FL}(2)	K_{480}	K_{440}(3)	K_Q(4)	η%(5)	η%(6)
132	0.061	0.064	0.041	0.054	–	2.41	2.35
135	0.073	0.071	–	0.055	–	1.95	1.28
155	0.058	0.050	0.043	0.049	0.093	2.58	1.40
1623	0.052	0.052	0.037	0.053	–	1.57	0.96
179	0.061	0.055	0.040	0.053	0.086	2.38	1.87
1815	0.059	0.061	0.047	0.058	0.106	1.76	1.67
1925	0.055	0.055	–	0.051	–	2.01	1.37

k in units of m^{-1}; (1) constant chlorophyll concentration; (2) chlorophyll variations included; (3) calculated and measured; (4) attenuation of total quantum irradiance; (5) average for water column; (6) average for top 5-10 m.

water column containing a constant level of pigment, fluorescing with a constant quantum efficiency, the decay rate with depth of the fluorescence peak height would match the decay rate of the excitation radiation. Values of fluorescence attenuation, K_{FL}, can be compared with the spectral values of attenuation, $K_T(\lambda)$, and total quantum irradiance, K_Q, as given in the Table. The fluorescence attenuation for varying pigment concentration, K_{FL^2}, lies between the minimum attenuation at 480 nm (hence maximum penetration) and attenuation of total quantum irradiance. Comparison with $K_T(\lambda)$ for all λ indicates good agreement between K_{FL} and the attenuation of radiation at 440 nm. There is no unique excitation wavelength for chlorophyll fluorescence, however, the above identification of the major excitation radiation is consistent with the fluorescence signature's being that of chlorophyll *a*. The depth of penetration of 1% of 440 nm light is between 70-80 m for these stations (as opposed to 45-55 m for total quantum irradiance) indicating that the excitation radiation can reach appreciable depths in the ocean resulting in the detection of passive fluorescence at depths up to 70 m and 80 m as illustrated in Figure 5. Once emitted, the fluorescence signature must obey the physical attenuation laws for red (680 nm) light. The attenuation due to pure sea-water alone will reduce the fluorescence signal to 10% of its original value in approximately 5 m. Passive fluorescence excited at a given depth can hence be considered to be representative of the chlorophyll content over a relatively small portion of the total water column.

The term $K_T(\lambda_E)$ in equation (6) can be obtained from a statistical regression of variables in equation 6 to give K_{FL^1} (*cf.* Table) when the pigment concentration is assumed to be constant with depth and K_{FL^2} when a depth varying pigment concentration is used. Using a constant depth value for total pigment leaves a regression residual of fluorescence ($\hat{F}_q(z)$) which shows depth structure, Figure 6, associated with the chlorophyll profile itself. After regression for a depth varying pigment regime there is some reduction of the residual and more of the chlorophyll structure has been accounted for. Fluorescence-pigment profiles obtained by normalisation of passive fluorescence to a varying excitation field can be favourably compared (Fig. 7) with artificially stimulated *in vivo* (active) fluorescence profiles (from the Aquatracka ®) and acetone extracted fluorescence profiles obtained from filtered water samples. Individual profiles in Figure 7 were all recorded on the same day at the same station but were not simultaneous. Some profiles were separated by a duration of several hours and hence differences can be seen in the position of the chlorophyll maximum.

Profiles of $\eta(z)$ can be obtained from equation (6). The implicit assumption here is not that the ratio of fluorescence to chlorophyll is non-linear but rather that variations in the ratio should relate to the taxonomic structure and physiological state of the plankton community (Butler, 1966; Kiefer, 1973). That potential relationship will be examined in a later paper. The present emphasis is on the ability to be able to measure fluorescence efficiency throughout the water column by means of the passive fluorescence emitted by plankton. Figure 8 gives the depth profile of η for one station in the Sargasso Sea. For this data set the excitation radiation at a given depth is not measured simultaneously but can be calculated from an earlier irradiance profile. The term $K_T(\lambda_E)$ in equation (6) is a function of C_p (equation 3) which can also be a function of depth. Values for η averaged throughout the water column for an average value of total pigments are given in the Table. Figure 8 shows normalized profiles of $\eta(z)$ when K is either held constant or allowed to vary with depth according to the pigment structure. Similar depth structure is seen in both profiles in Figure 8 although the errors associated with estimates are of the same order as the structure. At this stage no consideration has been given to variations in the total pigment composition (*e. g.* chlorophyll to phaeophytin ratios) which may also be depth dependent. The water column was relatively homogeneous in temperature and salinity for the top 300 m and hence the depth structure in Figure 8 does not appear to be related to any thermal structure of the water column. Average efficiency values within the top 10 m appear to be lower than those for the whole water column (*cf.* Table) although few values in the immediate surface layer (top 5 m) are available

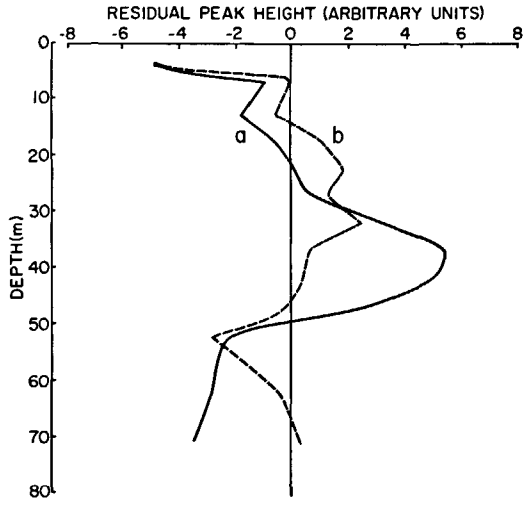

Figure 6
Depth variation of the residual of chlorophyll a fluorescence peak after exponential depth affects have been removed for a) solid line, constant chlorophyll concentration; b) broken line, with chlorophyll variations.

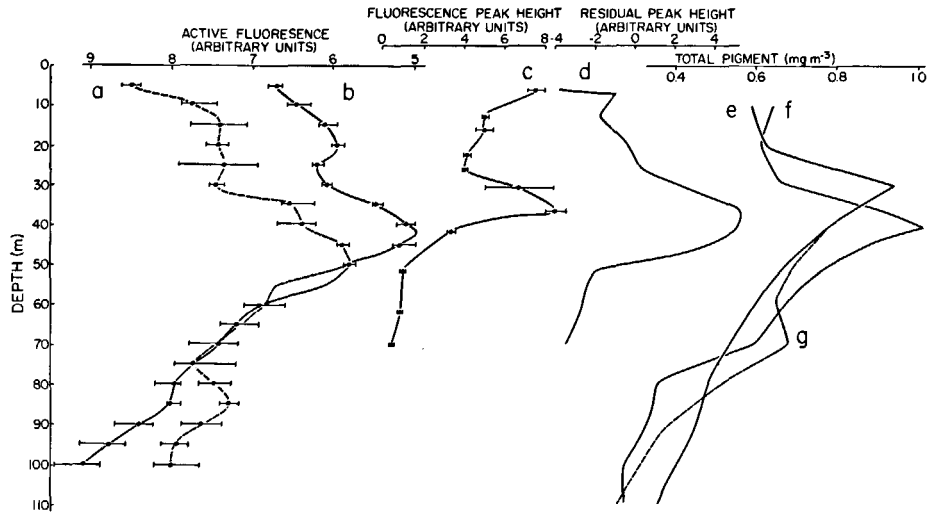

Figure 7

Comparison of active, passive and extracted fluorescence profiles. Profiles (a) and (b) were measured with an Aquatracka ® submersible fluorometer at noon and 17.00 hrs local time respectively. Profiles (c) and (d) are solar stimulated fluorescence profiles recorded between 14.30 and 15.00 hours, (c) as measured (d) with exponential depth variations removed. Profiles (e) (f) and (g) are total pigment concentrations obtained from acetone extracts from water samples obtained at 08.00-09.00; 14.00-15.00 and 19.00-20.00 hrs respectively.

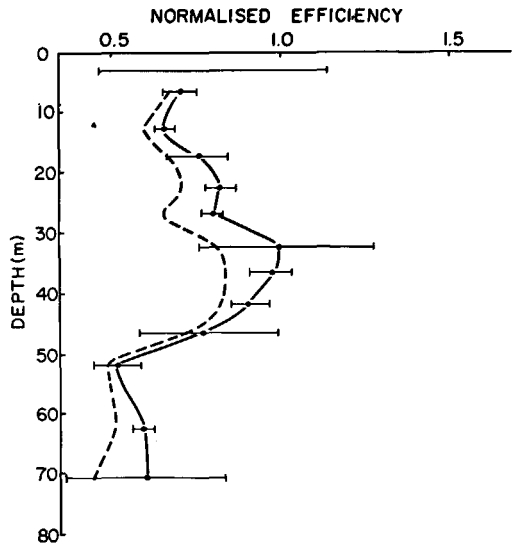

Figure 8

Depth variations of normalized chlorophyll a (total pigment) fluorescence quantum efficiency for constant specific attenuation coefficient (solid line) and for a chlorophyll dependent specific attenuation (dashed line).

since wave motion resulted in large errors as indicated in Figure 8.

The numerical values of quantum efficiency of fluorescence obtained from depth profiles of passive fluorescence lie within the limits of those obtained from theoretical analysis of surface fluorescence and laboratory estimations. The different estimates, however, often involve different assumptions. This analysis has used a simplified I-D model and has assumed throughout that both absorption and fluorescence can be related to the combined (chlorophyll and phaeophytin) pigment concentration. Apart from differences in methodology some instrumentation problems also remain. In particular, the very small fluorescence signal is of the same order of magnitude as the instrumentation dark current or noise level. This dark current is temperature-dependent and although "lifting" the fluorescence signal from the background level eliminates the baseline temperature dependence no provision has been made for the temperature changes in the absolute calibration of such a small signal. Although data can be expected to be consistent within a cruise errors may arise in comparing data from locations with widely different environmental temperatures. Kattawar and Vastano (1982) obtained fluorescence efficiencies between 0.44 and 0.53% using a 1-D model, Gordon (1979) typically between 0.66 and 0.79% using a 3-D model, Latimer *et al.* (1956) between 1.5 and 2.8% in laboratory work and Kiefer (1973) obtained an average measurement of natural phytoplankton given by Gordon (1979) to be 5%. The discrepancy between field/laboratory and theory has been attributed to the fact that calculations use the absorption coefficient of phytoplankton and covarying detritus not chlorophyll alone. This over-estimation of the absorption of energy leads to an under-estimation of the true (algal) fluorescence efficiency.

CONCLUSIONS AND DISCUSSION

The spectral bio-optical model for the Sargasso Sea gave a specific attenuation coefficient for phytoplankton pigments consistent with that attributed by Smith and Baker (1978) to phytoplankton and consistent with laboratory spectral absorption estimates by Lewis *et al.* (1984). A straight comparison of models however would indicate that the location had no independently-variable, detrital material ($K_{x2}=0$) and as such the attenuation would be caused by phytoplankton alone possibly due to the bloom on post bloom situation. The amount of phaeophytin recorded at each station is high, raising the possibility of errors due to the presence of pigments such as chlorophyll *b* (Spitzer *et al.*, 1982). Estimations of pigment composition by Parsons and Strickland (1963) formulae indicate that up to 42% of chlorophyll *b* could be present in the picoplankton contribution to the pigments. Such a simplistic estimation of chlorophyll *b* is not always considered reliable (Lorenzen, Jeffrey, 1980). Examination of high pressure liquid chromotography results (S. Roy, Dalhousie, pers. comm.) and species identification (C. Nalejwaiko, Toronto, pers. comm) indicated that no chlorophyll *b* was present in the water mass. The labora-

tory interpretation of spectral absorption of samples by Lewis *et al.* (1984) indicated that their spectral characteristics were consistent with the presence of detrital material, deduced from their high absorption in the blue. The statements on model findings and laboratory findings can still be consistent with the data if it is assumed that all the detrital material is optically covariant with the chlorophyll and that the overall spectral attenuation for this combination is much lower than that obtained by Smith and Baker (1978). It should be noted that the Sargasso data set is close to the transition between the two models used by Smith and Baker (1978) and may be a particular case for such models when ocean areas are highly productive (bloom and post bloom conditions).

The influence of biological material on the underwater light field can be seen not only in the absorption of light at the blue end of the spectrum but in the emission of fluorescence radiation at the red end of the spectrum. The solar radiation penetrating into the ocean can stimulate passive fluorescence to considerable depths (80 m) allowing variations in fluorescence due to changes in pigment concentration and efficiency to be profiled throughout the water column. Passive fluorescence measurements do not have the advantage of detecting chlorophyll during night-time as is possible with active fluorescence sensors. However, it does provide a means of examining the natural fluorescence of marine chlorophyll in undisturbed and natural lighting conditions. Such natural fluorescence may contain useful additional information about the photosynthetic state of marine plankton.

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