

Optical classification of natural waters¹

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Abstract

A technique has been developed that leads to an optical classification of natural waters in terms of the dissolved and suspended biogenous material present. As a first approximation, this classification has been made in terms of the total chlorophyll-like pigment concentration.

A relationship between the spectral diffuse attenuation coefficient for irradiance and the chlorophyll-like pigment concentration has been found with spectral irradiance data from diverse types of ocean waters. The specific spectral attenuation coefficient due to phytoplankton is shown to be consistent with laboratory measurements of the diffuse absorption coefficient of various lot cultures of phytoplankton.

Smith and Baker (1978) introduced the term bio-optical state to represent a measure of the total effect of biological material on the optical properties of natural waters. No generally accepted technique now exists for relating the biological constituents to the optical properties within the euphotic layer. We here 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.

The spectral characteristics of ocean properties can be represented by a few principal components. An alternative to multivariate analysis is needed that would allow each component to have some physically measurable biological significance. Smith and Baker (1978) considered the total diffuse attenuation coefficient for irradiance, K_T , without consideration for its spectral nature. We have now found that $K_T(\lambda)$ can be written as a linear function of the chlorophyll-like pigment concentration in the water column by using Beer's Law and taking into account nonlinear biological effects.

Spectral diffuse attenuation coefficient for irradiance

Smith and Baker (1978) gave detailed reasons for choosing the total diffuse at-

tenuation coefficient for irradiance to characterize the bio-optical state of ocean waters. These reasons are equally compelling when the spectral characteristics of ocean waters are considered. Furthermore, techniques for determining K_T as a function of wavelength, from measurements of spectral irradiance as a function of depth, have been developed (Tyler and Smith 1966, 1970; Morel and Calounenos 1973; Burr and Duncan 1972) and there are some spectral irradiance data available for analysis (Tyler and Smith 1970; Discoverer Exped. 1973: Scripps Inst. Oceanogr. Ref. 73-16; Morel and Prieur 1975).

$K_T(\lambda)$ 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 $E_d(z, \lambda)$:

$$E_d(z, \lambda) = E_d(0, \lambda)e^{-[K_T(\lambda)z]} \quad (1)$$

The value of $K_T(\lambda)$ can be written as

$$K_T(\lambda) = K_w(\lambda) + K_x(\lambda) + k_c(\lambda) \times C_K, \quad (2)$$

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} (mg pigment m^{-3})⁻¹] is the specific spectral irradiance attenuation coefficient due to chlorophyll-like pigments, C_K (mg pigments m^{-3}) is the average concentration of Chl *a* and pheopigments in the ocean

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water to a depth of 1 attenuation length, and $K_x(\lambda)$ (m^{-1}) is a variable representing the average contribution to spectral attenuation not directly attributable to chlorophyll-like pigments.

Nonlinear biological effects alter the expected linear relationship between K_T and C_K . On the basis of the results of Hobson et al. (1973), we have assumed two separate linear relationships of the form given by Eq. 2. One contains low to medium concentrations of chlorophyll-like pigments, 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 one.

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 1978: table 1, fig. 5), noting that there is a smaller body of spectral data available. Regression curves are fit at each wavelength (every 5 nm) from 350 to 700 nm:

$$K_T(\lambda) - K_w(\lambda) = k_1(\lambda) \times C_K, \quad C_K < 1; \quad (3a)$$

$$K_T(\lambda) - K_w(\lambda) = K_{x2}(\lambda) + k_2(\lambda) \times C_K, \quad C_K > 1. \quad (3b)$$

Combining 3a and b yields

$$k_1(\lambda) = K_{x2}(\lambda) + k_2(\lambda), \quad C_K = 1, \quad (3c)$$

where the subscripts 1 and 2 refer to the regions $C_K < 1$ and $C_K > 1$ respectively. The first region is composed of low C_K values where much of the detrital material covaries with chlorophyll. This is indicated by values for the noncovarying term, $K_{x1}(\lambda)$, which were generally within 1 or 2 SD of zero, and by the larger values for $k_1(\lambda)$ relative to $k_2(\lambda)$. The second group consists of higher C_K values where the $K_{x2}(\lambda)$ term is significant and where the relative contribution of detrital material to the slope $k_2(\lambda)$ is much less. Because the relative contribution of unidentified organic carbon becomes small for high values of C_K , we can consider

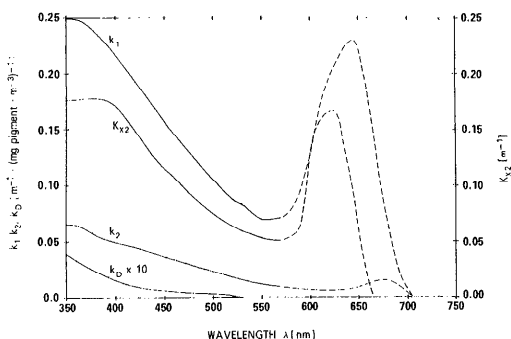


Fig. 1. Spectral values of specific attenuation coefficients $k_1(\lambda)$ and $k_2(\lambda)$ and spectral attenuation coefficient $K_{x2}(\lambda)$. $k_2(\lambda)$ is specific diffuse attenuation coefficient due to an average ensemble of marine phytoplankton. k_D ($\times 10$ to place it in scale of figure) is specific attenuation coefficient due to dissolved organic material (Stuermer 1975).

$k_2(\lambda)$ to be the specific attenuation coefficient due to chlorophyll-like pigments.

Our spectral data are fit with two lines, rather than a single line. An analysis of covariance indicates that the sum of squares about the single regression line for the pooled data was significantly greater than the sum of squares about the two regression lines.

By use of the $K_T(\lambda)$ derived from spectral irradiance data as a function of depth, we calculated the spectral values of $k_1(\lambda)$, $K_{x2}(\lambda)$, and $k_2(\lambda)$ between 350 and 570 nm. These constants are plotted in Fig. 1 and presented in Table 1 as a function of wavelength. The same technique that was used to obtain k_1 and k_2 for total irradiance (see fig. 5; Smith and Baker 1978) by making a least-squares regression fit to the data at each wavelength (every 5 nm) has been used here with the Vis Lab spectral irradiance data. We carried out a separate determination of $k_2(\lambda)$ above 570 nm, where our spectral data are limited, by using Eq. 3b and data from a few stations with high C_K values for which $K_T(\lambda)$ data between 570 and 750 nm had been obtained. This provided a relatively good determination of $k_2(\lambda)$, even though it is based on data from a few oceanographic stations.

The condition given by Eq. 3c pro-

Table 1. Spectral attenuation coefficient, $K_w(m^{-1})$ and $K_{x2}(m^{-1})$, and spectral values of the specific attenuation coefficients $k_1(\lambda)$ and $k_2(\lambda)$.

$\lambda[nm]$	$K_w(\lambda)$	$K_{x2}(\lambda)$	$k_1(\lambda)$	$k_2(\lambda)$	$\Delta K(\lambda)$
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

sides of Eq. 3c are equal, there is satisfactory internal consistency. Lack of equality in 3c implies a lack of consistency; i.e. inaccuracies in determining the spectral constants or the occurrence of spectral components which have not been included in the analysis or both. The relative lack of agreement between the left and right side of Eq. 3c, where

$$\Delta K = \frac{k_1(\lambda) - k_2(\lambda) - K_{x2}(\lambda)}{k_1(\lambda)}, \quad (4)$$

is shown in Table 1 (col 5). ΔK is <10% below 560 nm but rises to as high as 20% between 565 and 630 nm; above 630 nm the values given for $k_1(\lambda)$ and $K_{x2}(\lambda)$ may be in error by as much as a factor of two. These less reliable results are shown as the dashed portions of the curves in Fig. 1.

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 came from diverse oceanographic regions and thus cover 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 statistical average.

Preisendorfer (1976) has shown that the diffuse absorption coefficient, k , may be given in the form

$$k = [a^*(a^* + 2b^*)]^{1/2}, \quad (5)$$

where a^* and b^* are the absorption and back-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. 5 becomes

$$k(\lambda) \approx a^*(\lambda), \quad \text{for } b^*(\lambda) \ll a^*(\lambda). \quad (6)$$

The spectral diffuse absorption coeffi-

vides a measure of the internal consistency of our spectral analysis. To the extent that the independently determined

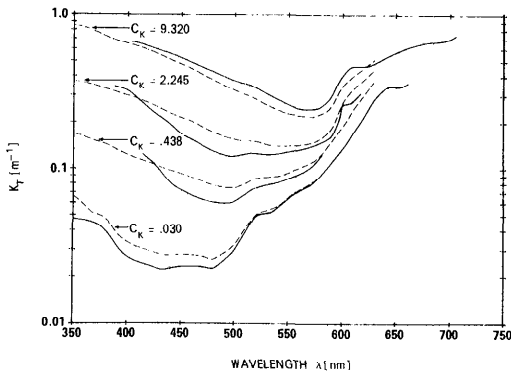


Fig. 3. Experimentally measured (solid curves) and calculated values (dashed curves) of the diffuse attenuation coefficient for irradiance, $K_T(\lambda)$, for several ocean waters varying in chlorophyll-like pigment concentrations. Dashed curves calculated from Eq. 3 and spectral values of parameters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

ment concentration has a significant, even dominant, effect on 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.

Equation 3c serves primarily as a boundary condition to link Eq. 3a and b at the value of the pigment concentration used to separate the data into high and low groups. This point was chosen so as to hold across the full wavelength spectrum, as well as to be consistent with the division point of Hobson et al. (1973). The data shown in Fig. 1 and listed in Table 1 are a result of this optimization.

Comparison with experimental data

The reliability of calculations made by Eq. 3 and the tabulated values of $K_W(\lambda)$, $k_1(\lambda)$, $K_{x2}(\lambda)$, and $k_2(\lambda)$ can be demonstrated by comparing such calculations with actual experimental data. In Fig. 3 the solid curves give experimentally determined values of $K_T(\lambda)$ for selected waters 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 Eq. 3, along with the parameters listed in Table 1, provides a reliable method for estimating $K_T(\lambda)$ from a knowledge of the chlorophyll-like pigment concentration. It should be emphasized again that the combined data used did not include areas noticeably affected by terrigenous material. The difference between the calculated and measured curves increases below 400 nm, where the calculated values underestimate the influence of dissolved organic material.

We do not have the ancillary biological information necessary to analyze our optical data for the purpose of quantitatively determining the influence of dissolved organic material (DOM) on the values of $K_T(\lambda)$. An 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 Eq. 3.

Lacking field data, we have used the data of Stuermer (1975; pers. comm.), shown on Fig. 1, as an upper limit estimate of $k_D(\lambda)$. For the range of DOM normally found in open ocean waters, these data suggest that DOM has a small effect on the optical properties except in the blue and far-blue region of the spectrum where its influence may be dominant. In principle, the indicated $k_D(\lambda)$ value can be multiplied by the concentrations of DOM and then added to Eq. 3. 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% of the total dissolved organic carbon; the measured values times 20 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 so it already partially accounts for the dissolved organic material.

Optical classification of ocean waters

An optical classification of ocean water types may be made with all the applica-

tions suggested by Jerlov's (1968, 1976) earlier method. The present scheme has the advantage of being related to the components that are major contributors to the ocean optical properties. It provides a good first approximation for spectrally characterizing the bio-optical state of ocean waters and provides a point of departure for more detailed analyses.

Figure 4 presents values of $K_T(\lambda)$, calculated using Eq. 3 and Table 1, for ocean water types ranging in chlorophyll-like pigment concentrations from 0.03 to 10 mg pigment m^{-3} . These curves show how the spectral characteristics of ocean waters are influenced by concentrations of chlorophyll-like pigments. At each 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).

With data from Table 1, a measurement of C_K is sufficient to calculate $K_T(\lambda)$ from Eq. 1. Knowing $E_d(0, \lambda)$ from direct measurement or estimating it from a knowledge of latitude, time of year, and cloud cover (Kondrat'ev 1969, 1973), we can then calculate, by means of Eq. 2, the spectral irradiance as a function of depth. $E_d(z, \lambda)$ can, in turn, be integrated to obtain an estimate of the total quanta or total energy as a function of depth and these values can be used to determine a diffuse attenuation coefficient for total quanta or total energy.

Remote sensing of the bio-optical state of ocean waters

A satellite affords the opportunity to examine important features of the marine ecosystem rapidly and repeatedly. 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.

For remote sensing purposes Eq. 3 can

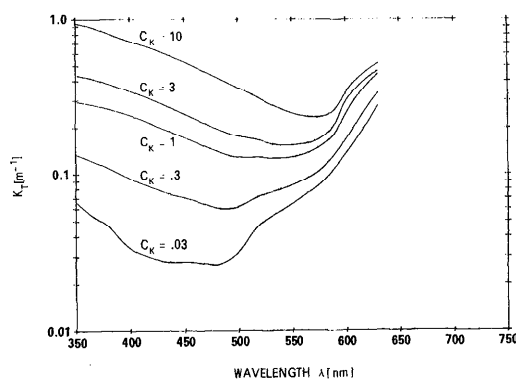


Fig. 4. Diffuse attenuation coefficient for irradiance, K_T , as a function of wavelength for various values of chlorophyll-like pigment concentration, C_K . Curves calculated from Eq. 3 and Table 1.

be considered an algorithm that links an ocean optical property to the pigment concentration. There are several theoretical methods available for relating K_T to the irradiance reflectance, $R(\lambda)$, of ocean waters (e.g. Duntley 1942; Gordon et al. 1975; Prieur 1976; Preisendorfer 1976). For the sake of illustration, we will adopt the simple expression (Morel and Prieur 1977)

$$R(\lambda) = 0.33 \frac{b'(\lambda)}{a(\lambda)}, \quad (8)$$

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

$$b'(\lambda) = b'_w(\lambda) + b'_p(\lambda). \quad (9)$$

The molecular back-scattering has been determined by Morel (1974) and the specific back-scattering coefficient of various ocean phytoplankton has been reported by Duntley et al. (1974). We have taken $b'_p(\lambda) = 10^{-3} [m^{-1} (mg \text{ Chl } a \text{ } m^{-3})^{-1}]$ independent of wavelength for the following calculations. For simplicity, we have assumed that phytoplankton account for all the back-scatter and have neglected scattering from covarying detrital material. We estimate $a(\lambda)$ by means of an approximation given by Preisendorfer (1976)

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 gain information about the material in these waters. If this potential is to be realized, the relationships between ocean optical properties and the biological parameters affecting these properties must be understood.

We have presented a technique 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. We have 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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