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# Optical Classification Of Natural Waters

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Raymond C. Smith and Karen S. Baker

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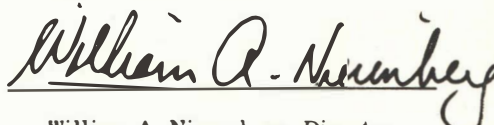
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## ABSTRACT

A technique leading to an optical classification of natural waters, in terms of dissolved and suspended biogenous material in these waters, has been presented. It has been shown that, as a first approximation, this classification can be made in terms of the total chlorophyll-like pigment concentration while the possibility of including other primary biological components, e.g., dissolved organic material, has been discussed.

A relationship between the spectral diffuse attenuation coefficient for irradiance and the chlorophyll-like pigment concentration has been found which is both physically and biologically meaningful. It was derived using spectral irradiance data from diverse ocean water types. In the process of this analysis, the specific spectral attenuation coefficient due to phytoplankton has been determined and is shown to be consistent with laboratory measurements of the diffuse absorption coefficient of various lot cultures of phytoplankton.

The optical identification of a water type in terms of important dissolved and suspended biological material is of interest per se and has a number of immediate practical applications including the quantitative description of ocean color and the remote sensing of chlorophyll by satellite.

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## **INTRODUCTION**

It has long been recognized that biological constituents, particularly phytoplankton pigments and associated degradation products, play a significant role in determining the optical properties of natural waters. In spite of this knowledge and the potential usefulness that may derive therefrom, no generally accepted technique exists for relating the optical characteristics of natural waters to the dissolved and suspended biogenous material. The principal objective of this work is to present a method for optically classifying natural waters, whose dissolved and suspended materials are primarily of biogenous origin, in terms of the total chlorophyll-like pigment concentration in these waters.

Using a multivariate analysis of optical data from a wide range of ocean waters as a point of departure, we have developed an alternative spectral analysis. This analysis follows our earlier work (Smith and Baker 1977) and shows that the total diffuse attenuation coefficient for irradiance as a function of wavelength can be written as a linear function of the chlorophyll-like pigment concentration in the water column. This is done by making use of Beer's law and by taking account of nonlinear biological effects which influence the optical properties. Several immediate applications of this analysis are discussed, including: the optical classification of natural waters in terms of their pigment concentration, the remote sensing of the bio-optical state of ocean waters, the quantitative relationship between the color of natural waters and pigment concentration.

We wish to thank R. W. Eppley for allowing us the use of unpublished data from the Southern California Bight Studies obtained by the Food Chain Research Group (Institute of Marine Resources, Scripps Institution of Oceanography) and for helpful advice and discussions. We also wish to thank R. W. Austin, D. Clark, D. A. Kiefer, J. E. Tyler, and W. Wilson for constructive discussions concerning this work.

## **MULTIVARIATE ANALYSIS OF OCEAN OPTICAL DATA**

Biological constituents, particularly phytoplankton pigments and associated degradation products, play a significant role in determining the optical properties of natural waters within the euphotic layer. We have used the term "bio-optical state" to represent a measure of the total effect of biological material on the optical properties of natural waters. It is the combined effect of the absorption and scattering due to suspended and dissolved biogenous material that establishes the bio-optical state of these waters. In the following discussion we will show that the bio-optical state of natural waters may be characterized physically by determining important optical properties as a function of wavelength.

For simplicity, and to address a separate set of problems, we previously (Smith and Baker 1977) considered only the total diffuse attenuation coefficient for irradiance.  $K_T$  is dependent upon the absorption and scattering properties of natural waters, and (like these inherent properties) is a function of wavelength. In particular, in waters for which dissolved and suspended materials are primarily of biogenous origin, the spectral character of  $K_T(\lambda)$  is largely dependent upon the chlorophyll-like pigment concentrations of phytoplankton. As a consequence, the spectral nature of  $K_T(\lambda)$  may be used to optically characterize natural waters in terms of phytoplankton pigment concentration and is of direct importance to the problem of remotely sensing the bio-optical state of ocean waters.

Suppose, for purposes of illustration, that the euphotic layer of natural waters had optical properties whose spectral characteristics were influenced only by pure water and chlorophyll a. Then, if we knew the diffuse attenuation coefficient for clear natural waters,  $K_w(\lambda)$ , and the specific diffuse attenuation coefficient due to chl a,  $k_c(\lambda)$ , these could be used to relate the chlorophyll a concentration to the total diffuse attenuation coefficient,  $K_T(\lambda)$ ,

$$K_T(\lambda) = K_w(\lambda) + k_c(\lambda) \cdot C_K \quad (1)$$

Thus we could construct a family of spectral curves for  $K_T(\lambda)$  from a knowledge of  $C_K$ . Conversely, if the world's oceans contained only pure water and chl a, a multivariate spectral analysis of experimentally determined  $K_T(\lambda)$ 's from waters containing low to high concentrations of chl a would, in principle, allow  $K_w(\lambda)$  and  $k_c(\lambda)$  to be extracted from the data.

Multivariate analysis is a method (Simonds 1963, Morrison 1967, Mueller 1976) of examining a number of sets of multivariate response data, e.g., sets of experimentally determined  $K_T(\lambda)$  data, and determining linear transformations of the data to a smaller number of parameters, e.g.,  $K_w(\lambda)$  and  $k_c(\lambda)$ , which contain essentially all the information in the original data. In practice, multivariate or eigenvector analysis does not normally extract "vectors" that represent quantities that are physically measurable, contrary to the suggestion in the above illustrative example. Rather, the analysis extracts spectral adjustment components which may be added to a mean spectral component in order to match any of the original experimental data. In addition to lacking a direct physical or biological interpretation, the usual components obtained from multivariate analysis combine physically (and/or biologically) meaningful components in such a way that they are not readily separable for individual analysis.

In spite of these limitations we have subjected our  $K_T(\lambda)$  data (see Smith and Baker 1977 for a discussion of these "Vis Lab" data) to a multivariate analysis. Mueller (1973, 1976) has also used multivariate analysis to study ocean color and has described the application of this statistical technique for optical oceanography in detail. An important result from both analyses is that only a few principal components are required to account for more than 99 percent of the variability among the original experimental data. In other words, only a few principal components are required in order to describe the full range of variation in ocean  $K_T(\lambda)$  data. Thus, once these principal components have been obtained and have been shown to be derived from data which is truly representative of the world's ocean waters, they may be used to describe the basic optical properties of various ocean waters.

Rather than utilizing this approach, we have chosen to use the multivariate analysis of optical data as a point of departure for an alternate analysis. We utilize the fact that the spectral characteristics of ocean properties can be represented by a few principal components. We depart from the usual procedures of multivariate analysis and have sought an analysis of ocean optical properties that would allow the bio-optical state of ocean waters to be described in terms of physically measurable biological parameters. This alternative analysis is as descriptive as the usual multivariate analysis and has the significant advantage of providing direct insight into important physical and biological processes affecting the optical properties of natural waters.

## SPECTRAL DIFFUSE ATTENUATION COEFFICIENT FOR IRRADIANCE

We have already given detailed (Smith and Baker 1977) reasons for choosing the total diffuse attenuation coefficient for irradiance  $K_T$  to characterize the bio-optical state of ocean waters:

1. Many authors (Riley 1956, Holmes 1965, Aruga and Ichimura 1968, Lorenzen 1972) have shown that a strong correlation exists between  $K_T$  and the chlorophyll  $a$  concentration.
2.  $K_T$  is the optical parameter that relates the spectral irradiance just beneath the ocean surface  $E_d(0,\lambda)$  to the downwelling spectral irradiance at depth  $E_d(Z,\lambda)$ , viz,

$$E_d(Z,\lambda) = E_d(0,\lambda) e^{-K_T(\lambda) \cdot Z} \quad (2)$$

3. Techniques for determining  $K_T$  by measuring energy or quanta as a function of depth, have been developed and are widely used (Jerlov and Nygard 1969, Smith 1969, Smith and Wilson 1972, Booth 1976). In addition, techniques for determining  $K_T$  as a function of wavelength, by measuring spectral irradiance as a function of depth, have been developed (Tyler and Smith 1966, 1970, Morel and Caloumenos 1973, Burr and Duncan 1972) and there is a representative amount of spectral irradiance data available for analysis (Tyler and Smith 1970, Morel 1973, Smith 1973, Morel and Prieur 1975).
4. For remote sensing applications  $K_T$ , by means of radiation transfer theory, can be related to the upwelling signal available to a remote sensor and in addition  $K_T^{-1}$  defines the depth from which about 90 percent of the remotely sensed signal originates (Gordon and McCluney 1975).

Morel has recently (1976) carried out an independent analysis of spectral irradiance with the aim of describing ocean color in terms of dissolved and suspended material, in particular, phytoplankton pigment concentrations. Morel's analysis is physically strict and makes use of the inherent optical properties of water (Preisendorfer 1976). Our analysis makes use of the apparent optical property  $K_T$  which directly provides, via Eq. 2, the spectral energy (and/or quanta) available for photosynthesis. It also provides direct input to mathematical models of phytoplankton dynamics.



The value of  $K_T(\lambda)$  may be determined as indicated in Eq. 3,

$$K_T(\lambda) = K_w(\lambda) + K_x(\lambda) + k_c(\lambda) \cdot C_K, \quad (3)$$

where  $K_T(\lambda)$  [ $m^{-1}$ ] is the total diffuse attenuation coefficient for spectral irradiance,  $K_w(\lambda)$  [ $m^{-1}$ ] is the diffuse spectral attenuation coefficient for clear ocean waters (e.g., Sargasso Sea),  $k_c(\lambda)$  [ $m^{-1}(\text{mg pigment} \cdot m^{-3})^{-1}$ ] is the specific spectral irradiance attenuation coefficient due to plankton (chlorophyll-like) pigments,  $C_K$  [ $\text{mg pigments } m^{-3}$ ] is the average concentration of chlorophyll *a* and phaeopigments in the ocean water to a depth of one attenuation length, and  $K_x(\lambda)$  [ $m^{-1}$ ] is the contribution of spectral attenuation not directly attributable to chlorophyll-like pigments.

We have already shown (Smith and Baker 1977) that nonlinear biological effects alter the expected linear relationship between  $K_T$  and  $C_K$ . In particular, the slope  $k_c$  is influenced by all the biological material, including detritus, associated with viable plant material which co-varies with  $C_K$ . As a consequence, it has been found that the expected linear relationship holds separately for two regions: one for low pigment concentration ( $C_K < 1$ ) and one for high pigment concentrations ( $C_K > 1$ ). Based upon the results of Hobson *et al.* (1973), we have assumed two separate linear relationships (i.e., Eq. 3) to describe two distinct types of ocean waters. One type contains low to medium chlorophyll-like pigment concentrations, where the ratio of viable to detrital plus viable organic carbon is relatively low. Another linear relationship holds in pigment rich ocean waters, where the ratio of viable to detrital plus viable organic carbon approaches 1.0.

In a manner analogous to our previous analysis for total irradiance  $K_T$ , we have analyzed our "Vis Lab" spectral irradiance data (Smith and Baker, Table 1 and Fig. 5, 1977) by fitting a regression curve to these data at each wavelength (every 5 nanometers) from 350 to 700 nanometers, viz:

$$K_T(\lambda) - K_w(\lambda) = k_1(\lambda) \cdot C_K \quad C_K < 1 \quad (4a)$$

$$K_T(\lambda) - K_w(\lambda) = K_{x2}(\lambda) + k_2(\lambda) \cdot C_K + K_B(\lambda) \quad C_K > 1 \quad (4b)$$

$$k_1(\lambda) = K_{x2}(\lambda) + k_2(\lambda) + K_B(\lambda) \quad C_K = 1 \quad (4c)$$

When our spectral data are fit with two lines, rather than a single line, the results of an analysis of covariance indicates that the sum of squares about the regression line for the pooled data (single line) was significantly greater than the sum of squares about the two regression lines.

This division of the analysis into two types, one with low and the other with high pigment concentrations, is somewhat arbitrary. Clearly there is a distinction between these two types but the division is not sharp, and one might reasonably expect a continuous change (and a spread) in the ratio of viable to total particulate organic carbon as  $C_K$  ranges from low to high concentrations. However, there are not sufficient spectral data for a more detailed analysis and the fit given here is optimum for these data.

It should be noted that there are fewer spectral data available for analysis than were available for the total irradiance  $K_T$  analysis.  $K_B$  is defined by Eq. 4c and is dependent upon the choice of the "boundary" concentration (taken here as  $1[\text{mg pigment} \cdot \text{m}^{-3}]$ ).

Thus, the total spectral diffuse attenuation coefficient has been defined for two distinct groups of data (Eqs. 4). One group is composed of low  $C_K$  values, where the relative contribution of detrital material to the slope of  $k_1(\lambda)$  is appreciable. Another is composed of  $C_K$  values where the relative contribution of detrital material to the slope  $k_2(\lambda)$  is significantly less. Because the relative contribution of unidentified organic carbon becomes small for high values of  $C_K$ , we can, as a first approximation, consider  $k_2(\lambda)$  to be the specific attenuation coefficient due to chlorophyll-like pigments.

By use of  $K_T(\lambda)$  data derived from spectral irradiance data as a function of depth, we have carried out this analysis for wavelengths between 350 and 700 nanometers. Then by using data from the Sargasso Sea to represent clearest ocean waters  $K_w(\lambda)$  we were able to obtain values for the spectral constants in Eqs. 4. The curves for these constants are plotted in Fig. 1 and are presented in Table 1 as a function of wavelength.

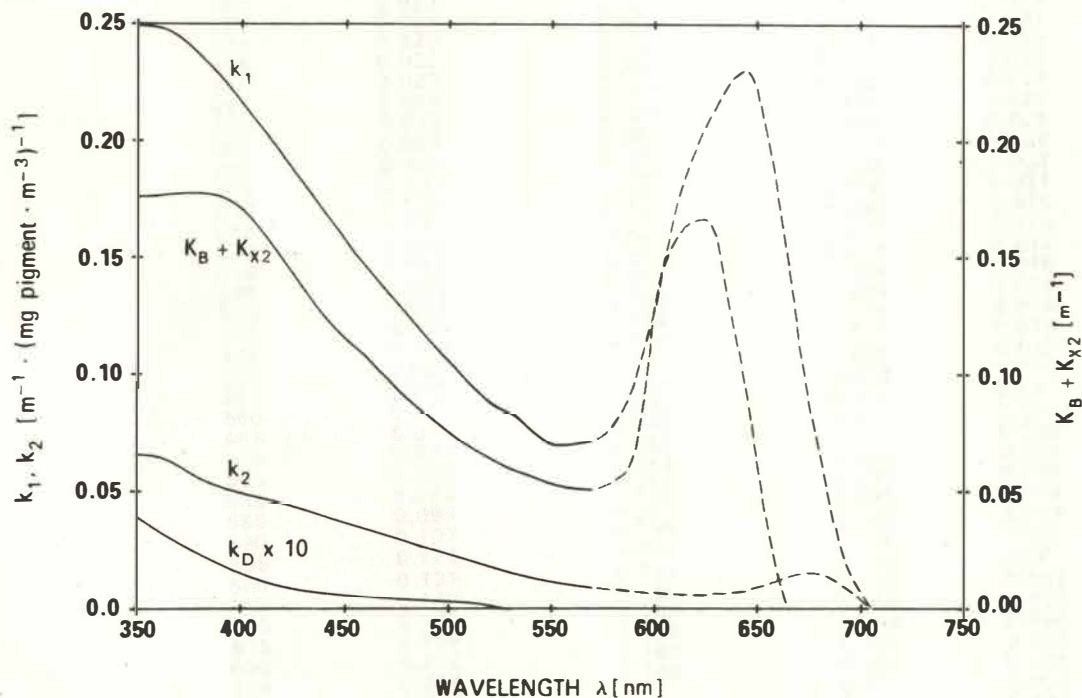


Fig. 1. Spectral values of the specific attenuation coefficients  $k_1(\lambda)$  and  $k_2(\lambda)$  [ $\text{m}^{-1} \cdot (\text{mg} \cdot \text{pigment} \cdot \text{m}^{-3})^{-1}$ ] and the spectral attenuation coefficient  $K_B(\lambda) + K_{x2}(\lambda)$ .  $k_2(\lambda)$  is the specific diffuse attenuation coefficient due to an average ensemble of ocean phytoplankton.  $k_D$  (multiplied times 10 to place it in the scale of this figure) is the specific attenuation coefficient due to dissolved organic material (Stuerner, 1975).  $K_B$  is defined by Eq. 4c and is dependent upon the choice of the "boundary" concentration (see text).

**Table 1.** Spectral attenuation coefficient  $K_w [m^{-1}]$  and  $K_B + K_{x_2} [m^{-1}]$  and spectral values of the specific attenuation coefficients  $k_1(\lambda)$  and  $k_2(\lambda)$ .

$\lambda [nm]$	$K_w(\lambda)$	$K_B(\lambda) + K_{x_2}(\lambda)$	$k_1(\lambda)$	$k_2(\lambda)$	$\Delta K(\lambda)$
350	0.059	0.177	0.249	0.066	0.024
355	0.055	0.177	0.249	0.066	0.024
360	0.051	0.177	0.249	0.066	0.024
365	0.045	0.178	0.248	0.063	0.028
370	0.044	0.179	0.245	0.061	0.020
375	0.043	0.179	0.240	0.058	0.013
380	0.040	0.179	0.237	0.055	0.014
385	0.036	0.179	0.232	0.053	0.000
390	0.031	0.177	0.227	0.051	-0.009
395	0.029	0.175	0.223	0.050	-0.009
400	0.027	0.172	0.216	0.049	-0.025
405	0.026	0.167	0.210	0.048	-0.027
410	0.025	0.162	0.205	0.047	-0.024
415	0.024	0.156	0.200	0.046	-0.013
420	0.024	0.150	0.194	0.045	-0.005
425	0.023	0.145	0.187	0.044	-0.010
430	0.022	0.137	0.181	0.042	0.006
435	0.022	0.132	0.175	0.041	0.007
440	0.022	0.125	0.168	0.039	0.021
445	0.023	0.121	0.163	0.038	0.022
450	0.023	0.116	0.158	0.037	0.030
455	0.023	0.112	0.150	0.036	0.013
460	0.023	0.110	0.146	0.034	0.011
465	0.023	0.104	0.141	0.033	0.029
470	0.023	0.100	0.135	0.031	0.027
475	0.022	0.095	0.130	0.030	0.038
480	0.022	0.091	0.125	0.029	0.034
485	0.024	0.087	0.120	0.027	0.042
490	0.025	0.084	0.115	0.026	0.043
495	0.027	0.080	0.110	0.025	0.045
500	0.029	0.077	0.105	0.024	0.035
505	0.033	0.074	0.102	0.022	0.056
510	0.037	0.071	0.096	0.021	0.039
515	0.043	0.069	0.093	0.020	0.045
520	0.048	0.066	0.088	0.019	0.033
525	0.050	0.064	0.085	0.017	0.047
530	0.050	0.061	0.084	0.016	0.085
535	0.052	0.060	0.080	0.015	0.062
540	0.055	0.059	0.076	0.014	0.042
545	0.059	0.056	0.073	0.013	0.049
550	0.063	0.055	0.070	0.012	0.044
555	0.067	0.054	0.070	0.011	0.070
560	0.071	0.053	0.070	0.011	0.087
565	0.074	0.052	0.071	0.010	0.120
570	0.077	0.053	0.072	0.009	0.133
575	0.082	0.054	0.074	0.009	0.154
580	0.088	0.056	0.077	0.008	0.160
585	0.099	0.059	0.085	0.008	0.213
590	0.107	0.066	0.095	0.007	0.223
595	0.121	0.091	0.110	0.007	0.105
600	0.131	0.131	0.125	0.007	-0.106
605	0.146	0.150	0.148	0.007	-0.060
610	0.170	0.159	0.168	0.007	0.014
615	0.188	0.165	0.184	0.006	0.069
620	0.212	0.167	0.195	0.006	0.109
625	0.244	0.169	0.205	0.006	0.146
630	0.277	0.161	0.213	0.006	0.213
635	0.300	0.137	0.222	0.007	0.350
640	0.327	0.117	0.227	0.007	0.449
645	0.339	0.095	0.231	0.008	0.554
650	0.336	0.061	0.225	0.009	0.686
655	0.337	0.037	0.205	0.011	0.765
660	0.390	0.015	0.180	0.012	0.850
665	0.425	0.002	0.156	0.014	0.896
670	0.460	0.0	0.118	0.015	0.873
675	0.485	0.0	0.088	0.016	0.823
680	0.510	0.0	0.068	0.015	0.779
685	0.540	0.0	0.045	0.014	0.693
690	0.570	0.0	0.028	0.011	0.596
695	0.600	0.0	0.015	0.008	0.460
700	0.630	0.0	0.008	0.004	0.450



The spectral values of  $k_1(\lambda)$ ,  $K_B(\lambda) + K_{x_2}(\lambda)$ , and  $k_2(\lambda)$  between 350 and 570 nanometers were obtained using all the Vis Lab spectral irradiance data in exactly the same manner that was used to obtain  $k_1$  and  $k_2$  for total irradiance (as illustrated by Fig. 5, Smith and Baker 1977) by making a least squares regression fit to the data at each wavelength (every 5 nanometers). Our spectral data above 570 nanometers is limited, primarily due to the rapid increase in the attenuation by water above this wavelength. This rapid increase in attenuation reduces the number of data points, when spectral irradiance data are taken at fixed depth intervals, from which to determine  $K_T(\lambda)$ . As a consequence our analysis is less reliable above 570 nanometers.

Because of this we carried out a separate determination of  $k_2(\lambda)$  from 570 to 750 nanometers. In this wavelength region we made use of Eq. 4b and data from a few stations with high  $C_K$  values and for which sufficient  $K_T(\lambda)$  data had been obtained. This provided a relatively good determination of  $k_2(\lambda)$ , even though it is based upon data from a few oceanographic stations. This separate determination of  $k_1(\lambda)$  and  $K_B(\lambda) + K_{x_2}(\lambda)$  is relatively less accurate than that for  $k_2(\lambda)$ .

In the process of determining  $k_1(\lambda)$ ,  $k_2(\lambda)$ , and  $K_B(\lambda) + K_{x_2}(\lambda)$ , an intercept value for the low group of data  $K_{x_1}(\lambda)$  was also determined. These values were generally within one or two standard deviations of zero. Yet we know, from our analysis of the more complex total irradiance data, that  $K_{x_1}$  is not zero. However, for simplicity and to be consistent with the accuracy of the present analysis, we have taken  $K_{x_1}(\lambda)$  equal to zero.

The condition given by Eq. 4c provides a measure of the internal consistency of our analysis. The left and right sides of Eq. 4c are independently determined. To the extent that they agree, there is satisfactory internal consistency. Lack of equality in Eq. 4c implies a lack of consistency, e.g., inaccuracies in determining the spectral constants and/or the occurrence of spectral components which have not been included in the analysis. Column 5 in Table 1 lists the relative lack of agreement between the left and right side of Eq. 4c,  $\Delta K$ , where

$$\Delta K = \frac{k_1(\lambda) - [k_2(\lambda) + K_B(\lambda) + K_{x_2}(\lambda)]}{k_1(\lambda)} \quad (5)$$

It can be seen that  $\Delta K$  is less than 10 percent below 560 nanometers but rises to as high as 20 percent between 565 and 630 nanometers. Above 630 nanometers the values given for  $k_1(\lambda)$  and  $K_B(\lambda)$  may be in error by as much as a factor of two. These less reliable results are shown as the dashed portion of the curves in Fig. 1.

It should also be pointed out that we do not have sufficient spectral irradiance data to allow a separation of the sum of terms  $K_B(\lambda) + K_{x_2}(\lambda)$  which is given by the intercept of the fit to Eq. 4b. This is an important limitation of the work reported herein because the spectral contribution of biogenous material that does not co-vary with chlorophyll-like pigment concentrations has not been determined. However, in principal, this can be determined with more complete biological and optical data.

Within these limitations we have achieved our desired result. For biogenous natural waters the spectral diffuse attenuation coefficient for irradiance has been cast into a form which is physically (satisfies Beer's Law) and biologically ( $k_2(\lambda)$  represents the spectral absorption of an average ensemble of phytoplankton) meaningful. Using the data from Table 1, a measurement of  $C_K$  is sufficient to calculate  $K_T(\lambda)$  and hence, by Eq. 2 and knowing  $E_d(0,\lambda)$ , to also calculate the spectral irradiance as a function of depth and all optical properties derivable therefrom. Before turning to the potential application of these results, it remains to compare  $k_2(\lambda)$  with laboratory data, to demonstrate the reliability of calculations made using Eqs. 4 and Table 1 and to discuss the limitations (and potential for improvement) of these results.

## SPECIFIC ATTENUATION COEFFICIENT FOR OCEAN PHYTOPLANKTON

In the above analysis  $k_2(\lambda)$  has been interpreted as a specific diffuse attenuation coefficient due to an average ensemble of ocean phytoplankton. The data used for this analysis was obtained from diverse oceanographic regions and ranged from the clear waters of the Sargasso Sea ( $0.03 \text{ mg pigment} \cdot \text{m}^{-3}$ ) to high productivity coastal waters ( $10 \text{ mg pigment} \cdot \text{m}^{-3}$ ). Thus the spectral data covers the full range of biogenous water types. To the extent that a single representative spectral curve can be extracted from the data representing these diverse waters, it must be considered as some kind of average.

$k_2(\lambda)$  is the specific attenuation coefficient for the sum of chlorophyll  $a$  and phaeophytin. As discussed by Smith and Baker (1977) we have combined the total chlorophyll-like pigments because they are not readily distinguishable by *in situ* spectroradiometric measurements. Thus the spectral values of  $k_2(\lambda)$  are given per unit pigment concentration, chlorophyll  $a$  plus phaeophytin.

The diffuse absorption coefficient for several representative ocean phytoplankton have been measured and reported by Duntley *et al.* (1974). Their data are reproduced in Fig. 2 along with  $k_2(\lambda)$  from our analysis.

Preisendorfer (1976, Vol. V, Sect. 9) has shown that the diffuse absorption coefficient  $k$  may be given in the form

$$k = [a^*(a^* + 2b^*)]^{1/2} , \quad (6)$$

where  $a^*$  and  $b^*$  are the absorption and backward scattering coefficients for diffuse flux. Duntley *et al.* (1974) have shown that for ocean phytoplankton  $b^* \ll a^*$ , within the spectral region of interest. Thus, Eq. 6 becomes

$$k(\lambda) \approx a^*(\lambda), \text{ for } b^*(\lambda) \ll a^*(\lambda) . \quad (7)$$

Thus, if our above analysis is correct, the specific diffuse attenuation coefficient due to chlorophyll-like pigments should be (within the approximations of Eqs. 6 and 7) equal to the spectral diffuse absorption coefficient of ocean phytoplankton.

The data presented in Fig. 2 show that  $k_2(\lambda)$  and the laboratory determined  $a^*(\lambda)$ 's have the same general spectral curve shape and have generally the same absolute numerical values. The closeness of these results lends support to our interpretation of  $k_2(\lambda)$ . In fact, there are a few reasons why we might expect these results to be even more divergent. First,  $k_2(\lambda)$  was extracted from oceanographic data covering the full range of biogenous water types while  $a^*(\lambda)$ 's were determined in the laboratory for a variety of phytoplankton lot cultures selected to be representative of oceanic waters. Second, the analysis of  $k_2(\lambda)$  does not eliminate completely the influence of covarying detrital material. Third, the present analysis does not allow one to distinguish the influence of dissolved organic material that covaries with the pigment concentration. It is probable that the remaining detrital material and dissolved organic material that covaries with  $C_x$  at high pigment concentrations is responsible for  $k_2(\lambda)$  being higher than  $a^*(\lambda)$  in the blue end of the spectrum. Fourth,  $a^*(\lambda)$  is given per unit chlorophyll  $\bar{a}$ , whereas  $k_2(\lambda)$  is given per unit chlorophyll  $\bar{a}$  plus phaeophytin. In spite of these reasons, the general agreement shown in Fig. 2 provides independent evidence that our interpretation of  $k_2(\lambda)$  is basically correct.

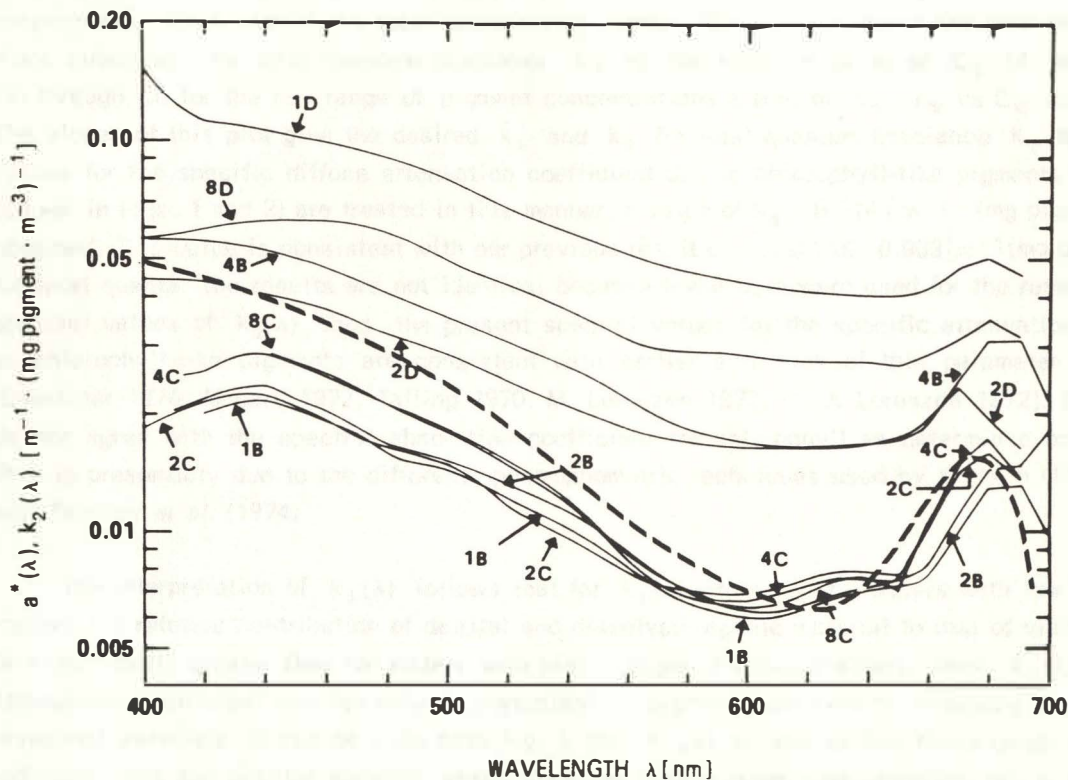


Fig. 2. Spectral diffuse absorption coefficient  $a^*(\lambda)$  for various ocean phytoplankton (solid curves) calculated from spectrophotometric data on lot cultures (Duntley, *et al.* 1974). Specific attenuation coefficient due to phytoplankton  $k_2(\lambda)$  (dashed curve), obtained by spectral analysis described in the text using spectral irradiance data from a variety of ocean areas, (Table 1, Smith and Baker 1977). The phytoplankton samples that were measured by Duntley, *et al.* are labeled as follows: 1B – *Nitzschia closterium*, 2B – *Lauderia borealis*, 4B – *Gymnodinium* species, 2C – *Monochrysis lutheri*, 4C – *Cyclotella nana*, 5C – *Skelotonema costatum*, 1D – *Gonyaulax polyedra*, 2D – *Gymnodinium splendens*, 8D – *Coccolithus huxleyi*.



In addition, the spectral values of  $k_2(\lambda)$  given here can be compared with the value of  $k_2$  for total irradiance  $K_T$  given earlier (Smith and Baker 1977) and hence with the work of previous investigators (Megard 1972, Talling 1970, M. Lorenzen 1972, C. J. Lorenzen 1972). The value of  $k_2$  for total irradiance  $K_T$  may be obtained from the spectral values of  $k_2(\lambda)$  as follows: (1) Eqs. 4a and 4b are used to obtain the spectral irradiance for various depths  $E_d(z, \lambda)$  for a selected value of  $C_K$  by means of Eq. 2, (2) The total quanta at each depth  $Q(z)$  [ $\text{photons} \cdot \text{m}^{-2} \cdot \text{sec}^{-1}$ ] can then be obtained by

$$Q(z) = \frac{1}{hc} \int_{350}^{700} E_d(z, \lambda) \cdot \lambda \cdot d\lambda \quad , \quad (8)$$

where the wavelength interval of 350 to 700 nanometers has been chosen in agreement with the recommendations of Working Group XV (1965), and  $h$  and  $c$  are Planck's constant and the velocity of light, respectively, (3) A plot of the total downwelling quanta  $Q(z)$  versus depth provides the diffuse attenuation coefficient for total quantum irradiance  $K_T$  for the selected value of  $C_K$ , (4) By repeating steps (1) through (3) for the full range of pigment concentrations a plot of  $K_T - K_w$  vs  $C_K$  may be constructed. The slopes of this plot give the desired  $k_1$  and  $k_2$  for total quantum irradiance  $K_T$ . When the spectral values for the specific diffuse attenuation coefficient due to chlorophyll-like pigments given in Table 1 (shown in Figs. 1 and 2) are treated in this manner, a value of  $k_2 = 0.014 [\text{m}^{-1} \cdot (\text{mg pigment} \cdot \text{m}^{-3})^{-1}]$  is obtained. This value is consistent with our previous result of  $k_2 = 0.016 \pm 0.003 [\text{m}^{-1} (\text{mg pigment} \cdot \text{m}^{-3})^{-1}]$  for total quanta. The results are not identical because fewer data were used for the result obtained using spectral values of  $k_2(\lambda)$ . Thus, the present spectral values for the specific attenuation coefficient due to chlorophyll-like pigments are consistent with earlier estimates of this parameter for total quanta (Bannister 1974, Megard 1972, Talling 1970, M. Lorenzen 1972, C. J. Lorenzen 1972). Our spectral data do not agree with the spectral absorption coefficient for chlorophyll as determined by Yentsch (1960). This is presumably due to the different spectrophotometric techniques used by Yentsch (1960) as compared with Duntley *et al.* (1974).

The interpretation of  $k_1(\lambda)$  follows that for  $k_2(\lambda)$ . However, for waters with low pigment concentration, the relative contribution of detrital and dissolved organic material to that of viable plant pigment is significantly greater than for waters with higher pigment concentrations. Thus,  $k_1(\lambda)$  is the specific attenuation coefficient due not only to phytoplankton pigments but also to covarying organic detrital and dissolved materials. It can be seen from Fig. 1 that  $k_1(\lambda)$  is four to five times larger than  $k_2(\lambda)$ . This indicates that the detrital material which covaries with pigment concentration has a significant, even dominant, effect upon the optical properties of biogenous oceanic waters except in relatively productive regions where the ratio of viable phytoplankton carbon to total particulate organic carbon approaches one.

The parameter  $K_B(\lambda)$  serves primarily as a "boundary condition" to link Eqs. 4a and 4b, and it is also a function of the value of the pigment concentration used to separate the data into high and low groups. The pigment concentration chosen for this separation point was required to meet the following conditions: (1) that Eq. 4c hold across the full wavelength spectrum, (2) that the chosen chlorophyll  $a$  concentration be consistent with reported carbon to chlorophyll ratios so as to be consistent with the results of Hobson *et al.* (1974). Several pigment separation points, consistent with condition two, were tried in order to optimize condition one. The data shown in Fig. 1 and listed in Table 1 are a result of this optimization.

Dissolved organic material (DOM), sometimes referred to as "gelbstoff," is known to influence optical properties of natural waters, especially in the blue and far blue region of the spectrum. We do not have the necessary ancillary biological information necessary to analyze our optical data for the purpose of quantitatively determining the influence of DOM on the values of  $K_T(\lambda)$ . A potential extension of the analysis presented here would be to determine a specific attenuation coefficient due to DOM  $k_D(\lambda)$  and to add such a term to Eqs. 4.

Lacking field data, we have used the data of Stuermer (1975 and private communication), shown in Fig. 1, as an upper limit estimate of  $k_D(\lambda)$ . These data suggest that DOM has a small effect upon the optical properties of natural waters except in the blue and far blue region of the spectrum. For the range of DOM normally found in open ocean sea waters, the influence of DOM is significant, frequently dominant, in the blue region of the spectrum. In the present analysis, any DOM which happens to co-vary with  $C_K$  has been included in the constant  $k_1$ , and thus we cannot properly separate the influence of DOM on the optical signal. In principle, this separation could be obtained from appropriate biological and optical data and this remains for further investigation.

## COMPARISON WITH EXPERIMENTAL DATA

The reliability of calculations made using Eqs. 4 and the tabulated values of  $K_w(\lambda)$ ,  $k_1(\lambda)$ ,  $K_B(\lambda) + K_{x_2}(\lambda)$ , and  $k_2(\lambda)$  may be demonstrated by comparing calculations with actual experimental data. This comparison is shown in Fig. 3 where the solid curves give experimentally determined values of  $K_T(\lambda)$  for selected water types and the dashed curves give calculated values of  $K_T(\lambda)$  for the appropriate pigment concentrations corresponding to these waters.

The agreement between the calculated and experimental curves is satisfactory and indicates that Eqs. 4, along with the parameters listed in Table 1, provide a reliable method for estimating  $K_T(\lambda)$  from a knowledge of the chlorophyll-like pigment concentration. The difference between the calculated and measured curves increases below 400 nanometers, where the calculated values underestimate the influence of dissolved organic material. Further, it should be emphasized again that, the combined data used to derive the values given in Table 1 were obtained from waters whose dissolved and suspended material was largely of biogenous origin. Areas noticeably affected by terrigenous material were avoided or excluded. Thus, our analysis as presented, does not apply to such waters. In spite of these limitations, the present analysis has wide applicability and usefulness and provides a point of departure for more detailed analyses.

## APPLICATIONS

Equations 4 and Table 1 provide a relationship between pigment concentration and the diffuse attenuation coefficient for irradiance which is applicable to biogenous natural waters. Further, we have shown that  $k_2(\lambda)$  may be interpreted as the specific attenuation coefficient for an average ensemble of oceanic phytoplankton. These results have a variety of immediate applications.

## OPTICAL CLASSIFICATION OF OCEAN WATERS

Equations 4 and Table 1 allow an optical classification of ocean water types to be made with all the applications suggested by Jerlov's (1968) earlier classification. In addition, such a classification has the advantage of being related to the components in ocean waters which are major contributors to the ocean optical properties. The present work, while outlining an ocean optical classification based directly upon pigment concentration, and hence, indirectly upon the biological productivity of natural waters, is incomplete because we have not fully accounted for dissolved organic material which is a second major biological component influencing ocean optical properties or for terrigenous material. In spite of these limitations, the present work provides a good first approximation for spectrally characterizing the bio-optical state of ocean waters.

Figure 4 presents values of  $K_T(\lambda)$ , calculated from Eqs. 4 and Table 1, for a variety of ocean water types ranging in chlorophyll-like pigment concentrations from 0.03 to 10 mg pigment  $\cdot$  m $^{-3}$ . These curves indicate how the spectral characteristics of ocean waters are influenced by concentrations of chlorophyll-like pigments. It should also be noted, as discussed above and by Smith and Baker 1977, that the specific attenuation coefficient  $k_1(\lambda)$  is influenced by all biogenous material that covaries with  $C_K$ . As a con-

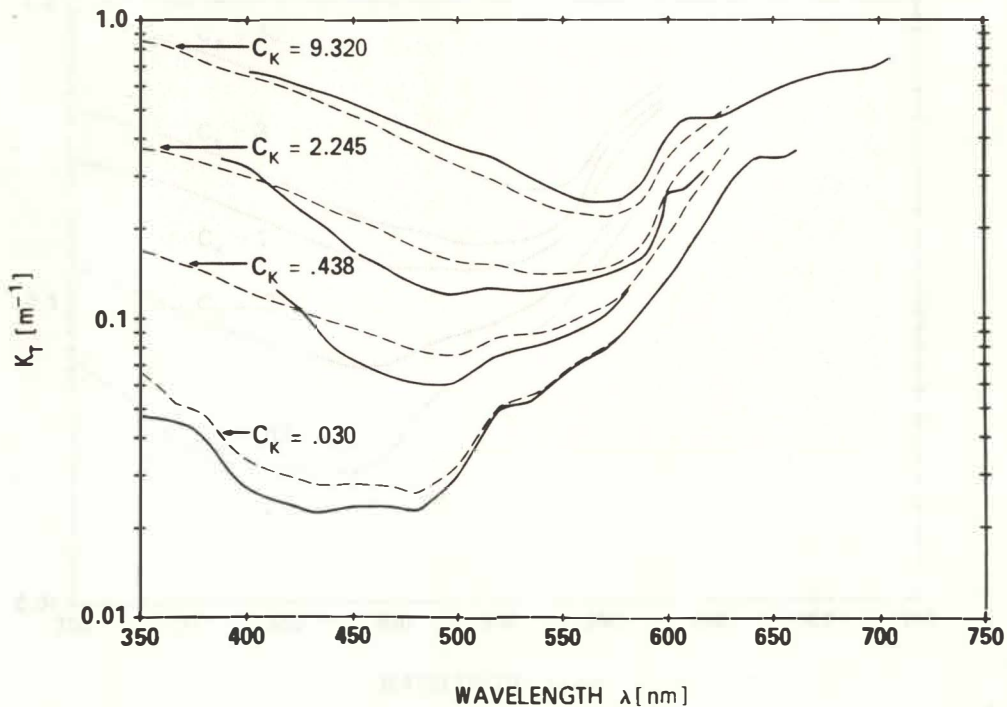


Fig. 3. Experimentally measured (solid curves) and calculated values (dashed curves) of the diffuse attenuation coefficient for irradiance  $K_T(\lambda)$  for several ocean waters varying in chlorophyll-like pigment concentrations. The dashed curves were calculated from Eqs. 4 and the spectral values of the parameters listed in Table 1.



sequence, the curves in Fig. 4 are also influenced by the material that covaries with the chlorophyll-like pigment concentration. This includes some fraction of particulate organic carbon (POC) and dissolved organic material (DOM). Unfortunately, we do not have sufficient biological data on POC and DOM, accompanying our optical measurements, to estimate their independent influence on the optical properties of ocean water.

As a rough indication of how dissolved organic material influences  $K_T(\lambda)$ , we have included in Fig. 1 a spectral curve of the specific attenuation coefficient due to DOM from the data of Stuermer (1975 and private communication). In principle, the indicated  $k_D(\lambda)$  value can be multiplied by the concentrations of DOM and then added to Eqs. 4 so as to include the spectral influence of DOM on  $K_T$ . In practice, this procedure will overestimate the influence of DOM for two reasons. First, Stuermer's data are for the fulvic acid fraction of DOM which was assumed to represent about 5 percent of the total dissolved organic carbon. Thus the measured attenuation coefficient times twenty can be considered an upper limit for the specific attenuation coefficient due to DOM. Second, our measured  $k_1(\lambda)$  (and to a lesser extent  $k_2(\lambda)$ ) will include the effect of any DOM that covaries with  $C_K$ , and hence has already partially accounted for the dissolved organic material. Thus, at present we can account for the influence of DOM on  $K_T$  only roughly and further experimental work is necessary in order to accurately include the  $k_D(\lambda)$  component in Eqs. 4.

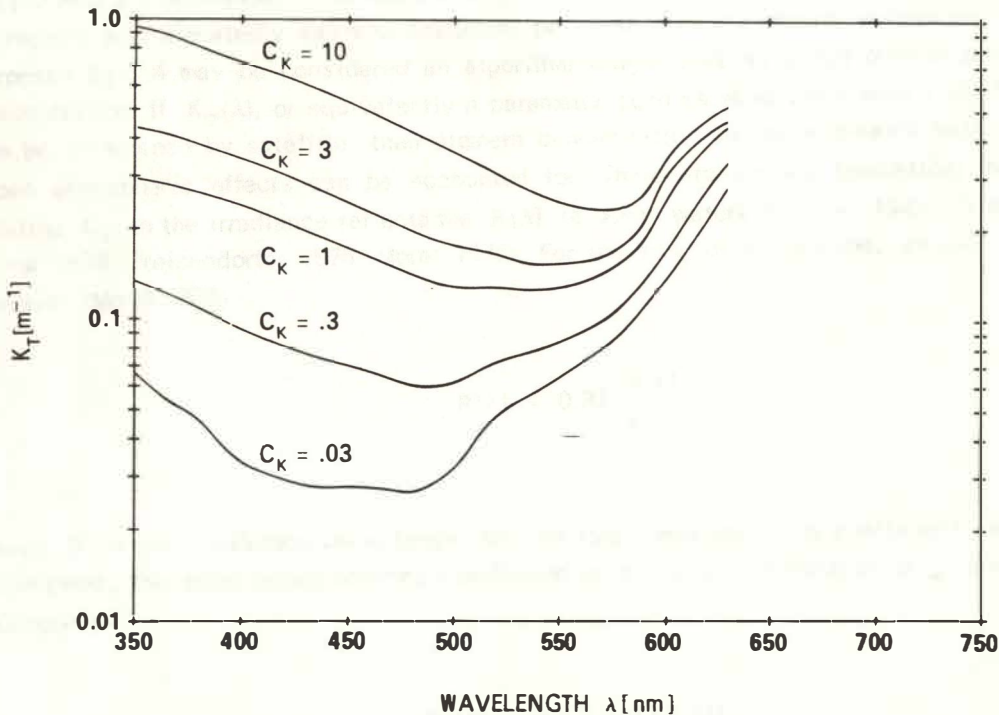


Fig. 4. Diffuse attenuation coefficient for irradiance  $K_T [m^{-1}]$  as a function of wavelength for various values of chlorophyll-like pigment concentration  $C_K [mg \text{ pigment} \cdot m^{-3}]$ . The curves were calculated using Eqs. 4 and Table 1.

Thus, as shown in Fig. 4, the diffuse attenuation coefficient for irradiance may be calculated as a function of wavelength from a knowledge of  $C_K$ . If the spectral irradiance just below the ocean surface is known from direct measurement or can be estimated from a knowledge of latitude, time of year and cloud cover (Kondrat'ev 1969, 1973), then the spectral irradiance as a function of depth may also be obtained by means of Eq. 2.  $E_d(Z, \lambda)$  can, in turn, be integrated to obtain an estimate of the total quanta or total energy as a function of depth and these values may be used to determine a diffuse attenuation coefficient for total quanta or total energy.

The minimum values of  $K_T(\lambda)$  for the calculated curves shown in Fig. 4 can be determined as a function of  $C_K$ . With increasing depth the downwelling spectral irradiance takes on a maximum value at a wavelength  $\lambda_{E_{max}}$  determined by the wavelength of the minimum value of  $K_T(\lambda)$ . These values of  $\lambda_{E_{max}}$  considered as a function of chlorophyll concentration are in agreement with the data presented by Morel and Smith (Fig. 3, 1974).

## REMOTE SENSING OF THE BIO-OPTICAL STATE OF OCEAN WATERS

In an earlier paper (Smith and Baker 1977) we defined the bio-optical state of ocean waters and discussed how the determination of the bio-optical state of ocean waters by satellite affords the opportunity to rapidly and repeatedly examine important parameters of the marine ecosystem. For remote sensing purposes Eqs. 4 may be considered an algorithm which links an ocean optical property to the pigment concentration. If  $K_T(\lambda)$ , or equivalently a parameter such as reflectance which can be related to  $K_T(\lambda)$ , can be determined by satellite, then pigment concentration can be estimated with useful accuracy provided atmospheric effects can be accounted for. There are several theoretical methods available for relating  $K_T$  to the irradiance reflectance  $R(\lambda)$  of ocean waters (Duntley 1942, 1974, Gordon *et al.* 1975, Prieur 1976, Preisendorfer 1976, Morel 1976). For the sake of illustration, we will adopt the simple expression (Morel 1976)

$$R(\lambda) = 0.33 \frac{b'(\lambda)}{a(\lambda)} \quad (9)$$

where  $R$  is the irradiance reflectance,  $b'$  the total backscattering coefficient, and  $a$  the absorption coefficient. The total backscattering coefficient is the sum of molecular  $b'_w$  and particle  $b'_p$  backscattering

$$b'(\lambda) = b'_w(\lambda) + b'_p(\lambda) \quad (10)$$

The molecular backscattering has been determined by Morel (1974) and the specific backscattering coefficient of various ocean phytoplankton has been reported by Duntley *et al.* (1974). For illustration purposes, we have taken  $b'_p(\lambda) = 10^{-3} [m^{-1} \cdot (mg\ chl\ a \cdot m^{-3})^{-1}]$  and independent of wavelength for the following calculations. In addition, for simplicity, we assume that phytoplankton account for all the backscatter and have neglected scattering from covarying detrital material. Also, we estimate  $a(\lambda)$  by means of an approximation given by Preisendorfer (Vol. 5, Sect. 10, 1976)

$$a(\lambda) \approx \frac{3}{4} K_T(\lambda) \quad (11)$$

With these approximations, Eqs. 4, 8, 9, and 11 may be used to calculate  $R(\lambda)$  for a range of chlorophyll-like pigment concentrations. The result of these calculations are shown in Fig. 5.

When the results of calculating  $R(\lambda)$  using these equations are compared with directly measured values of  $R(\lambda)$ , the calculated  $R(\lambda)$  shapes are in good agreement with the experimental ones while the absolute values for the reflectances disagree by as much as several percent. Because of the above approximations, this is to be expected. More accurate agreement is possible with a more precise treatment of the equation of radiative transfer linking  $K_T(\lambda)$  and  $R(\lambda)$ . A more accurate treatment, linking  $K_T(\lambda)$  and  $R(\lambda)$ , will be addressed in a subsequent article by the authors and has already been discussed in part by Morel (1976). The additional complexity is unnecessary for our present purpose where we wish only to demonstrate how  $R(\lambda)$  can be directly and meaningfully related to the chlorophyll-like pigment concentration in the water.

## OCEAN COLOR AND PIGMENT CONCENTRATION

Austin *et al.* (1977) have discussed the problem of ocean color and phytoplankton and have described a technique for quantitatively specifying ocean color at sea by means of hues from the Munsell

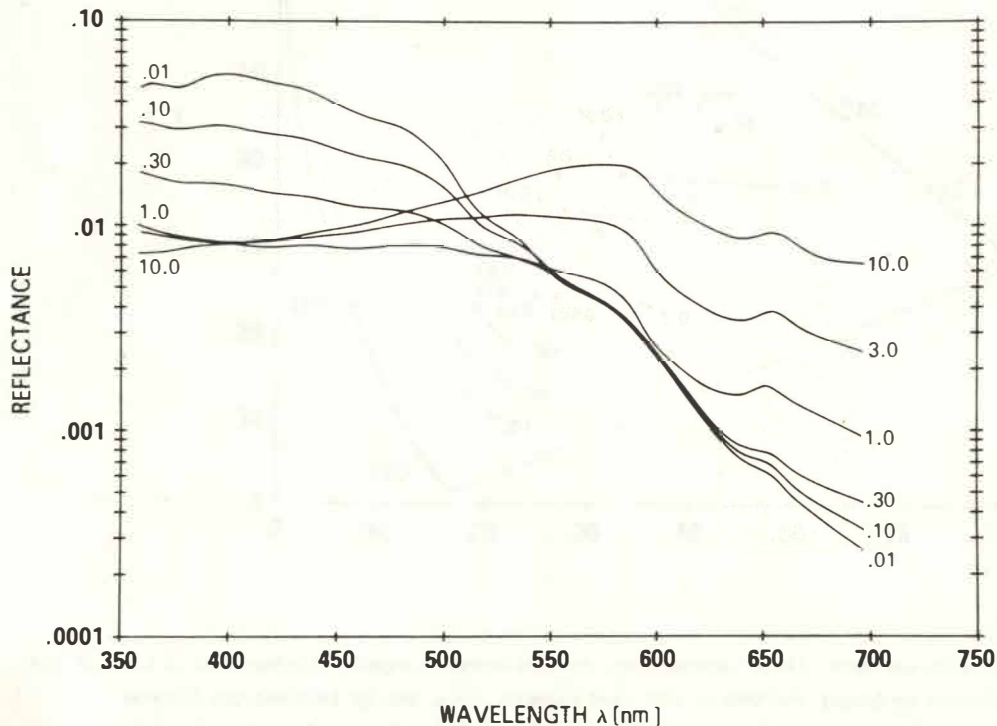


Fig. 5. Irradiance reflectance  $R(\lambda)$  as a function of wavelength for various values of chlorophyll-like pigment concentration  $C_K$  [ (mg pigment  $\cdot$  m $^{-3}$ ) ]. These curves were calculated using Eqs. 4, 8, 9, 11 and Table 1.



Book of Colors. In addition, they have discussed how ocean color may be calculated from a knowledge of the irradiance reflectance  $R(\lambda)$  (also, see Jerlov 1968).

In Fig. 6 we have plotted the color coordinates of the reflectances given in Fig. 5 for various values of  $C_K$  on the CIE chromaticity diagram, along with the Munsell specifications of hue suggested by Austin *et al.* for describing ocean color. The locus of points for various values of  $C_K$  show directly in a quantitative way the relationship between ocean color and pigment concentration. It can be seen that the dominant wavelength (obtained by drawing a line from standard illuminant "C" through the point in question to the dominant wavelength given on the pure spectrum locus) varies from 470 nanometers for  $C_K = 0.01 \text{ mg pigment} \cdot \text{m}^{-3}$  to 560 nanometers for  $C_K = 10 \text{ mg pigment} \cdot \text{m}^{-3}$ . Since, as Austin *et al.* (1977) have pointed out, the chroma and value of ocean color are highly dependent upon the environmental and viewing factors, they are not indicative of intrinsic water color, and have, therefore, not been included in their Munsell notation for ocean color.

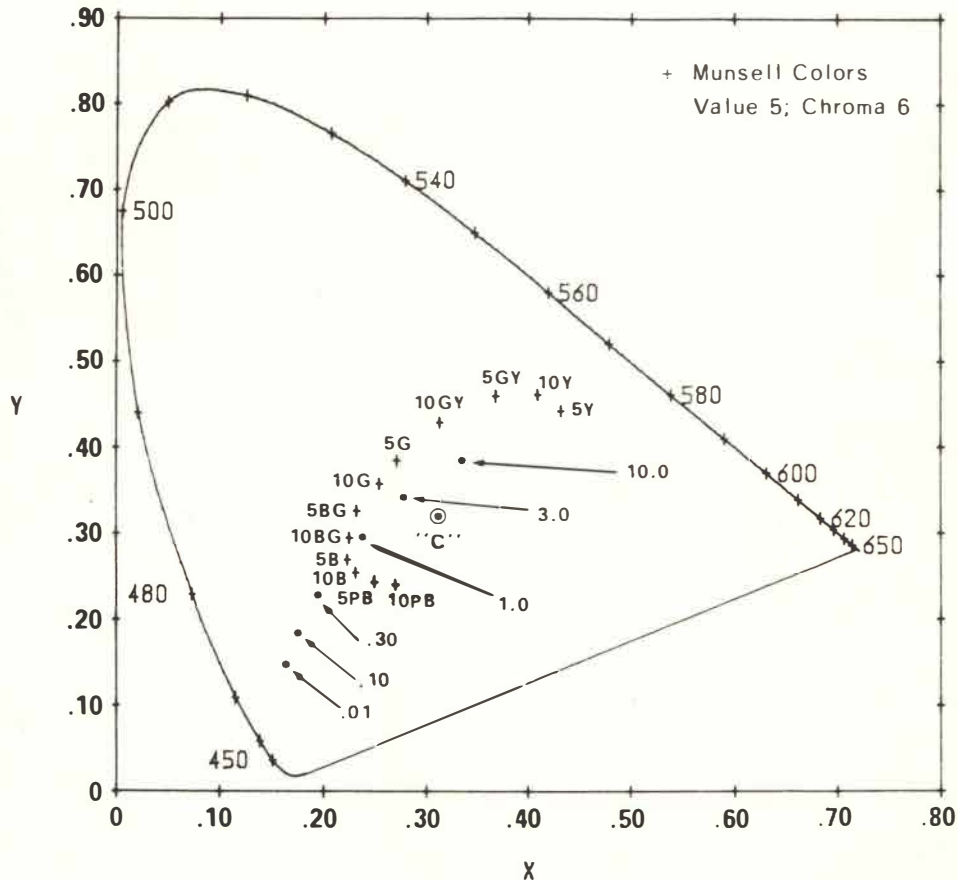


Fig. 6. C.I.E. chromaticity diagram (committee on colorimetry, 1964), with the loci of spectrally pure wavelengths represented by the curve labeled from 450 to 650 nm, based on standard source C as achromatic stimulus. Tristimulus values of reflectance, for various values of  $C_K$  [ $\text{mg pigment} \cdot \text{m}^{-3}$ ], are plotted and labeled. Munsell (1967) specifications for ocean color hue, as suggested by Austin, *et al.* (1976), are also plotted and labeled.

## SUMMARY

The spectral characteristic from natural waters of upwelling radiant energy, which has penetrated to depth and been backscattered, contains information with respect to the dissolved and suspended material in these waters. It is possible to detect this upwelled signal with appropriate spacecraft sensors and thus, potentially, to obtain information with respect to the material in these waters remotely. If this potential is to be realized, the relationships between ocean optical properties and the biological parameters affecting these properties must be understood.

A possible technique has been presented for relating the spectral diffuse attenuation coefficient for irradiance to the chlorophyll-like pigment concentration in a way that is both physically and biologically meaningful. It has been shown that  $C_K$  can be quantitatively related not only to  $K_T$  but also to the spectral reflectance  $R(\lambda)$  and to a specific description of ocean color. Within the limitations discussed above, this provides a basis for the remote sensing of chlorophyll-like pigment concentrations in ocean waters.

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