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Spectral absorption by marine particles of coastal waters of Baja California[1]

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Abstract

During March 1979 spectral absorptance for the suspended particles of the coastal waters of Baja California was determined by measuring the diffuse transmittance of filters containing the particles with a simply designed spectrophotometer. The absorptance for the upper water of 20 stations varied by over an order of magnitude, but the spectra were generally similar in shape and indicated that phytoplankton pigments were the dominant absorbers. A region of major spectral change was found between 400 and 435 nm, where a shift in maximal absorptance toward shorter wavelengths was correlated with increased concentrations of pheopigments relative to chlorophyll. A multivariate analysis of the data yielded two spectra for the specific absorptance in units of $m^2 \cdot mg\ pigment^{-1}$ of those particles containing chlorophyll and those containing pheopigments. The specific absorptance for chlorophyll-containing particles is compared with previous measurements in the field and laboratory; the specific absorptance for pheopigment-containing particles has not been measured before.

In March 1979 RV *Velero IV* occupied 20 stations within the coastal waters of Baja California to collect data necessary for the analysis of imagery collected by the Nimbus 7 satellite. Included in the optical and biological measurements were determinations of the spectral absorption of visible light by marine particles, needed to determine the contribution by phytoplankton to particle absorption and the contribution of particle absorption to the spectral composition of the submarine light field. Although the spectral absorption of pigments extracted from marine particles has been frequently measured (Yentsch and Ryther 1959; Yentsch 1960; Lorenzen 1972), published studies of the absorption by particles themselves have come solely from the work of Yentsch (1957, 1960, 1962, 1979). The determinations of in situ absorption are of particular importance to ocean color analysis since the absorption of extracted pigments will not include contributions by nonextractable colored materials such as minerogenic particles and the water-soluble pigments of the cyanobacteria and microscopic red algae. Also the absorption spectrum of extracted pigments differs from spectra of those pigments in vivo.

We measured particle absorption during the cruise by the method of Trüper and Yentsch (1967). Glass-fiber filters containing collected particles were placed in a scanning spectrophotometer, and the absorptance of the particles was obtained by subtracting the optical density of a blank filter from that of the filter containing the sample. While Yentsch's earlier studies present the absorptance spectra in terms of relative optical density, we present the absorptance quantitatively in units of reciprocal meters. The spectra were recorded and stored digitally by a microprocessor and then subjected to statistical analysis.

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Methods

Spectral attenuance—The attenuance of sampled particles was measured in a

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single beam spectrophotometer assembled so that a vertical monochromatic beam passed through a filter in a sample compartment immediately above an end-on photomultiplier tube. The analog signal from the photometer was first amplified and then digitized and stored. The design of the spectrophotometer and the transformation of the photometer signal have been described by Butler (1962, 1972). As he pointed out, such a single beam instrument has certain advantages over commercial dual beam instruments. In particular, spectral attenuance can be measured for highly turbid materials in which the intensity of diffusely transmitted light may be below the sensitivity of the dual beam instrument. The vertical light path and associated sample compartment also allow easy handling of biological samples. For the application described here, we exploited these advantages by cutting sample filters in half and stacking one half on top of the other, thus obtaining a much larger signal of attenuance. Such a procedure is helpful in the sampling of oligotrophic waters where larger volumes of seawater must otherwise be filtered to obtain significant attenuance.

The spectrophotometer was assembled from commercial components. The tungsten light source and single grating monochromator are from Bausch and Lomb, and the photomultiplier tube and photometer from Gamma Scientific. The output from the photometer was boosted by a home-built, signal-conditioning amplifier, and the amplified signal was digitized, scaled, and stored with a microprocessor (Fig. 1). Spectra were then smoothed by applying a digital filter which consisted of a running average of a 5-nm band width. Replicate measurements of attenuance indicate that the precision of the measurement is about 0.02 log units.

Data transformation—The sample was scanned between wavelengths of 400 and 700 nm at a rate of 1 nm·s^{-1}. The signal was first sampled at 0.1-s intervals but then averaged for 1-s intervals to obtain

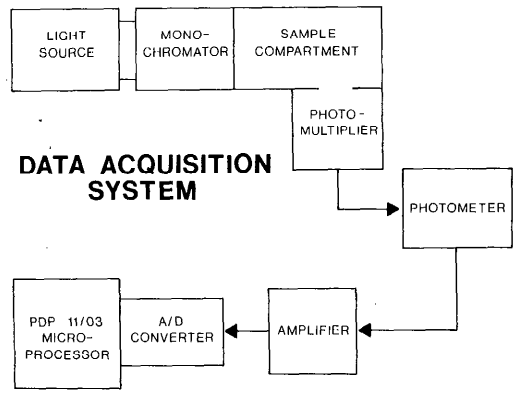

Fig. 1. Schematic representation of data acquisition system.

values of attenuance at 1-nm intervals. The semi-integral attenuance coefficient E_p (Shibata 1958), was obtained with the equation

$$E_p(\lambda) = \frac{\log V_b(\lambda) - \log V_s(\lambda)}{X} \qquad (1)$$

where $E_p(\lambda)$ is the semi-integral attenuance coefficient, $V_b(\lambda)$ and $V_s(\lambda)$ are voltages of the photometer for the blank and sample, and X is the pathlength in meters. $E_p(\lambda)$ is the exponent found in Beers' Law for the attenuation of a radiant flux, F, flowing through a medium of finite thickness, X:

$$F_X = F_0 10^{-E_p X}. \qquad (2)$$

The ratio of clearance area of the filter to the volume of seawater sampled represents a reciprocal pathlength of forward-flowing collimated light and determines the value of $1/X$. The dimensions of the attenuance coefficient defined by Eq. 1 are m^{-1}. Such a simple calculation allows comparison of the attenuance of particles collected from different waters.

Drawing on the arguments of Shibata (1958) one can show that the attenuance measured by such methods will be about equal to the absorptance of the sample if the radiance distribution of the diffusely reflected and transmitted light is the same for the blank (b) and sample (s) filters and if the absorptance of the blank is negligible. Representing the radiant

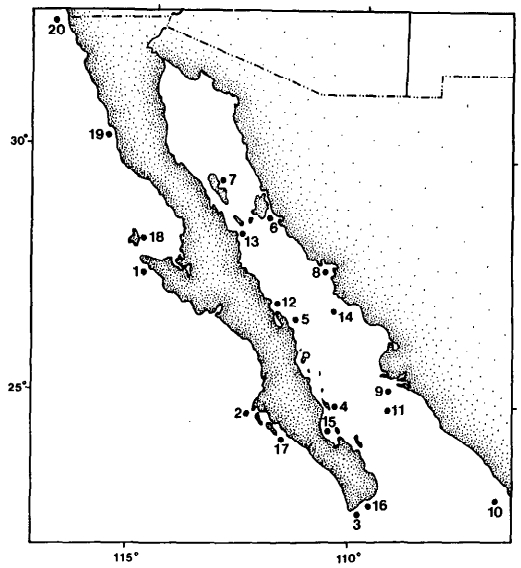

Fig. 2. Locations of stations occupied during March 1979 cruise.

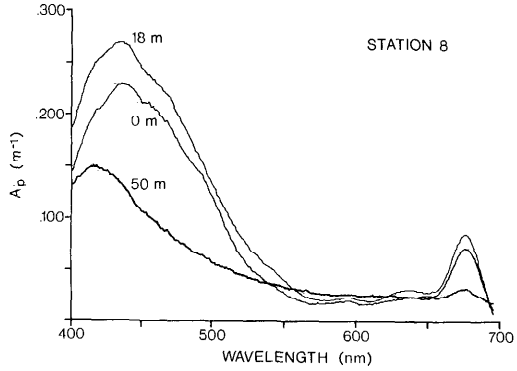

Fig. 3. Absorptance coefficient as a function of wavelength at station 8.

flux of collimated light incident to a filter as $F(0,\lambda)$, the radiant flux of reflected and transmitted light as $F(R^* + T^*,\lambda)$, and the radiant flux of absorbed light as $F(A,\lambda)$, one describes the conservation of radiant energy:

$$F(0,\lambda) = F(R^* + T^*,\lambda) + F(A,\lambda). \quad (3)$$

If f_b and f_s are the fraction of reflected and transmitted light detected by the photomultiplier, then the voltages of the photometer for blank and sample are

$$V_b(\lambda) = f_b F_b(R^* + T^*,\lambda) \quad (4)$$

and

$$V_s(\lambda) = f_s F_s(R^* + T^*,\lambda). \quad (5)$$

Substituting Eq. 4 and 5 into Eq. 1 yields

$$E_p(\lambda) = \frac{1}{X} \log \frac{f_b F_b(R^* + T^*,\lambda)}{f_s F_s(R^* + T^*,\lambda)}. \quad (6)$$

If f_b approximately equals f_s and if $F_b(R^* + T^*,\lambda)$ is approximately equal to $F(0,\lambda)$ then Eq. 6 becomes

$$E_p(\lambda) \approx \frac{1}{X} \log \frac{F(0,\lambda)}{F_s(R^* + T^*,\lambda)}. \quad (7)$$

Since the absorptance of a sample is defined as

$$A_p(\lambda) = \frac{1}{X} \log \frac{F(0,\lambda)}{F(R^* + T^*,\lambda)}, \quad (8)$$

then

$$E_p(\lambda) \approx A_p(\lambda). \quad (9)$$

Chlorophyll a and pheopigments—In addition to determining $A_p(\lambda)$, we measured the concentrations of chlorophyll *a* and pheopigments for the samples. The sample filters were ground in 90% acetone. After centrifugation the supernatant extract was placed in a cuvette and scanned with an Aminco Bowman scanning spectrophotofluorometer. The uncorrected excitation spectra for chlorophyll *a* and pheopigments were measured by scanning between 380 and 450 nm with the excitation monochromator and recording the emission centered at 676 nm. The concentrations of chlorophyll *a* and pheopigments were then determined by measuring the relative fluorescence intensity for excitation wavelengths of 416 and 435 nm. Relative values obtained at the two wavelengths were then introduced into dichromatic equations which we derived for the spectrophotofluorometer by scanning extracts containing exclusively chlorophyll *a* (435-nm excitation maximum) or pheopigments (416-nm excitation maximum) of known concentration. The shape of the fluorescence excitation spectrum indicated that neither chlorophyll *b* nor *c* contributed to the fluorescence.

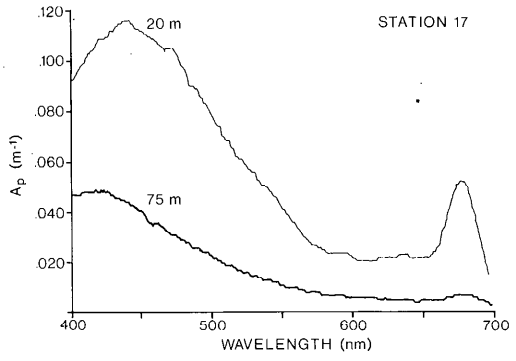

Fig. 4. As Fig. 3, but at station 17.

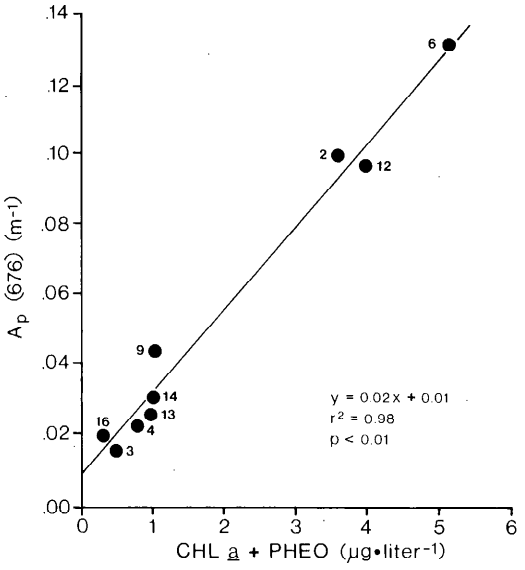

Fig. 5. Absorptance coefficient at 676 nm vs. sum of concentrations of chlorophyll *a* and pheopigments. Station numbers indicated next to points.

Results

Absorptance coefficients and the chlorophyll pigments—Spectral absorptance was measured for the upper water at 15 stations within the coastal waters of Baja California (Fig. 2). Previous studies (Zeitzschel 1970; Kiefer and Austin 1974) indicated that particulate organic material in these waters originates predominantly from marine primary production rather than freshwater or terrestrial sources. Waters were sampled from the surface and most often two other depths. Figures 3 and 4 show typical spectra of $A_p(\lambda)$ for stations 8 and 17. As was evident at all stations, the spectrum for $A_p(\lambda)$ in surface waters is qualitatively similar to that of phytoplankton. The red absorption maximum at 676 nm is uniquely characteristic of the chlorophyll *a* pigments and the broad blue absorption is characteristic of the combined absorption of chlorophylls and other algal pigments. The absorptance of particles from deeper waters, such as 50 and 75 m at stations 8 and 17, are lower than those for shallower waters and have relatively weak absorption in the red.

The predominant contribution by phytoplankton to the absorptance is evident when we examine the correlation between $A_p(\lambda)$ and concentrations of chlorophyll *a* and pheopigments. Such a relationship is shown graphically in Fig. 5 where $A_p(676)$ is plotted as a function of the sum of the concentrations of the two classes of chlorophyll *a* pigments. The coefficient of determination for a linear regression analysis of all samples was 0.98.

Spectral changes effected by pheopigments—The spectra in Figs. 3 and 4 show a shift to shorter wavelengths of the absorptance peaks for the particles collected at greater depth. Since the deeper waters most often have a relatively larger fraction of chlorophyll *a* pigments as pheopigments (Lorenzen 1965, 1967; Kawarado and Sano 1973; Jeffrey 1974), we examined the possibility that such a shift was effected by the presence of particles which contain the degradation products. Such a possibility was supported by the fact that a shift to shorter wavelengths in the blue was also evident in the $A_p(\lambda)$ of surface waters containing large fractions of pheopigment. As mentioned earlier, pheopigments in acetone fluoresce maximally when excited at 416 nm while chlorophyll *a* fluoresces maximally when excited at 435 nm. In Fig. 6 we have plotted the ratio $A_p(416) : A_p(435)$ vs. the ratio Pheo : Chl *a*. The coefficient of determination for such a regression was 0.91, indicative of a significant covariation.

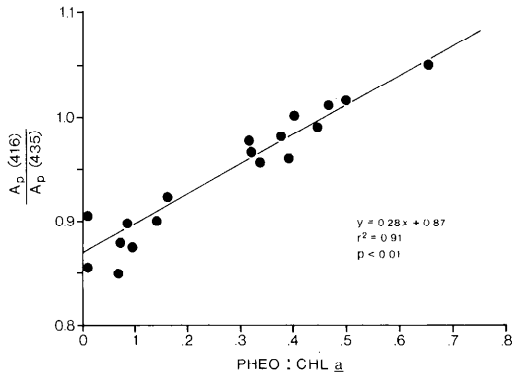

Fig. 6. Ratio of absorptance coefficient at 416 nm to that at 435 nm as a function of ratio of pheopigment concentration to chlorophyll concentration.

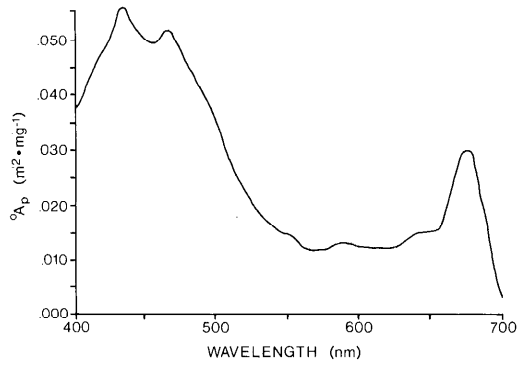

Fig. 7. Calculated specific absorptance coefficient for those pigments which covary with chlorophyll *a*.

Specific absorptance by particles containing chlorophyll and pheopigment—The apparent contribution by pheopigments to spectral changes in $A_p(\lambda)$ in the blue region of the spectrum led to further investigation into the absorption properties of the two classes of chlorophyll-like molecules. Since $A_p(\lambda)$, chlorophyll, and pheopigments were measured at several depths at many stations, we applied a multiple regression analysis to the data. The only successful analysis treated measured values of $A_p(\lambda)$ as the sum of the absorptance by two classes of particulates, one covarying with the concentration of chlorophyll *a* and the other covarying with the concentration of pheopigments. This relationship is expressed algebraically by

$$A_p(\lambda,i) = {}^{\circ}A_C(\lambda,i)C(i) + {}^{\circ}A_{Ph}(\lambda,i)Ph(i) \quad (10)$$

where $A_p(\lambda,i)$ is the absorptance coefficient for particulates of water sample i, which contains concentrations of chlorophyll, $C(i)$, and pheopigment, $Ph(i)$. ${}^{\circ}A_C(\lambda,i)$ and ${}^{\circ}A_{Ph}(\lambda,i)$ are specific absorptance coefficients for particles containing the two pigments. Since the absorptances are normalized to unit concentrations of chlorophyll *a* and pheopigment, their dimensions are $m^2 \cdot mg\ pigment^{-1}$. These specific absorptance coefficients were determined statistically at each wavelength between 400 and 700 nm by application of a least-squares best fit. The spectrum of ${}^{\circ}A_C(\lambda)$ is shown in Fig. 7 and the spectrum of ${}^{\circ}A_{Ph}(\lambda)$ is shown in Fig. 8. ${}^{\circ}A_C(\lambda)$ has maximum values at 435 nm and 460 nm and a red maximum at 676 nm; its minimum occurs at 590 nm. The spectrum of ${}^{\circ}A_{Ph}(\lambda)$ contains little structure with a maximum value at 400 nm and with the hint of the expected red absorption band at 676 nm. The specific absorptance coefficient of particles which covary with pheopigment is several times larger than the absorptance coefficient of particles which covary with chlorophyll.

Discussion

Absorptance and the volume absorption coefficient—Shibata (1958) first used an opal glass plate as a light diffuser in a spectrophotofluorometer for measurements of the attenuance of light by biological materials that also scatter light. Yentsch (1962) substituted a membrane filter for the opal glass light diffuser to measure the relative attenuance by marine particles, and Trüper and Yentsch (1967) have described measurements of spectral attenuance by photosynthetic bacteria collected on a glass-fiber filter. We have added to the methods of these investigators by constructing a spectrophotometer with a vertical light path which makes placement and stacking of filters easy (Fig. 1), by collecting and

storing the spectra digitally with a microprocessor (Fig. 1), and by normalizing measurements of absorptance so that values measured from different waters can be compared.

Because the scattering intensity and thus the radiance distribution of the light field used to measure particle attenuance is different from that of the submarine light field, the values for $A_p(\lambda)$ will not be equal to in situ values for either the diffuse volume absorption coefficient for particles, $a^*_p(\lambda)$, or the volume absorption coefficient for particles in collimated light, $a_p(\lambda)$. However, the absorptance coefficients that we measured for particles from the Gulf of California do estimate the volume absorption coefficient for these particles or the diffuse volume absorption coefficient. The absorptances that we have measured are proportional to the volume absorption coefficient (Butler 1962):

$$a_p(\lambda) = \frac{2.3A_p(\lambda)}{\beta(\lambda)}. \qquad (11)$$

In the case of the diffuse volume absorption coefficient

$$a^*_p(\lambda) = D(\pm,\lambda)a_p(\lambda) = \frac{2.3D(\pm,\lambda)A_p(\lambda)}{\beta(\lambda)}. \qquad (12)$$

The factor 2.3 converts $\log_{10}$ to ln units, $D(\pm,\lambda)$ is the distribution function for forward- (+) or backward-flowing (−) irradiance, and $\beta(\lambda)$ is the pathlength amplification factor. The distribution function, which depends on the radiance distribution of the light field within a lamina of diffusing material, has a minimum value of 1 for collimated light and a value of 2 for a completely diffuse light (Preisendorfer 1961). The pathlength amplification factor is the ratio of the optical thickness of the diffusing material to its geometric thickness. The pathlength amplification factor has a minimum value of 1 for materials that do not scatter light and values >100 for thick materials that scatter light intensely (Butler 1962).

To estimate $\beta(\lambda)$ for stacked halves of glass-fiber filters we compared calculated

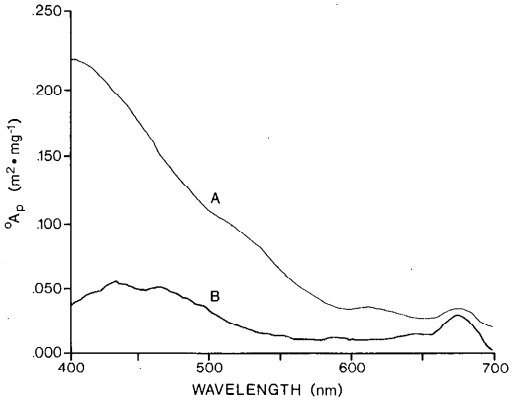

Fig. 8. Calculated specific absorptance coefficient for those pigments which covary with (A) pheopigments and with (B) chlorophyll *a* (note change of scale from Fig. 7).

values of specific absorptance coefficient for particles which contain chlorophyll *a* (Fig. 7) with measured values of the specific volume absorption coefficient for two cultures of phytoplankton, the small diatom *Thalassiosira pseudonana* and the small chrysophyte *Monochrysis lutheri* (unpubl. from Kiefer et al. 1979). The introduction of spectral values of $^\circ a_p(\lambda)$ and $^\circ A_C(\lambda)$ into Eq. 11 yielded a value of $\beta(\lambda)$ of about 6. By substituting this value for $\beta(\lambda)$ in Eq. 11, we can estimate the values of $a_p(\lambda)$ (Figs. 3–6), $a_C(\lambda)$ (Fig. 7), and $a_{Ph}(\lambda)$ (Fig. 8) for marine particles from the Gulf of California. These volume absorption coefficients will now be compared with other estimates.

Comparisons of spectral values of $^\circ a_C(\lambda)$ *and* $^\circ a_{ph}(\lambda)$—The specific spectral absorption for pigment-containing particles has been calculated from spectroradiometric measurements at sea. Smith and Baker (1978) estimated the specific diffuse absorption coefficient from measurements of the diffuse attenuation coefficient for downwelling irradiance, and Morel and Prieur (1977) and Prieur and Sathyendranath (1981) calculated the specific absorption coefficient for collimated light from measurements of both diffuse reflectance and attenuation. Although the specific absorption coefficient calculated from values of $A_p(\lambda)$ shown in

Fig. 7 is similar in shape and magnitude to those presented by these workers, there are differences. The spectrum of $^{\circ}a^{*}_{p}(\lambda)$ presented by Smith and Baker (1978) lacks the structure found in Fig. 7, and values are somewhat higher. For example, at 440 nm they obtained a value for $^{\circ}a^{*}_{p}(\lambda)$ of 0.039 while our value for $^{\circ}a_{C}(\lambda)$ is 0.022. The larger values for their coefficients and the lack of structure within their spectra may be due in part to contributions by the pheopigments (Fig. 8). Prieur and Sathyendranath (1981) calculated $^{\circ}a_{p}(\lambda)$ for the absorption by particles containing both chlorophyll *a* and pheopigments as well as for particles that do not contain chlorophyll or its degradation products. The shape of spectral absorption by particles containing photosynthetic pigments which they calculated is very similar to that for $^{\circ}A_{C}(\lambda)$ shown in Fig. 7. Their value for $^{\circ}a_{p}(\lambda)$ at 440 nm is 0.018 $m^2 \cdot mg^{-1}$, which is close to our estimate of 0.022. Since their spectrum has no features indicating the presence of pheopigments, the degraded chlorophylls presumably were at relatively low concentration in the surface waters that they sampled.

Quantitative evaluation of the absorption coefficient of particles containing pheopigments (Fig. 8) has not been previously attempted. Although the spectrum presented here was determined by a regression analysis of relatively few stations and thus requires substantiation, we feel that the general features of the spectrum should be discussed. The spectrum is relatively structureless, and its shape is different from that of the pheopigments in extract. Such a difference is most likely to be caused by the presence of relatively high concentrations of other pigments, such as the carotenoids, in those particles containing the pheopigments. This is best appreciated by comparing the small absorption peak for pheopigments at 676 nm with the much larger blue absorption.

We suggest that the spectrum presented here is typical of small detrital particles found within the euphotic zone, and we support such a suggestion by noting the similarities between this spectrum and that which we have measured for large fecal particles collected in sediment traps. The role of detrital material in absorbing short-wavelength light was discussed by Yentsch (1979). He presented an attenuance difference spectrum for a culture of *Skeletonema costatum* and a seawater sample containing detritus and phytoplankton. This difference spectrum shows the same shape as that in Fig. 8.

Finally, it is evident from the data shown in Figs. 6 and 8 that particles containing pheopigments contribute to water color. The presence of increasing concentrations of pheopigments seems to be correlated with a shift to shorter wavelengths in the blue region of the spectrum (Fig. 6). In addition, the particles which contain pheopigments probably contribute quantitatively to the absorption of blue light in the upper waters of the ocean. Such a contribution can be estimated from the value of specific absorptance coefficients shown in Fig. 8. The concentration of pheopigments in the mixed layer is about 15–20% of the concentration of total chlorophyll pigments. Since in the blue region of the spectrum the specific coefficient for pheopigment-containing particles is about four times that of the chlorophyll-containing particles, we estimate that about 40% of the blue absorption by particles comes from those containing pheopigments.

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