Light absorption by phytoplankton, photosynthetic pigments and detritus in the California Current System

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Abstract—Pigment-specific absorption by total particulates, detritus and phytoplankton was measured throughout the euphotic zone at > 275 stations on three cruises off California in late 1991 and early 1992. A new spectral fluorescence method for assessing photosynthetically active absorption in natural samples was developed and applied. Spatial variability in specific absorption coefficients at the mesoscale was found to be as high as previously observed between mid- and high-latitudes, while differences between cruises were very low. In surface waters, the highest values of specific absorption were found in warm, low-pigment surface waters offshore and in the Southern California Bight. Vertical sections reveal that low values occur near the surface only where the pycnocline and nitracline slope toward the sea surface. The highest values of phytoplankton specific absorption occurred at shallow optical depths for stations with deep nitraclines, whereas the lowest values always occurred close to or below the depth of the nitracline. Specific absorption generally increased with increasing temperature, but there were large differences in the relationships between cruises. In the context of previous laboratory observations, these results imply that nutrient availability plays a greater role than direct temperature effects in controlling natural variance in phytoplankton specific absorption. Specific absorption of photosynthetically active phytoplankton pigments was found to be less variable than that of total phytoplankton and showed no systematic trends with temperature, optical depth, or distance from the nitracline. This result leads to a new version of a bio-optical model for primary production which is based only on the photosynthetically active component rather than total phytoplankton absorption.

INTRODUCTION

Light absorption by particulate material, including phytoplankton, is an important source of optical variability in the surface waters of the ocean. This variability has consequences for light attenuation, primary production, remote sensing of pigment biomass and mixed layer heating. For these reasons and because of the advent of remote sensing capabilities, there is increasing demand for a fundamental knowledge of the magnitude, range and sources of variability in particulate optical properties in marine surface waters. Remote sensing offers the potential for synoptic assessment of phytoplankton pigment biomass and primary production, but this requires that variability in particulate absorption properties must be incorporated into models and algorithms at a variety of spatial and temporal scales.

Previous work has shown the importance of chlorophyll concentration on variability in

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diffuse attenuation (e.g., Smith and Baker, 1978; Morel, 1988) and reflectance ratios or ocean color (Morel and Prieur, 1977; Gordon *et al.*, 1983, 1988; Mitchell and Holm-Hansen, 1991). However, many of the algorithms resulting from this type of work have not explicitly included variability in absorption properties, limiting our ability to extend algorithms from one region to another (Mitchell and Holm-Hansen, 1991; Carder *et al.*, 1991; Sosik *et al.*, 1992). For analysis of this problem, it is useful to consider the total absorption $(a(\lambda))$, an inherent optical property, in terms of its constituent components:

$$a(\lambda) = a_w(\lambda) + a_p(\lambda) + a_s(\lambda) \tag{1}$$

and

$$a_p(\lambda) = a_{ph}(\lambda) + a_d(\lambda), \tag{2}$$

where λ is wavelength, $a_w(\lambda)$ is the absorption due to the water itself, and $a_p(\lambda)$ and $a_s(\lambda)$ are absorption by particulate material and soluble material in the water. The absorption by the particulate fraction is further decomposed in (2) into absorption by viable phytoplankton $a_{ph}(\lambda)$ and by all remaining material, generally referred to as detrital particulates, $a_d(\lambda)$. With respect to estimating phytoplankton pigment concentrations and light attenuation or reflectance as a function of pigment concentration, simple algorithms will lead to errors if the pigment-specific absorption by any of the components varies. Since pigment concentration is the dominant source of variance in particle absorption, it is convenient to define pigment-specific coefficients for describing the remaining variance; for example:

$$a_{ph}{}^*(\lambda) = \frac{a_{ph}(\lambda)}{(\text{chl} + \text{phaeo})}, \tag{3}$$

where $a_{ph}^*(\lambda)$ has units of area per mass of pigment (e.g., m^2 (mg chl+phaeo)$^{-1}$) and chl+phaeo represents the concentration of chlorophyll *a* plus phaeopigment (phaeo).

Variability in $a_{ph}^*(\lambda)$ is also important for accurate modeling of primary production from light and pigment data. Light absorption by phytoplankton pigments is critical for photosynthesis, so the process of light absorption is often explicitly included in models of primary production (e.g., Kiefer and Mitchell, 1983). For these purposes, we also propose that it is useful to further decompose absorption by the phytoplankton into two components:

$$a_{ph}(\lambda) = a_{ps}(\lambda) + a_{pp}(\lambda), \tag{4}$$

where $a_{ps}(\lambda)$ represents absorption by phytoplankton pigments which effectively transfer excitation energy to the photochemical reaction centers and $a_{pp}(\lambda)$ is absorption by photoprotective accessory pigments or other cell components not coupled to photochemistry.

Considerable evidence now exists in the literature documenting variability in $a_{ph}^*(\lambda)$ for laboratory cultures of phytoplankton. Differences have been found between species (Morel and Bricaud, 1986; Bricaud *et al.*, 1988; Mitchell and Kiefer, 1988a) as well as within a species grown under different environmental conditions. Within species, effects have been well documented for changes in growth irradiance, with highest values of $a_{ph}^*(\lambda)$ observed for high light intensities (e.g., Dubinsky *et al.*, 1986; Mitchell and Kiefer, 1988a; Berner *et al.*, 1989; Stramski and Morel, 1990). For nutrient-limited, steady-state

growth, $a_{ph}^*(\lambda)$ varies inversely with growth rate (Herzig and Falkowski, 1989; Chalup and Laws, 1990; Sosik and Mitchell, 1991). Additionally, recent evidence shows a similar inverse relationship between $a_{ph}^*(\lambda)$ and growth rate for temperature-limited cells (Sosik and Mitchell, 1994; Moisan et al., 1994). Nutrient-starved batch cultures have also been observed to exhibit high values of $a_{ph}^*(\lambda)$ (Cleveland and Perry, 1987).

This variability in $a_{ph}^*(\lambda)$ both between and within species is due to differences in pigmentation and to pigment packaging effects. Package effects are most extreme in large, highly pigmented cells because of attenuation by surrounding pigment molecules. This effect has been analyzed theoretically (Duysens, 1956; Morel and Bricaud, 1981, 1986; Kirk, 1983) and has been well documented in the laboratory (Dubinsky et al., 1986; Bricaud et al., 1988; Mitchell and Kiefer, 1988a; Berner et al., 1989; Sosik and Mitchell, 1991). The result is generally lower $a_{ph}^*(\lambda)$ with flatter peaks for phytoplankton cells which have significant package effects by virtue of larger cell size or higher intracellular chlorophyll a concentrations. Since $a_{ph}^*(\lambda)$ is specific only to chlorophyll a (or chlorophyll a plus phaeopigment), $a_{ph}^*(\lambda)$ will also vary even for cells with the same chlorophyll a content and cell size if the relative abundance of accessory pigments varies. This effect will be strongly spectral and is most significant in regions of the spectrum where accessory pigment absorption is highest (see Sosik and Mitchell, 1994).

Based on the filter technique first used by Yentsch (1957, 1962), several quantitative methods for estimating $a_p(\lambda)$ in the ocean have been proposed (Kiefer and SooHoo, 1982; Mitchell and Kiefer, 1984, 1988a; Bricaud and Stramski, 1990; Cleveland and Weidemann, 1993). A major difficulty in applying this method to phytoplankton is that natural particulates include a substantial amount of non-phytoplankton material which absorbs visible wavelengths (Mitchell et al., 1984; Mitchell and Kiefer, 1988b). Kishino et al. (1985) proposed a methanol extraction procedure to remove phytoplankton pigments from the filtered material so that $a_d(\lambda)$ can be estimated. An estimate of $a_{ph}(\lambda)$ is then determined by difference $[a_p(\lambda) - a_d(\lambda)$; equation (2)]. Other techniques include statistical and numerical modeling methods to decompose $a_p(\lambda)$ into $a_{ph}(\lambda)$ and $a_d(\lambda)$ components (Morrow et al., 1989; Roesler et al., 1989; Bricaud and Stramski, 1990).

Since the development of these quantitative methods, there have been several studies considering ecological implications of observed variability in absorption properties of natural particulate material, especially with regard to pigment specific absorption by phytoplankton (Lewis et al., 1985; Mitchell and Kiefer, 1988b; Yentsch and Phinney, 1989; Bricaud and Stramski, 1990; Hoepffner and Sathyendranath, 1992; Babin et al., 1993). Generally, lower values of $a_{ph}^*(\lambda)$ have been observed for mesotrophic to eutrophic waters with cell size, pigment packaging and pigment ratios all being invoked as sources of variability in both $a_p^*(\lambda)$ and $a_{ph}^*(\lambda)$.

Although important ecological insight has been gained from these studies using particulate absorption techniques, none of these approaches is ideal for determining phytoplankton absorption which is most relevant for photosynthesis. This is primarily because $a_{ph}(\lambda)$ estimates include absorption by phytoplankton pigments which are not active in photosynthesis [see equation (4)]. Accessory pigments such as zeaxanthin, lutein and β-carotene do not transfer excitation energy effectively to the photosynthetic reaction centers and are thought to serve a photoprotective role (e.g., Siefermann-Harms, 1987; Demmig-Adams and Adams, 1992). This absorption represents an added source of variability not directly related to photosynthesis.

In contrast, chlorophyll a fluorescence excitation spectra have the potential to provide

direct information about the spectral characteristics of photosynthetic activity. Neori *et al.* (1986, 1988) compared the spectral shapes for chlorophyll *a* fluorescence and for photosynthetic oxygen production for a variety of algae and concluded that fluorescence provides a viable alternative for estimating photosystem II action spectra compared to the more laborious O_2 evolution method. Since photosystem II is responsible for photosynthetic hydrolysis and O_2 evolution, the use of chlorophyll *a* fluorescence as a proxy is a potentially powerful method to assess the relative spectral shape for photosynthetically active light absorption. An alternative method proposed to estimate active absorption is based on pigment reconstruction techniques (Bidigare *et al.*, 1989, 1992). This method may be limited, however, in the accuracy with which *in vitro* spectra for pigments represent their *in vivo* counterparts, and also because package effects are not included in simple reconstruction. In addition, active absorption estimates based on pigment reconstruction are not corrected for variations in energy transfer efficiency for each pigment.

With the goal of determining and understanding spatial variability in pigment-specific absorption by the different components of the particulate material, we conducted a series of surveys off California. The hydrographic conditions in this region are highly variable and the circulation patterns are complex (Hickey, 1979; Jackson, 1986; Lynn and Simpson, 1987). In surface waters, the main jet of the California Current flows equatorward in a zone between 200 and 500 km offshore, generally moving closer to the coast in the south. This region marks on eddy-rich transition zone between oceanic and coastal waters (Lynn and Simpson, 1987). Water from the sub-arctic Pacific (cold, low salinity, high oxygen) and from the North Pacific (warm, high salinity) are both sources for the southward flow in this region. Poleward transport near the coast is common in the fall and winter north of Point Conception and throughout much of the year in the Southern California Bight (Hickey, 1979; Lynn and Simpson, 1987). The California Current bends eastward near 32°N and some of the water turns northward and, combined with water of more equatorial characteristics (warm, high salinity, low oxygen), feeds the nearshore countercurrent. If the optical properties of natural populations of phytoplankton are influenced by their physical and chemical environment, it should be apparent in a region of such oceanographic diversity.

In this paper, we describe the range and patterns of variability in specific absorption for total particulates and for detritus and phytoplankton determined by the extraction method of Kishino *et al.* (1985). We also present a novel method for assessing photosynthetically active absorption using a combination of particulate absorption, chlorophyll *a* fluorescence and pigment measurements. We show that $a_{ph}^*(\lambda)$ is highly variable in the California Current System and is related to the hydrographic and chemical environment at the time of sampling and, in contrast, $a_{ps}^*(\lambda)$ is relatively constant and more independent of environmental variables. The implications of these observations for the construction of photosynthetic models is considered.

MATERIALS AND METHODS

Sampling

Sampling was conducted on three cruises in 1991 and 1992 off California (see Fig. 1). The first two cruises were conducted in collaboration with the California Cooperative Oceanic Fisheries Investigation (CalCOFI), an on-going program with quarterly cruises in
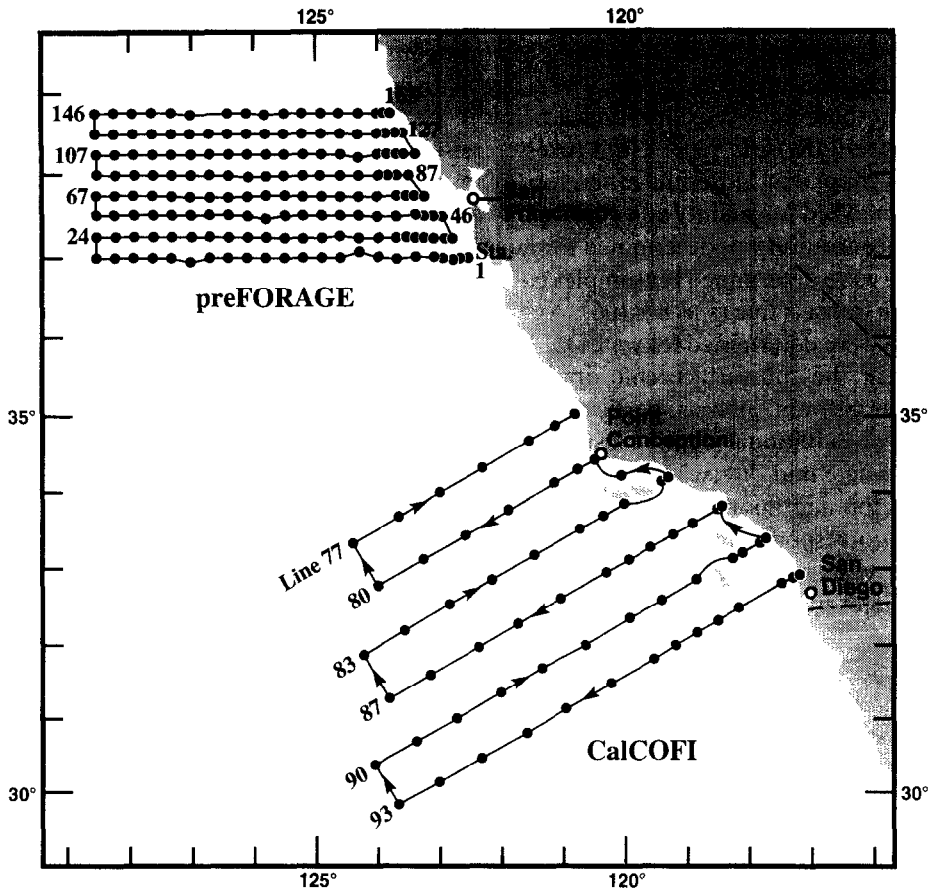
Fig. 1.   Map of the CalCOFI and preFORAGE sites with cruise tracks and sta. locations indicated. The CalCOFI area was visited first in the autumn of 1991 and again in winter 1992. The preFORAGE cruise took place in early spring of 1992.

the study area. CalCOFI cruise 9110 on the R.V. *New Horizon* took place between 28 September and 14 October 1991, and cruise 9202 returned to the same stations between 28 January and 13 February 1992 on the R.V. *David Starr Jordan*. The third cruise was a two-ship preliminary survey for the NOAA Fishery Oceanography Research and Groundfish Ecology program (preFORAGE). Sampling on preFORAGE cruise 9203 was conducted on the R.V. *David Starr Jordan* leg from 14 March to 2 April 1992.

On the CalCOFI cruises, hydrocasts were conducted at each of the stations, with water generally collected from 20 depths in the top 500 m. Temperature, salinity and concentrations of chlorophyll a, phacopigment, NO_3^-, NO_2^-, PO_4^{3-}, SiO_4^{2-} and dissolved O_2 were determined on all samples as part of the routine CalCOFI sampling protocol (Scripps Institution of Oceanography, 1992a,b). Samples were collected from every other bottle from the top ten for particulate absorption and fluorescence measurements (no fluorescence on CalCOFI 9110). In addition, a second hydrocast was conducted immediately following the main cast to collect a larger water sample from 4 m depth for absorption, fluorescence and pigment analysis. Once each day, at the station just before local apparent

noon, water for primary productivity incubations was collected with a CTD rosette package at six depths corresponding to approximately 95, 37, 16, 4.5, 2.5 and 0.15% of surface light estimated from the Secchi depth. In addition, *in situ* optical profiles were also made at these mid-day stations (see below).

On preFORAGE 9203, CTD rosette casts were conducted at all stations with water bottles tripped at 11 depths in the top 200 m and at 500 m or 1000 m. All water samples were analyzed for salinity and chlorophyll *a* and phaeopigment concentrations. Dissolved O_2 concentration was determined for most samples and nutrients (NO_3^-, NO_2^-, PO_4^{3-} and SiO_4^{2-}) were determined for samples collected at the mid-day stations and at all stations on the fifth transect line (stas 87–106). At all stations, particulate absorption and fluorescence spectra were determined for water samples collected from at least two depths: near surface and near the sub-surface chlorophyll maximum. On line 5, where sampling included detailed nutrient analysis, particulate optical properties were analyzed for water samples from two additional depths, usually above and below the chlorophyll maximum. At stations near mid-day, where samples were collected for primary productivity incubations, absorption and fluorescence spectra were measured on six euphotic zone samples from depths corresponding to approximately 93, 34, 16, 4.4, 2.2 and 0.14% of surface PAR. The rosette casts at these stations were preceded by an optical cast with an underwater radiometer to determine target depths (see below).

Optical profiles. On all three cruises, *in situ* optical measurements at the mid-day stations consisted of continuous profiles in the top 200 m with a Biospherical Instruments MER 1012 underwater spectral radiometer. Narrow band (~ 10 nm full-width half-power) downwelling vector irradiance was measured at 410, 441, 488, 520, 565, 633 and 683 nm. Sampling also included upwelling radiance (441, 488, 565, 633, 683 nm), scalar downwelling PAR, pressure and temperature. Optical depth at 488 nm [$OD(488,z)$] for the sample depths was determined from the underwater irradiance profiles as $OD(488,z) = -\ln(E(488,z)/E(488,0^-))$, where $E(488,0^-)$ represents the irradiance just below the surface, and z is depth. Since near-surface irradiance data are often compromised by problems such as ship shadow and surface waves, $E(488, 0^-)$ was determined by extrapolating to the interface using the rate of attenuation determined for the top 5 m of the cast below any obvious surface artifacts. To extend the information of $OD(488)$ to include all stations sampled for particulate absorption, we have used the spectral model of Morel (1988) to estimate $OD(488)$ from measured chlorophyll *a* and phaeo concentrations. The model was applied to estimate a diffuse attenuation coefficient, $K(488)$, for each discrete depth z where pigment concentrations were determined. The $OD(488)$ at a particular depth Z was then determined as $OD(488, Z) = \Sigma(K(488,z)\Delta z)$ for all z between 0 and Z, where Δz was calculated as half the distance between the sample depths immediately above and below each z. Although there is a tendency for the calculated values to overestimate, the results agree favorably with $OD(488,Z)$ determined from measured irradiance profiles (Fig. 2).

Analysis of discrete samples

Nutrient concentrations were measured with an autoanalyzer, dissolved oxygen by Winkler titration, and salinity with an inductive salinometer following established procedures (Scripps Institution of Oceanography, 1992a,b). Samples for pigments were
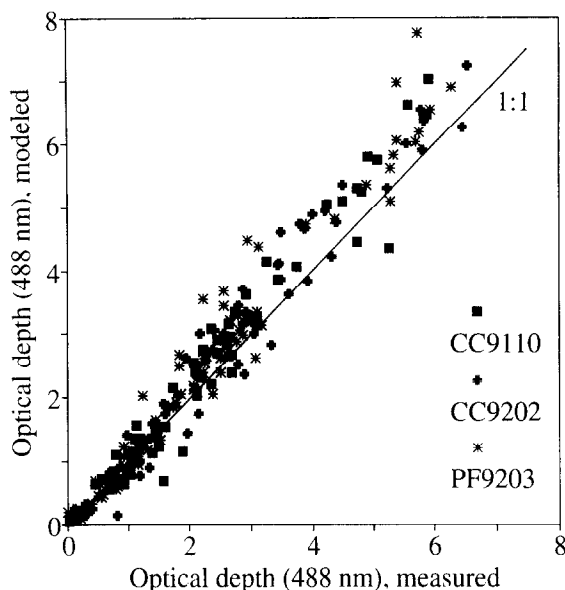
Fig. 2. Scatter plot of measured optical depth at 488 nm for discrete sample depths and optical depth calculated from measured pigment concentrations with the model of Morel (1988). Observations from all three cruises are included for a total of 246 points. The overall relationship is close to 1:1 (slope = 1.12) with $r^2 = 0.97$.

collected on Whatman GF/F filters and refrigerated for at least 24 h in 90% acetone. Concentrations of chlorophyll a and phaeopigment were determined from fluorescence of the extracts before and after acidification using a Turner Designs fluorometer calibrated with pure chlorophyll a. Some comments on issues concerning this technique for pigment determination can be found at the end of the Methods section.

Particulate absorption spectra. All absorption measurements were made on fresh samples at sea. Particulates were collected from water samples on Whatman GF/F filters. The absorption of these filters relative to a blank filter saturated with seawater was measured in a Perkin Elmer Lambda six dual beam spectrophotometer following the guidelines of Mitchell (1990). Scans were conducted between 300 and 750 nm with a 4 nm slit. Following measurement of the initial particulate absorption spectrum, the filters were extracted in methanol using the procedure of Kishino *et al.* (1985) and then resaturated with filtered seawater. Following this extraction, the absorption of the filters relative to blank filters also treated with methanol and resaturated with filtered seawater was determined in the spectrophotometer. These spectra represent absorption by non-methanol extractable detrital material $(a_d(\lambda))$. An estimate of the phytoplankton component of the total particulate absorption pool was then determined by difference [see equation (2)] (Kishino *et al.*, 1985). All spectra were shifted to have zero absorbance at 750 nm to correct for spectrally constant differences between sample and reference filters which occur during routine particulate absorption determinations. Following this normalization, absorption spectra were corrected for pathlength amplification using the Quantitative Filter Technique (QFT) of Mitchell (1990). Absorption spectra were smoothed by

filtering out variations with frequencies greater than 0.039 nm^{-1} using Fourier transform techniques. Pigment-specific absorption for total particulates $(a_p^*(\lambda))$, phytoplankton $(a_{ph}^*(\lambda))$ and detritus $(a_d^*(\lambda))$ were calculated by normalizing to the concentration of chlorophyll a plus phaeopigment. See the end of this section for some consideration of issues relating to these analysis procedures.

Chlorophyll a fluorescence spectra. Chlorophyll a fluorescence excitation spectra were measured at sea on whole seawater samples in 1 cm cuvettes using a Spex Industries Fluoromax spectrofluorometer equipped with a stirring accessory and a red sensitive photomultiplier. Following the method of Neori *et al.* (1986), samples were treated with 3-(3,4-dichlorophenyl)-1,1-dimethylurea (DCMU) and excitation spectra were determined from 300 to 700 nm with an excitation slit of 5 nm while emission was monitored at 730 nm with a 20 nm slit. To minimize stray light reaching the detector, a Schott glass long pass filter (RG715) was mounted between the sample and the emission monochromator. Blank scans of 0.2 μm filtered seawater were subtracted from sample spectra. In addition, all spectra were corrected for simultaneous measurement of lamp output (data acquired in ratio mode) and further corrected using the quantum counter 2,7-bis-(diethyl-amino)phenazoxonium perchlorate (purchased as laser grade Oxazine 1 perchlorate from Eastman Kodak, but also available as Basic Blue) as described by Kopf and Heinze (1984). Excitation spectra were processed using a median filter with a 5 nm moving window followed by the same Fourier transform filtering applied to the absorption spectra.

The DCMU-enhanced fluorescence excitation spectra $(F_{DCMU}(\lambda))$ were used to determine the component of the total phytoplankton absorption which is active in photosynthesis as a function of wavelength $(a_{ps}(\lambda))$. Since fluorescence measurements represent only relative spectral shape, it is necessary to normalize the spectra to obtain a quantitative estimate of absorption. As in previous work (Sakshaug *et al.*, 1991; Johnsen and Sakshaug, 1993), we have chosen to use 675 nm for this normalization since accessory pigment absorption is minimal at the red peak. Unlike Sakshaug *et al.* (1991), who used the method for cultures, we have applied a correction to $a_{ph}(675)$ for absorption by the phaeopigments in natural samples. Absorption at 675 nm can be approximated as the sum of two components:

$$a_{ph}(675) = a_{chl}(675) + a_{phaeo}(675), \tag{5}$$

where $a_{chl}(675)$ represents the absorption by chlorophyll a and $a_{ph}(675)$ is the absorption by degradation products of chlorophyll a (phaeopigments). These absorption components can be expressed as the product of a specific absorption coefficient and the concentration for each pigment:

$$a_{ph}(675) = a_{chl}^*(675) \cdot chl + a_{phaeo}^*(675) \cdot phaeo. \tag{6}$$

With the assumption that all the chlorophyll a present can actively transfer energy to the photosynthetic reaction centers, we can write:

$$a_{ps}(675) = a_{ph}(675) - a_{phaeo}^*(675) \cdot phaeo, \tag{7}$$

from which it is possible to determine $a_{ps}(675)$ based on measurements of $a_{ph}(675)$ and phaeopigment concentration if $a_{phaeo}^*(675)$ is known. To estimate $a_{phaeo}^*(675)$, we pooled all the pigment and $a_{ph}(675)$ determinations from CalCOFI 9202 and preFOR-AGE 9203 (the two cruises on which $F_{DCMU}(\lambda)$ data were collected) and determined the
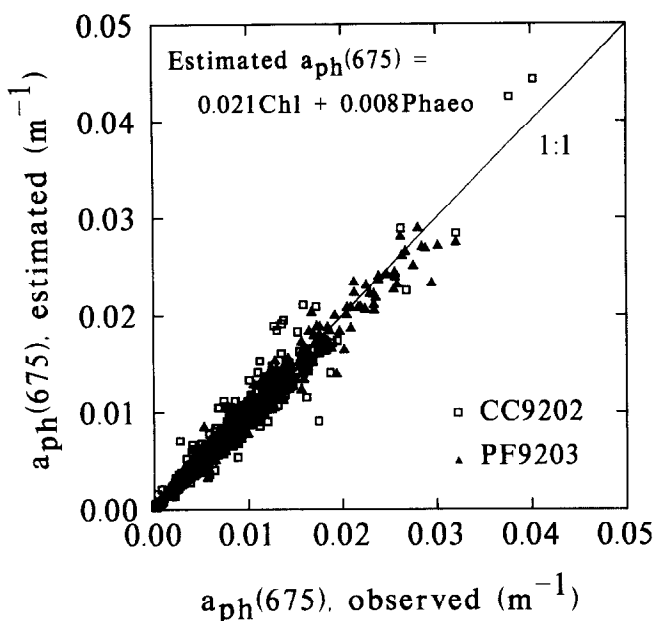
Fig. 3. Values of $a_{ph}(675)$ estimated from the pigment-specific model detailed in the text [equation (6)] plotted against the measured values used to derive the model for CalCOFI 9202 and preFORAGE 9203 ($r^2 = 0.95$; $N = 865$).

least-squares fit to equation (6) with $a^*_{chl}(675)$ and $a^*_{phaeo}(675)$ as adjustable parameters (Fig. 3). The result was a value for $a^*_{chl}(675)$ of 0.021 m^2 (mg chlorophyll $a)^{-1}$, which is consistent with results from laboratory studies of pure phytoplankton cultures which contain negligible amounts of phaeopigments, and a value of 0.008 m^2 (mg phaeopigment)$^{-1}$ for $a^*_{phaeo}(675)$. In principle, these coefficients should vary because of package effects or the presence of other pigments, but these effects are minimized at red wavelengths compared to the blue to green region of the spectrum.

Once the value of $a_{ps}(675)$ is determined from equation (7), it is possible to normalize the entire fluorescence excitation spectrum so that the value at 675 nm is equal to $a_{ps}(675)$:

$$a_{ps}(\lambda) = F_{DCMU}(\lambda) \cdot \frac{a_{ps}(675)}{F_{DCMU}(675)},$$

(8)

where $F_{DCMU}(\lambda)$ is the quantum corrected fluorescence excitation spectrum. Photosynthetically active specific absorption ($a^*_{ps}(\lambda)$) was calculated by normalizing to the concentration of chlorophyll a only.

Methodological issues concerning absorption estimates

The magnitude of absorption estimated by the methods described above depends on the interpretation of optical density measurements made for particles collected on glass fiber filters. An important issue in this interpretation is the choice of correction algorithm for pathlength amplification effects. While several different corrections have been published

in the literature and there can be significant differences between them (e.g., Bricaud and Stramski, 1990), we have chosen to apply the algorithm determined by Mitchell (1990). This particular algorithm was derived using a variety of phytoplankton types and recent work using additional phytoplankton species resulted in a very similar algorithm with final values agreeing within 10% (Cleveland and Weidemann, 1993). It should be noted, however, that new work with the extremely small cells of *Prochlorococcus marinus* suggests that even this algorithm may not be universally applicable (Moore *et al.*, 1995). A second issue concerning filter-based measurements is the interpretation of absorption values for wavelengths greater than 750 nm. While there may be a small amount of absorption at 750 nm in the total particulate and detrital fractions (Bricaud and Stramski, 1990), it is our opinion that assigning a null value of 750 nm is preferable to allowing known methodological errors due to spectrally flat baseline shifts.

While these issues affect the magnitude of all our absorption estimates, there are some concerns which apply specifically to absorption by the phytoplankton component of the particulates. The methanol extraction method of Kishino *et al.* (1985) can potentially result in estimates which differ from the true $a_{ph}(\lambda)$ since methanol is not a perfect discriminator for viable pigments. Detrital pigments which extract readily in methanol (e.g., phaeopigments) are included in the phytoplankton fraction, and phycobiliproteins which are present for light harvesting in cyanobacteria but cannot be extracted in organic solvents are included in the detrital fraction. Despite these potential problems, this method is an improvement over simply using total particulate absorption to provide information about phytoplankton and it is free of the variety of difficult assumptions inherent in the methods used for statistical deconvolution of measured total particulate absorption into phytoplankton and non-phytoplankton components.

With respect to estimation of photosynthetically active absorption, there are some definite advantages to the fluorescence method described here. The $F_{DCMU}(\lambda)$ measurements capture the spectral quality of photosystem II activity accounting for factors such as pigment packaging and variations in energy transfer efficiency among pigments. Difficulties arise, however, in determining the absolute magnitude of the absorption spectrum for light which is potentially active in photosynthesis. By choosing the red absorption peak from the $a_{ph}(\lambda)$ estimates to normalize the spectra, we have minimized effects due to varying accessory pigment absorption. There can be significant absorption due to chlorophyll *b* and phaeopigment in this region of the spectrum, however, and we have specifically incorporated a correction for the contribution to $a_{ph}(675)$ from phaeopigment [see equation (7)]. While the overall effect of this correction is a small source of variability in $a_{ps}^*(\lambda)$, the absolute accuracy is limited by our assumption of constant $a_{phaeo}^*(675)$ and also by the accuracy of the estimates of phaeopigment concentration (see below). It must also be noted that, with this method for scaling of $F_{DCMU}(\lambda)$ to determine $a_{ps}(\lambda)$, all potential sources of error in $a_{ph}(675)$ are transferred to our estimates of $a_{ps}(\lambda)$.

Another important assumption we have made is that all of the chlorophyll *a* is potentially active in photosynthesis and it should be emphasized that these estimates of $a_{ps}(\lambda)$ may in some sense be overestimated. While absorption by accessory pigments which do not transfer excitation energy to chlorophyll *a* is not included, there is still the potential for losses due to fluorescence or heat dissipation. We view this not necessarily as a limitation, but rather as how we have chosen to define $a_{ps}(\lambda)$. Finally, it should also be noted that in our interpretation of $F_{DCMU}(\lambda)$ measurements, for lack of more complete information, we have assumed that there are minimal differences in the spectral distri-

bution of light harvested by photosystems I and II [see Johnsen and Sakshaug (1993) for a discussion of this issue].

In addition to the general problems of the methanol-extraction and fluorescence techniques, there are also issues related to the pigment normalization used to determine specific absorption values. Standard fluorometric techniques can underestimate the actual chlorophyll a concentration for waters with phytoplankton assemblages which include chlorophyll b-containing cells; total phaeopigment may similarly be overestimated under these conditions (Gibbs, 1979; Lorenzen, 1981; Vernet and Lorenzen, 1987; Gieskes, 1991). Furthermore, even in the absence of chlorophyll b, phaeopigment concentration determined from bulk fluorescence techniques is necessarily a crude estimate which reflects the average abundance of many chromophores (see, e.g., Klein and Sournia, 1987; Vernet, 1991), where the abundance of each is weighted by its respective specific absorption coefficient and fluorescence yield. While these problems should be recognized as limiting the absolute accuracy of our specific absorption estimates, it is unlikely that they are responsible for more than a fraction of the observed variability. Since both chlorophyll a and phaeopigments extract in methanol and contribute to $a_{ph}(\lambda)$, we have chosen to normalize these spectra [as well as $a_p(\lambda)$] by the summed concentration (chlorophyll a + phaeopigment). For $a_{ps}(\lambda)$, we used only chlorophyll a concentration for normalization to specific absorption, although further work is needed to determine whether there may be a low yield of fluorescence at 730 nm from natural chlorophyll a degradation products.

RESULTS

General characteristics

The areas sampled on these cruises covered a variety of oceanographic conditions. On each cruise a region of equatorward surface flow corresponding to the California Current was present offshore as expected. The band of highest velocities was generally further offshore on CalCOFI 9202 compared to CalCOFI 9110; on preFORAGE 9203 it bisected the sample area. The poleward countercurrent inshore of the main southward flow was pronounced on all cruises with both intensity and spatial extent greater than typical for the seasons sampled. These conditions were concurrent with elevated sea level and sea surface temperature compared to the long-term mean, and the CalCOFI region was also characterized by relatively low chlorophyll a, primary production and macrozooplankton biomass. These conditions have been described as manifestations of El Niño in this region (Hayward, 1993).

Surface temperatures ranged from 15 to 21°C, 13–16°C and 12–15°C on CalCOFI 9110, CalCOFI 9202 and preFORAGE 9203, respectively; surface salinity generally varied between 32.5 and 33.5; and NO_3^- concentrations ranged from undetectable to occasionally as high as 1.5 μM in surface waters. Nitracline depth, defined as the first depth where NO_3^- exceeded 0.5 μM, ranged from 0 to greater than 100 m. Despite generally deep nitraclines on all cruises, there were some differences between cruises. On CalCOFI 9110, only one station (77.49) had a nitracline which intersected the sea surface while, on CalCOFI 9202, nearly 25% of the stations had NO_3^- in excess of 0.5 μM at the surface. Surface chlorophyll a concentrations ranged from 1–2 mg m^{-3}, at a few nearshore stations where a surface maximum was observed, to 0.1 mg m^{-3} in oligotrophic offshore waters, where a pronounced sub-surface maximum was encountered at depths ranging from 50 to 100 m.

Depth profiles and temperature–salinity relationships found on CalCOFI 9202 were representative of the extent of conditions encountered on all three cruises (Fig. 4).

Typical relationships among the particulate absorption components are shown in Fig. 5 for a 5 m sample from an offshore station in the California Current. Total particulate absorption spectra show peaks near 440 nm and 675 nm corresponding to absorption by phytoplankton pigments and generally increasing absorption toward ultraviolet wavelengths, primarily due to absorption by detrital material. Photosynthetically active absorption $[a_{ps}(\lambda)]$ is a variable fraction of $a_{ph}(\lambda)$, with small differences at the red peak due to phaeopigment absorption [see equation (7)] and larger differences in the blue–green region of the spectrum due to absorption by phytoplankton pigments which do not efficiently transfer energy to photosystem II. These general characteristics are common to most a_p, a_d, a_{ph} and a_{ps} spectra collected (see Fig. 6).

Variability in specific absorption

Despite common spectral characteristics described above, the absolute value of specific absorption was found to be highly variable in the California Current System particularly on the two cruises off southern California. Even near surface spectra span a wide range of values with $a_p^*(440)$ varying from 0.02 to 0.13 m^2 mg^{-1}, $a_d^*(440)$ from <0.01 to 0.05 m^2 mg^{-1}, $a_{ph}^*(440)$ from 0.02 to 0.10 m^2 mg^{-1} and $a_{ps}^*(440)$ from 0.02 to 0.06 m^2 mg^{-1}. All surface spectra collected on CalCOFI cruise 9202 are shown in Fig. 6. When both were available (>85% of CalCOFI stations), the surface spectrum represents the average of the surface sample from the main hydrocast and the subsequent 4 m sample collected at the same station. CalCOFI 9202 exhibits the typical range of magnitudes encountered on all three cruises, although the total range was somewhat larger on CalCOFI 9110 and smaller on preFORAGE 9203 (see below).

Despite the high variability observed within cruises, cruise mean surface specific absorption spectra were very similar regardless of cruise area or time of year (Fig. 7). These spectra are the average of surface samples from 60, 64 and 159 stations for cruises CalCOFI 9110, CalCOFI 9202, and preFORAGE 9203, respectively, and thus are expected to represent well the areas sampled. At red wavelengths, specific absorption values for total particulates, detritus, phytoplankton and photosynthetic pigments are indistinguishable among the three cruises. There are some differences in the blue–blue-green portion of the spectra, but they are relatively small compared to within cruise variability (compare Figs 6 and 7).

The large within-cruise variability is important for modeling of primary production at smaller spatial scales. Light of blue–green wavelengths is of particular interest, since these wavelengths penetrate to the greatest depths in the ocean and are effectively utilized for photosynthesis. For this reason, we chose the blue absorption peak at 440 nm as an index of the range and magnitude of variability observed in $a_{ph}^*(\lambda)$ and $a_{ps}^*(\lambda)$ for each of the cruise areas. For the same surface samples used to compute the mean spectra shown in Fig. 7, histograms of $a_{ph}^*(440)$ values show distinct features (Figs 8A, C, E; Table 1). On CalCOFI 9110, the widest range was observed, with the distribution skewed toward the highest values (Fig. 8A). Lower modes and more Gaussian distributions were observed on CalCOFI 9202 and preFORAGE 9203, with the least variability on preFORAGE 9203 (Figs 8C and E). A comparison of $a_{ph}^*(440)$ distributions for samples collected below the nitracline shows smaller differences between cruises (Figs 8B, D, F; Table 1). For these
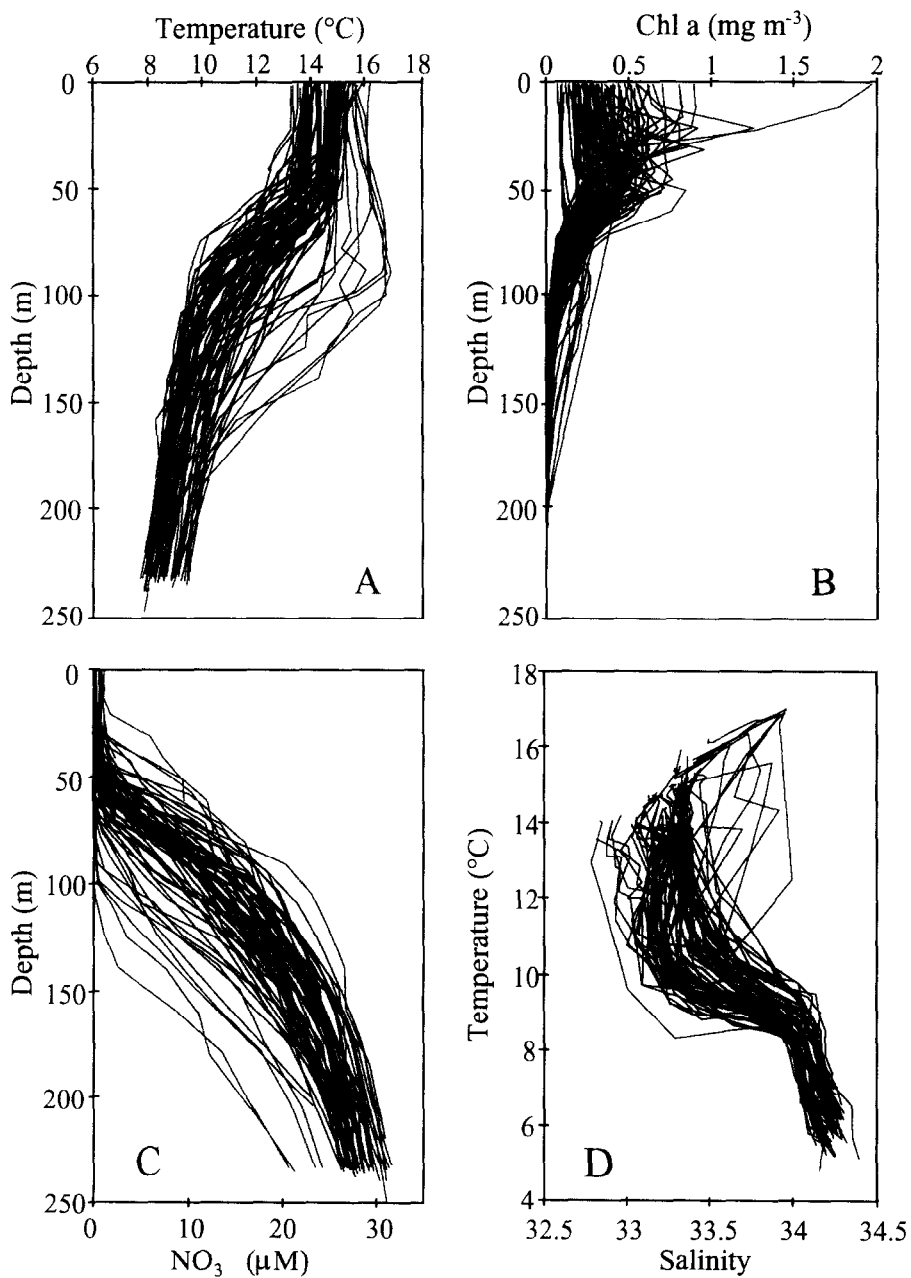
Fig. 4. Depth profiles and temperature–salinity relationships for all stations from CalCOFI cruise 9202. (A) Temperature; (B) chlorophyll a; (C) NO_3 concentration; (D) temperature–salinity plot.
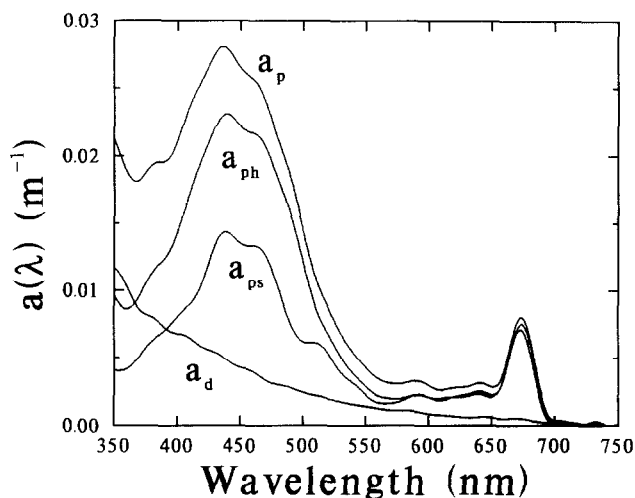
Fig. 5. An example of typical absorption spectra from an offshore station in the California Current System. Total particulate absorption (a_p) and the detrital (a_d), phytoplankton (a_{ph}) and photosynthetically active (a_{ps}) components are indicated.

samples, mode and mean values were similar for all three cruises and are consistently lower than those observed for the near-surface samples.

For $a_{ps}^*(440)$, data were available only for cruises CalCOFI 9202 and preFORAGE 9203 and different patterns from $a_{ph}^*(440)$ were evident (Fig. 9). Histograms for these two cruises show that $a_{ps}^*(440)$ values were lower and less variable compared with surface $a_{ph}^*(440)$. This was true for both $a_{ps}^*(440)$ surface samples and samples below the nitracline (Fig. 9). Differences between means and modes from surface and below the nitracline were small and values were generally similar to $a_{ph}^*(440)$ below the nitracline (compare Figs 8B, D and F with Figs 9A–D; see also Table 1).

Spatial patterns of variability in specific absorption

$a_{ph}^*(440)$. On all three cruises, both vertical and horizontal patterns of variability in $a_{ph}^*(\lambda)$ were evident and were similar to physical and chemical patterns. We have chosen to present results from CalCOFI cruise 9202 since patterns were strongest on the CalCOFI cruises and this late January to mid-February cruise is our most complete data set. On this cruise, the main southward flow of the California Current meandered through the offshore waters of the survey area, generally delineating a boundary for warmer, low chlorophyll offshore surface waters (Figs 10A–C). In the Southern California Bight, where flow was poleward, surface temperatures were also warmer, and surface chlorophyll a values were generally lower than off Point Conception and throughout much of the transition zone between the main current and the inshore countercurrent (Figs 10A–C). Similar patterns were evident in the surface values of $a_{ph}^*(440)$ (Fig. 10D). Highest values were observed in offshore waters, particularly in the southern portion of the sampled area and in the Southern California Bight. Values were lowest off Point Conception and extending into the transition zone.

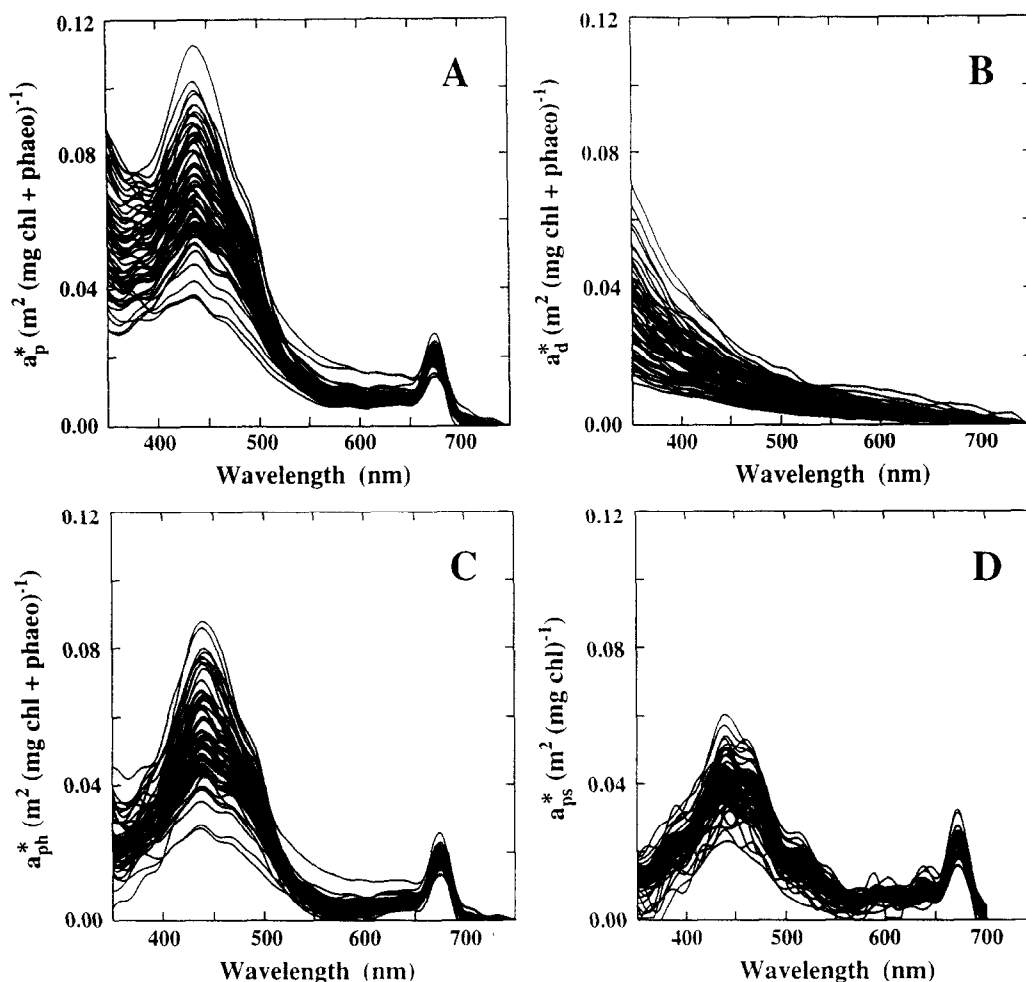Strong patterns were also evident in onshore–offshore vertical sections through this

Fig. 6. Pigment-specific absorption spectra from surface samples collected on CalCOFI cruise 9202 with one spectrum plotted for each station occupied. (A) Total particulate specific absorption; (B) pigment-specific absorption for detrital material; (C) phytoplankton specific absorption; (D) photosynthetically active specific absorption.

region. For the second transect line (Line 90), vertical gradients in potential density (σ_θ) and temperature showed isolines generally sloping upward toward the coast in the top 200 m (Fig. 11A, temperature not shown). This pattern was also evident in the sections of NO_3^- concentration and $a_{ph}^*(440)$. High values of $a_{ph}^*(440)$ were found near the surface in offshore waters where the nitracline tended to be the deepest and also where the nitracline deepened in the north-flowing countercurrent (Fig. 11C, D). In addition, where the highest gradient in σ_θ occurred in the euphotic zone (near Stas 90.70 and 90.53 for example), the nitracline shoaled and there were strong gradients in $a_{ph}^*(440)$. The lowest surface values of $a_{ph}^*(440)$ on this transect occurred near Sta 90.53, where mixed layer NO_3^- concentrations were the highest (0.3 μM). A sub-surface chlorophyll a maximum was
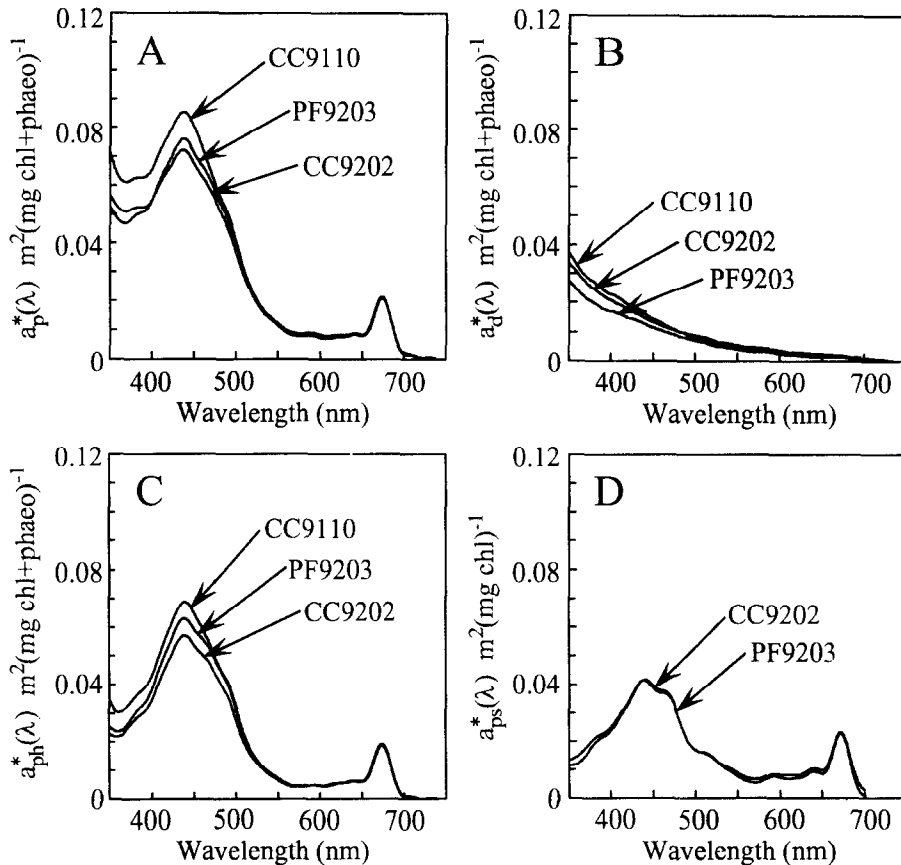
Fig. 7. Mean surface specific absorption spectra for each of the three cruises showing low between cruise variability. (A) Total particulates; (B) detritus; (C) phytoplankton; (D) photosynthetically active pigments.

present at most stas on Line 90 with a general decrease in magnitude and increase in depth further offshore (Fig. 11B). At Stas 90.53–90.70, however, chlorophyll a values were highest near the surface associated with the lowest surface $a^*_{ph}(440)$ values and the shoaling of the pycnocline and nitracline.

$a^*_{ps}(440)$. In comparison to $a^*_{ph}(440)$, $a^*_{ps}(440)$ showed low variability in both the vertical and horizontal. On the CalCOFI 9202 cruise, surface values of $a^*_{ps}(440)$ generally ranged between 0.03 and 0.05 m^2 (mg chlorophyll+phaeopigment)$^{-1}$ and gradients were small (Fig. 12A). A band containing some of the lowest values <0.04 m^2 (mg chlorophyll a)$^{-1}$ very near the coast and extending off Point Conception was evident, but overall the variability was low relative to that observed for $a^*_{ph}(440)$. A similar result was found in the vertical. For the same transect examined in Fig. 11, we found some values just over 0.05 m^2 (mg chlorophyll+phaeo)$^{-1}$ extending through the mixed layer near Stas 90.70 and 90.80, but most values ranged between 0.03 and 0.05, and vertical patterns were weak (Fig. 12B).
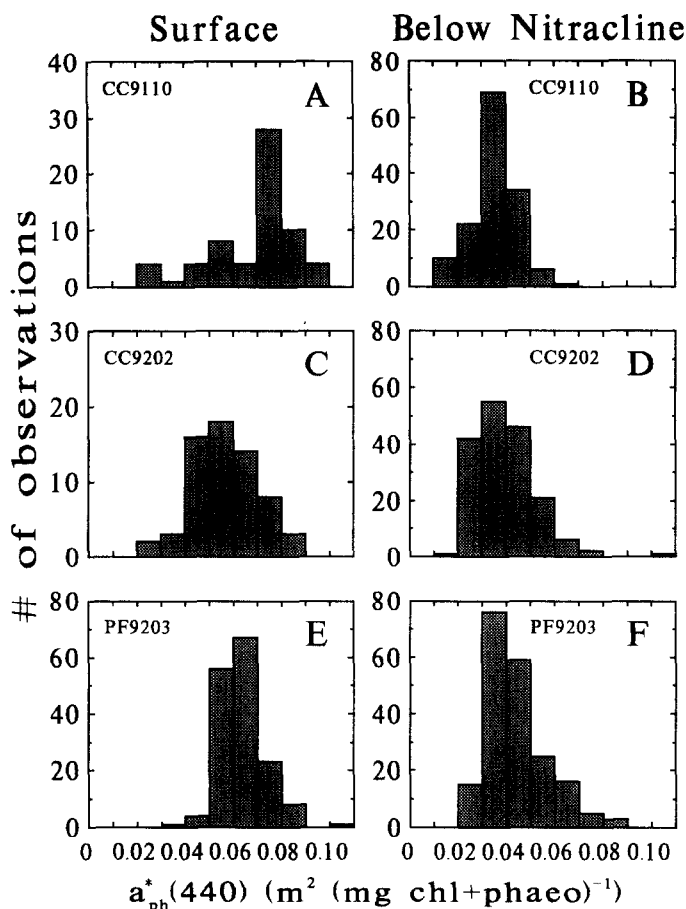
Fig. 8. Frequency distribution for phytoplankton specific absorption at the blue peak ($a_{ph}^*(440)$) for all surface samples and all samples collected from below the nitracline on each of the three cruises. (A) CalCOFI cruise 9110 surface samples; (B) CalCOFI cruise 9110 samples below the nitracline; (C) CalCOFI cruise 9202 surface samples; (D) CalCOFI 9202 samples below the nitracline; (E) preFORAGE 9203 surface samples; (F) preFORAGE cruise 9203 samples below the nitracline.

Variability with light, nutrients and temperature

It is also possible with this data set to examine overall patterns of variability in specific absorption with respect to some factors potentially important for phytoplankton photosynthesis and growth. The relationship of $a_{ph}^*(440)$ to optical depth and distance from the nitracline is shown for each of the three cruises in Fig. 13. In all cases, lower values of $a_{ph}^*(440)$ tend to occur at high optical depth as well as near and below the nitracline. On CalCOFI 9110, however, some low values are also found at small optical depths for stations where the nitracline outcropped in the mixed layer; thus, distance from the nitracline is a better predictor of the magnitude of $a_{ph}^*(440)$ (Fig. 13A, B). On CalCOFI 9202, when more stations had NO_3^- concentrations of 0.5 μM or greater at the surface, there is more scatter with distance below the nitracline compared with the previous cruise (Fig. 13C). Variability with optical depth is similar to that observed for CalCOFI 9110.

Nutrient data were not acquired for all stations on preFORAGE 9203, so it is difficult to generalize about patterns for the entire cruise but, for the stations where nitracline depth can be estimated, we found a relationship similar to that observed for CalCOFI 9110. Near-surface values of $a_{ph}^*(440)$ were less variable on preFORAGE 9203 relative to either of the southern California cruises, and a better relationship with optical depth was found, although compared to other depths, scatter is higher at shallow optical depths (Fig. 13F). In contrast to $a_{ph}^*(440)$, $a_{ps}^*(440)$ does not vary systematically with either optical depth or proximity to the deep source of inorganic nutrients for either of the cruises on which $a_{ps}(\lambda)$ was measured (Fig. 14).

With respect to temperature, there were general trends, but the relationships varied greatly between cruises (Fig. 15). In all cases, low values of $a_{ph}^*(440)$ occurred in samples with temperatures in roughly the lower half of the cruise range. For waters with higher temperatures, $a_{ph}^*(440)$ was more variable and tended to increase with temperature. This occurred for temperatures $> \sim 15°C$ on CalCOFI 9110, $\sim 13°C$ on CalCOFI 9202 and $\sim 12°C$ on preFORAGE 9203. As for the other variables, $a_{ps}^*(440)$ showed no systematic trends with temperature (Fig. 15C, E).

Variability in spectral shape

Variations in the spectral shape of the phytoplankton absorption component may also provide some insight into sources of variability in the magnitude of $a_{ph}^*(\lambda)$, because it is influenced by taxonomy and physiology. Despite the general similarities in spectral shape for all phytoplankton absorption samples, the ratio of the blue to the red peaks (approximately 440 and 675 nm) varied by more than a factor of two and had distinct spatial patterns. For all the cruises, $a_{ph}(440):a_{ph}(675)$ values generally ranged between 2 and 4.5. On CalCOFI 9202, surface ratios >3 were found only in offshore waters and in the countercurrent within the Southern California Bight, while very near the coast and off

Table 1. *Mean, S.D.* (s) *and sample number* (N) *for* $a_p^*(440)$, $a_d^*(440)$, $a_{ph}^*(440)$ *and* $a_{ps}^*(440)$ *for all surface samples and for all samples collected below the nitracline for each of three cruises conducted in the California Current System*

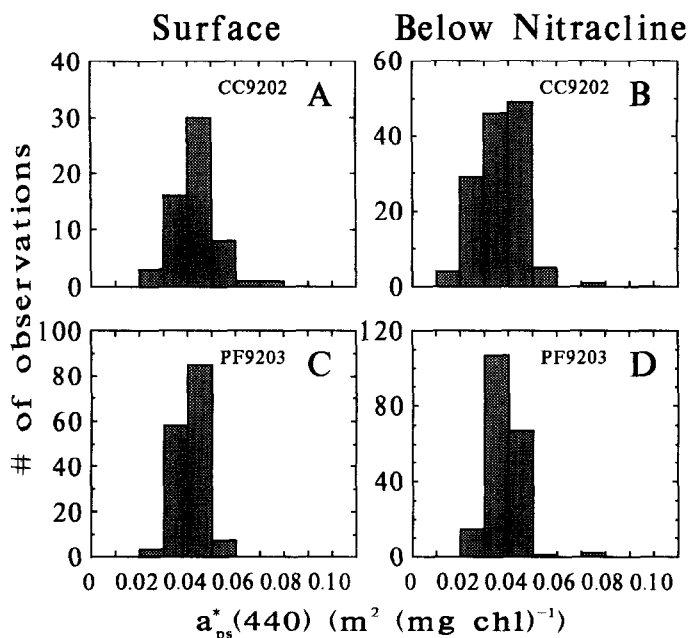|	Surface				Below the nitracline			
	$a_p^*(440)$	$a_d^*(440)$	$a_{ph}^*(440)$	$a_{ps}^*(440)$	$a_p^*(440)$	$a_d^*(440)$	$a_{ph}^*(440)$	$a_{ps}^*(440)$
CalCOFI 9110								
mean	0.087	0.021	0.069	nd	0.051	0.015	0.036	nd
s	0.028	0.036	0.017	nd	0.015	0.012	0.009	nd
N	66	63	63	nd	147	142	142	nd
CalCOFI 9202								
mean	0.072	0.015	0.057	0.043	0.061	0.021	0.039	0.037
s	0.016	0.005	0.013	0.009	0.021	0.017	0.012	0.009
N	64	64	64	59	180	170	170	134
preFORAGE 9203								
mean	0.076	0.013	0.063	0.041	0.055	0.010	0.043	0.038
s	0.012	0.005	0.009	0.005	0.016	0.007	0.012	0.006
N	160	160	160	153	210	199	199	192

Fig. 9.   Same as Fig. 8, except for photosynthetically active absorption (a_{ps}^*(440)). (A) CalCOFI cruise 9202 surface samples; (B) CalCOFI cruise 9202 samples below the nitracline; (C) preFOR-AGE cruise 9203 surface samples; and (D) preFORAGE cruise 9203 samples below the nitracline.

Point Conception, values were generally <2.5 (Fig. 16A). For the same transect line shown in Fig. 11, vertical patterns were also very similar to those for a_{ph}^*(440). There were distinct decreases with depth in the offshore region and Southern California Bight as well as strong horizontal gradients near the surface between Stas 80 and 45 (Fig. 16B). For $a_{ps}^*(\lambda)$, the blue-red ratio was lower and less variable than for $a_{ph}^*(\lambda)$, with values rarely falling outside the range 1.5–2.0 for all samples collected (not shown).

DISCUSSION

Variability in the magnitude of specific absorption spectra

From this study in the California Current System, we have found that within-cruise variability in pigment-specific absorption coefficients is much higher than between cruises (compare Figs 6 and 7). This is true for the same area in two different seasons and for waters off southern California compared with northern California. The similarity of cruise means was found despite differences in shapes of the frequency distributions for each cruise (Fig. 8). We propose that for regional to basin-scale bio-optical questions, these mean specific absorption coefficients may adequately characterize the California Current System. This hypothesis must be further tested for a broader range of conditions.

In contrast to the small differences between cruise means, the absolute range of values encountered on any one cruise was large. Restricting evaluation to surface waters, the range of values observed was as large as the average differences between this mid-latitude region and the coastal waters of the Antarctic Peninsula (Sosik *et al.*, 1992). For $a_p^*(\lambda)$, we
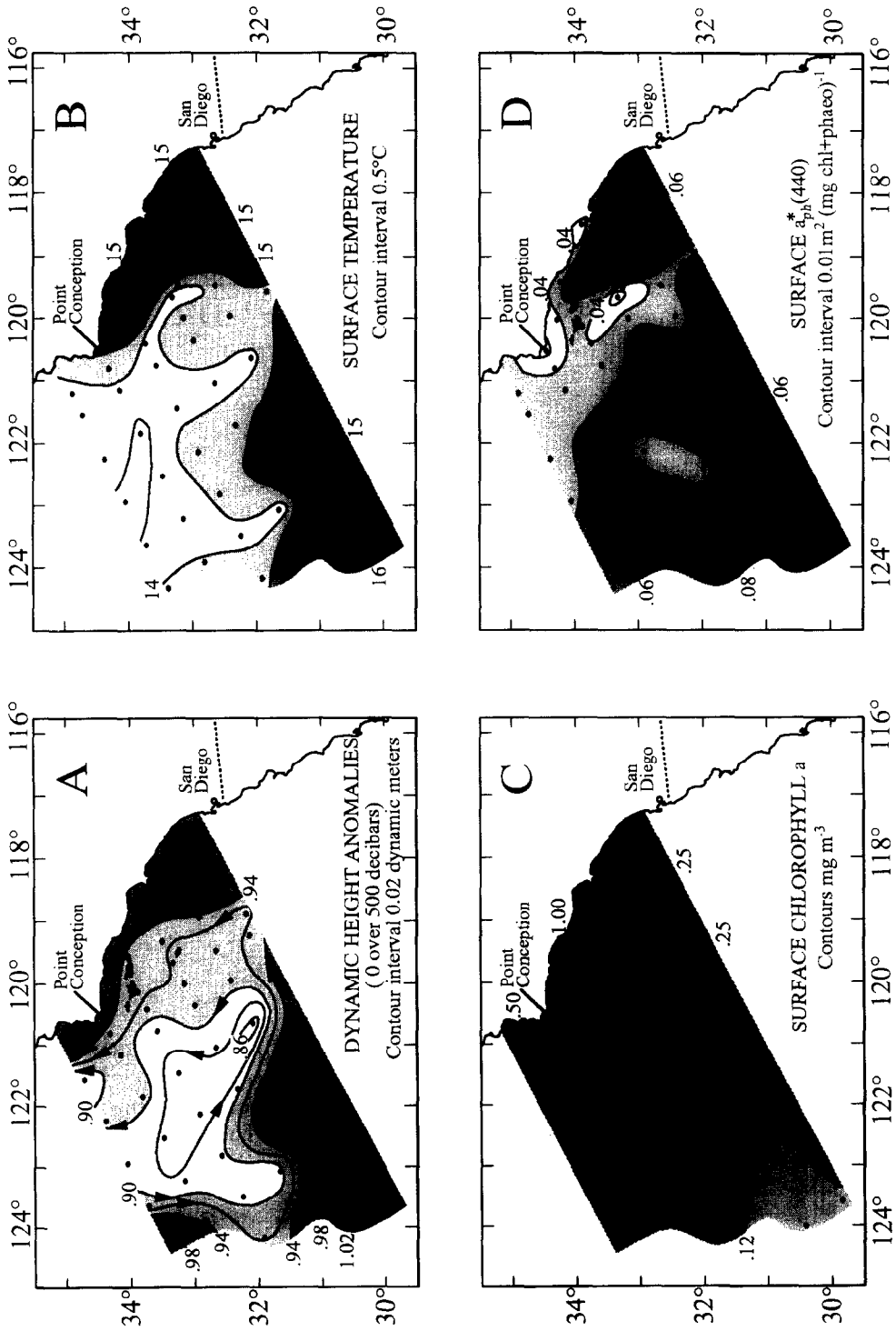
Fig. 10. Surface maps showing current structure and distributions in January–February of 1992 (CalCOFI cruise 9202). (A) Surface dynamic height anomalies relative to 500 db: (B) surface temperature: (C) surface chlorophyll a concentrations: (D) surface phytoplankton specific absorption at 440 nm.
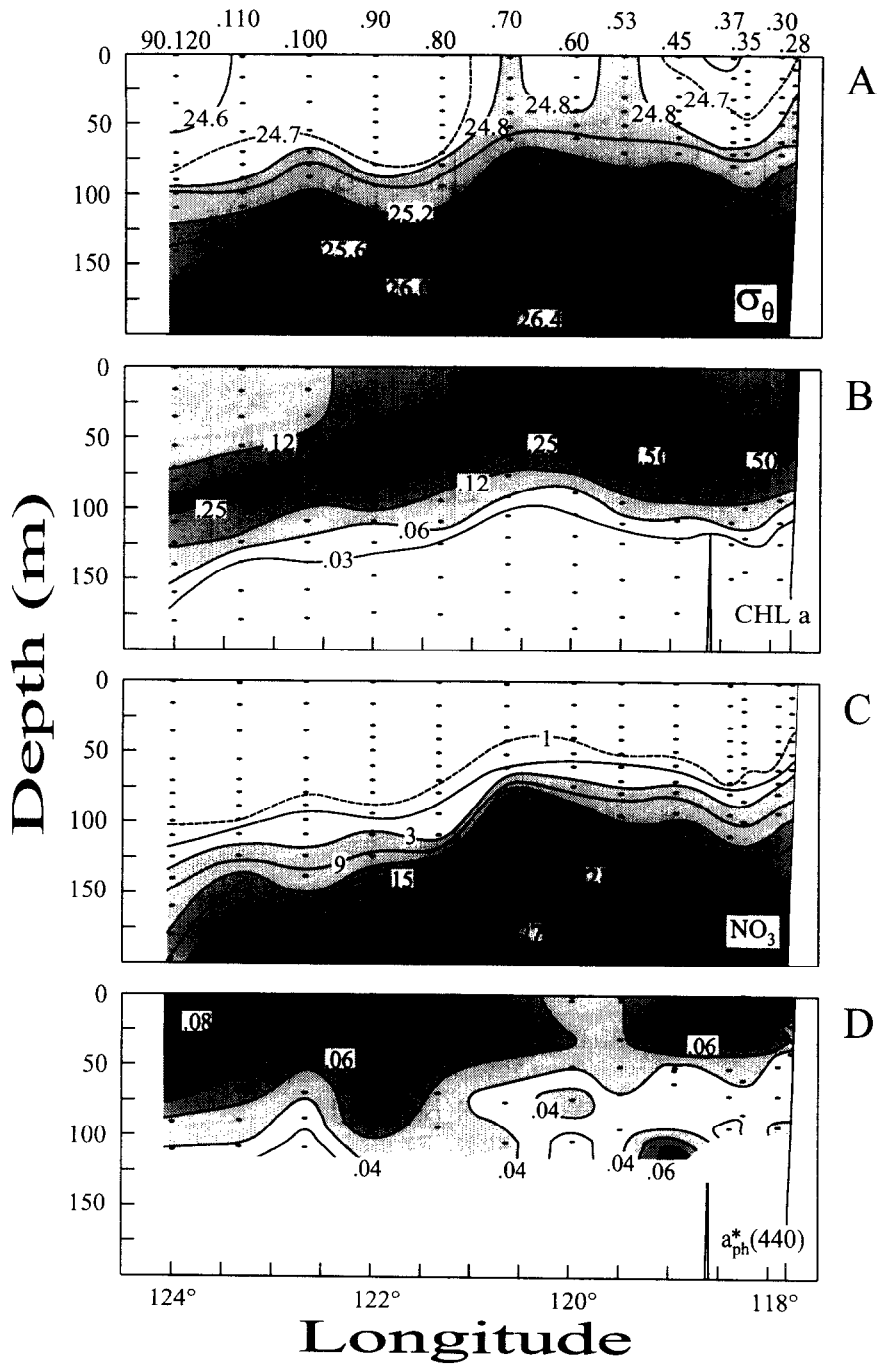
Fig. 11. Vertical sections for line 90 (second transect from the south) for the same cruise as in Fig. 10 (CalCOFI 9202). (A) Potential density; (B) chlorophyll a concentration in mg m^{-3}; (C) NO$_3^-$ concentration in μM; (D) phytoplankton specific absorption at 440 nm in m^2 (mg chlorophyll+phaeopigment)$^{-1}$.
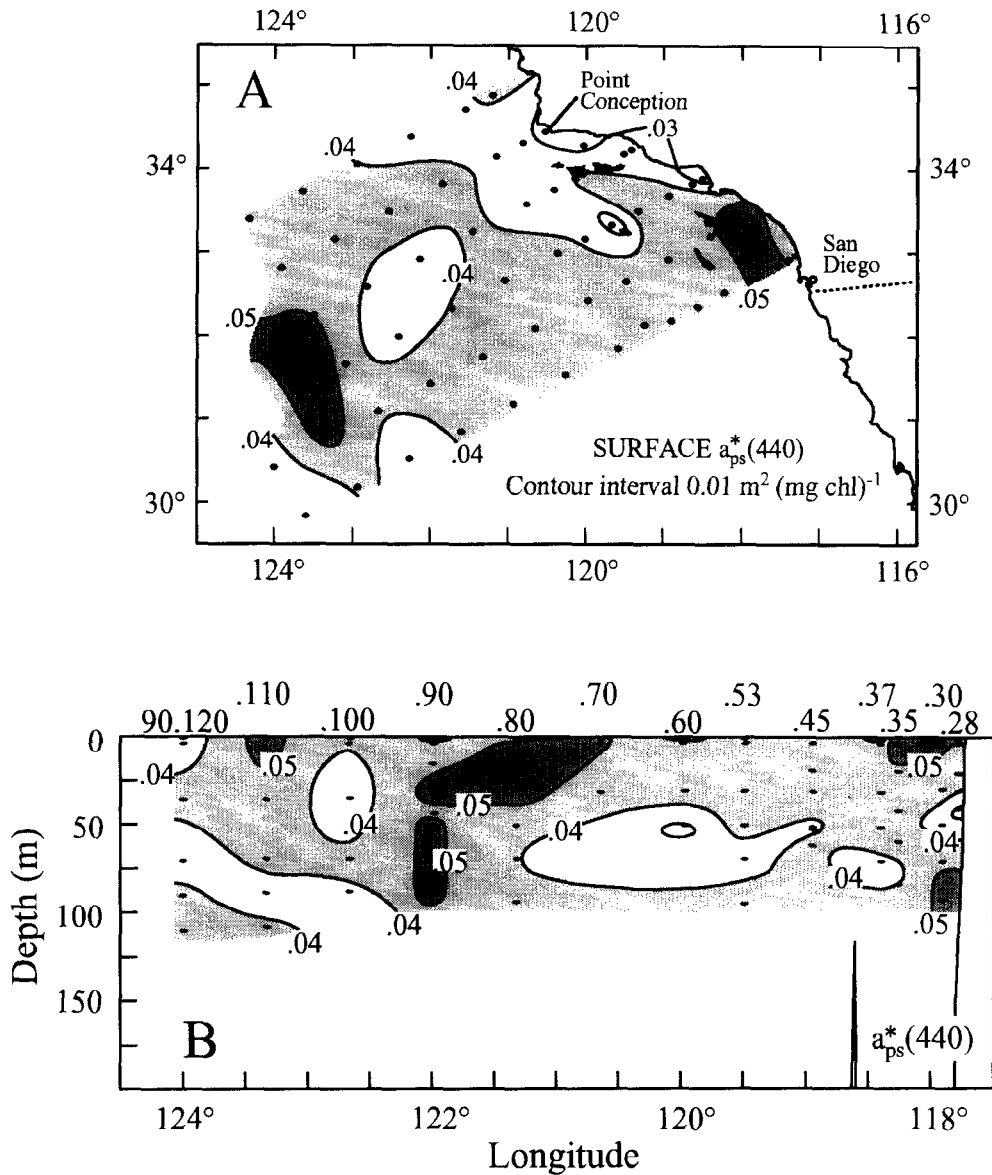
Fig. 12.   Distributions of photosynthetically active specific absorption at the blue peak (440 nm) for the same cruise as in Figs 10 and 11 (CalCOFI 9202). (A) Surface map; (B) vertical section through same transect as in Fig. 11 (line 90).

found many values much greater than previously reported for the central North Pacific (Mitchell and Kiefer, 1988b) and Antarctic (Mitchell and Holm-Hansen, 1991), although some of this difference may be methodological, since the QFT algorithm of Mitchell (1990) results in $a_p(\lambda)$ values up to 20% higher than the algorithm of Mitchell and Kiefer (1988a). For $a_{ph}^*(\lambda)$, variability of a similar magnitude has been reported for the Sargasso Sea (Bricaud and Stramski, 1990) and for the Gulf of Maine and Georges Bank region
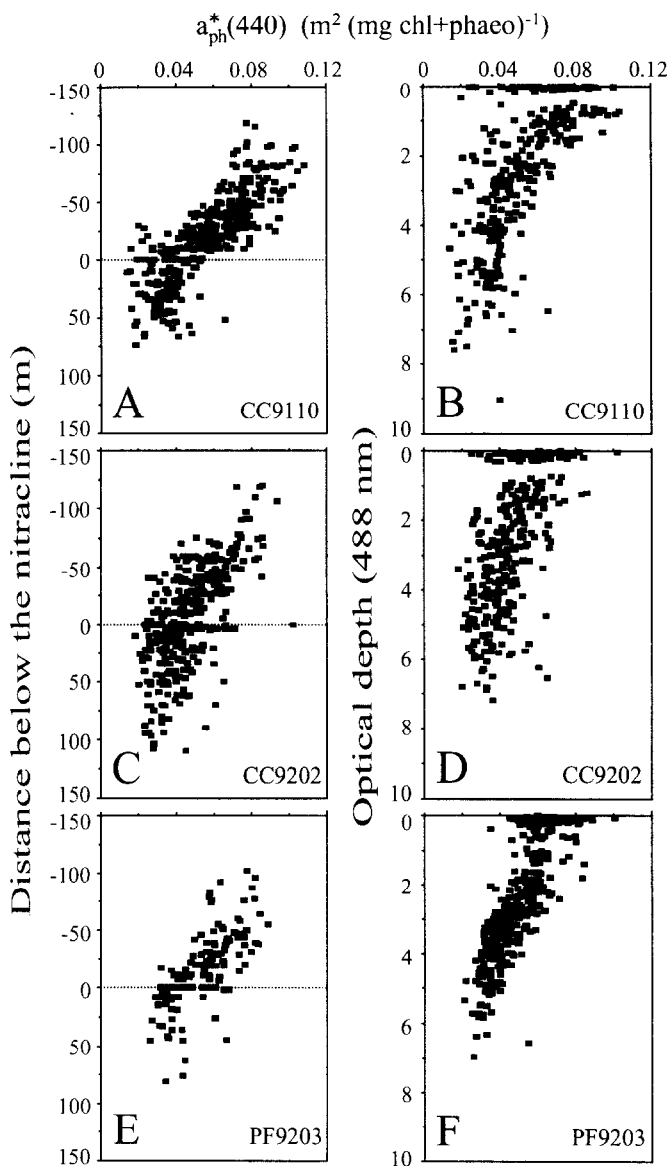
$$a_{ph}^*(440) \quad (m^2 \ (mg \ chl+phaeo)^{-1})$$

Fig. 13. Phytoplankton specific absorption at 440 nm plotted against distance below the nitra-cline and optical depth at 488 nm for each of the cruises. Samples from all depths are included. The depth of the nitracline (first depth where NO_3^- concentration exceeded $0.5 \ \mu M$) is indicated by the dashed line at 0; negative and positive values indicate depths above and below the nitracline, respectively. (A) Nitracline relationship for CalCOFI cruise 9110; (B) optical depth relationship for CalCOFI cruise 9110; (C) nitracline relationship for CalCOFI cruise 9202; (D) optical depth relationship for CalCOFI cruise 9202; (E) nitracline relationship for preFORAGE cruise 9203; (F) optical depth relationship for preFORAGE cruise 9203.
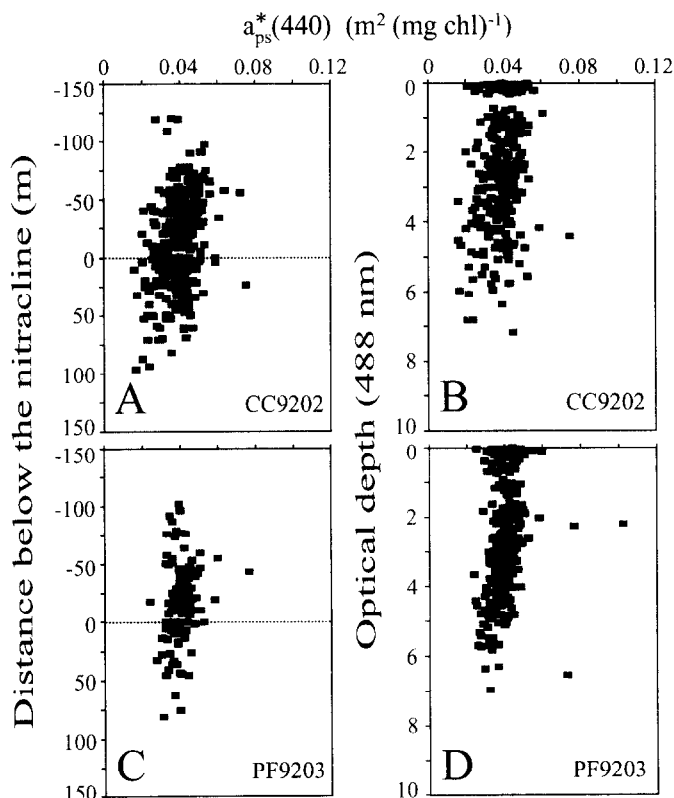
Fig. 14. Same as Fig. 13, but for photosynthetically active absorption at 440 nm and only for the last two cruises. (A) Nitracline relationship for CalCOFI cruise 9202; (B) optical depth relationship for CalCOFI cruise 9202; (C) nitracline relationship for preFORAGE cruise 9203; (D) optical depth relationship for preFORAGE cruise 9203.

(Hoepffner and Sathyendranath, 1992) although, in the latter case, only the concentration of chlorophyll a was used to normalize $a^*_{ph}(\lambda)$, making comparison difficult. For the purposes of determining specific absorption properties for bio-optical models and algorithms which are expected to provide accurate results at the mesoscale, the variability we have observed in the California Current is significant and understanding the sources of this variability should be a high priority.

Sources of variability in $a^*_{ph}(\lambda)$

Particularly for $a_{ph}(\lambda)$, we are interested in elucidating the sources of natural variability with the ultimate goal of developing better parameterization of the photosynthetic light absorption process. As an initial step toward this goal, we have examined patterns of variability in relation to the physical and chemical environment at the time of sampling. The similar patterns observed between the physical structure of the current system and the magnitude of $a^*_{ph}(440)$ show that there is a strong relationship between the physical or chemical regime and the bio-optical properties of the phytoplankton community (Figs 10 and 11).
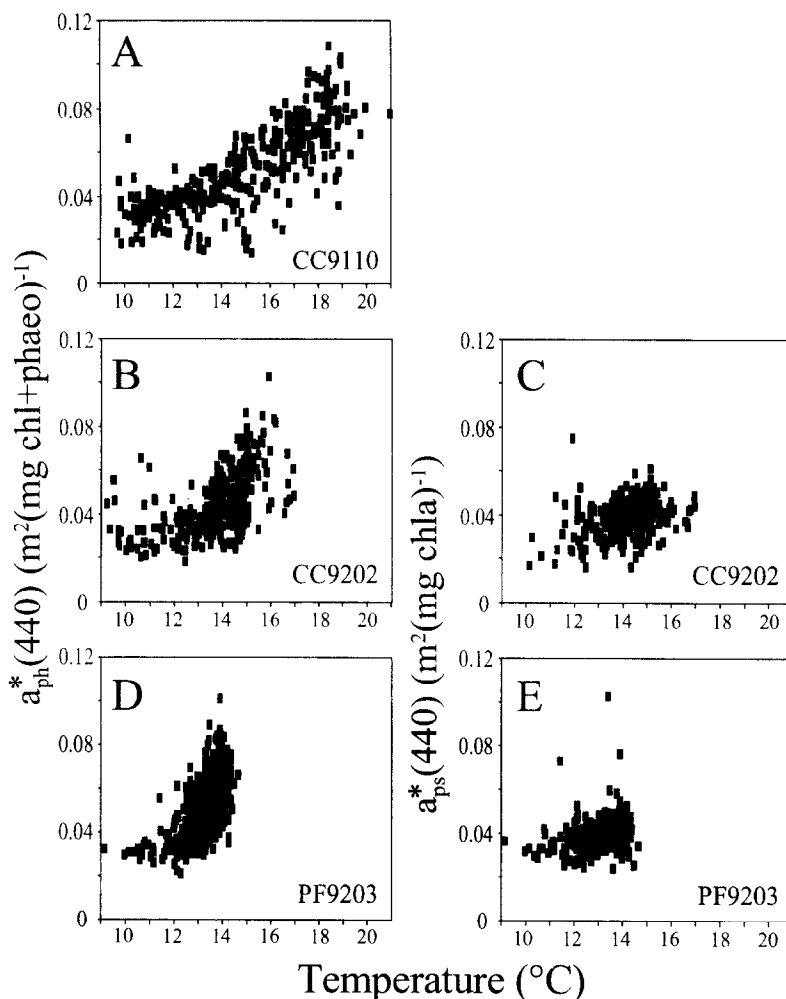
Fig. 15. Phytoplankton and photosynthetically active specific absorption at 440 nm as a function of temperature for all samples analyzed on each of the cruises. (A) Phytoplankton absorption on CalCOFI cruise 9110; (B) phytoplankton absorption on CalCOFI cruise 9202; (C) photosynthetically active absorption on CalCOFI cruise 9202; (D) phytoplankton absorption on preFORAGE cruise 9203; (E) photosynthetically active absorption on preFORAGE cruise 9203.

From controlled studies of laboratory cultures, for which $a_{ph}^*(\lambda)$ can be determined more precisely than for natural assemblages of phytoplankton, it has been shown that the primary sources of variability are changes in pigment package effects and in pigment ratios. These factors are functions of cellular pigmentation and cell size, which exhibit interspecific differences as well as differences resulting from physiological acclimation to varying growth conditions (light, temperature and nutrient availability).

Under natural conditions, the light, nutrient and temperature environment experienced by the phytoplankton are functions of the physical regime and are potentially important sources of variability in $a_{ph}^*(\lambda)$. We have chosen to examine this issue using the optical
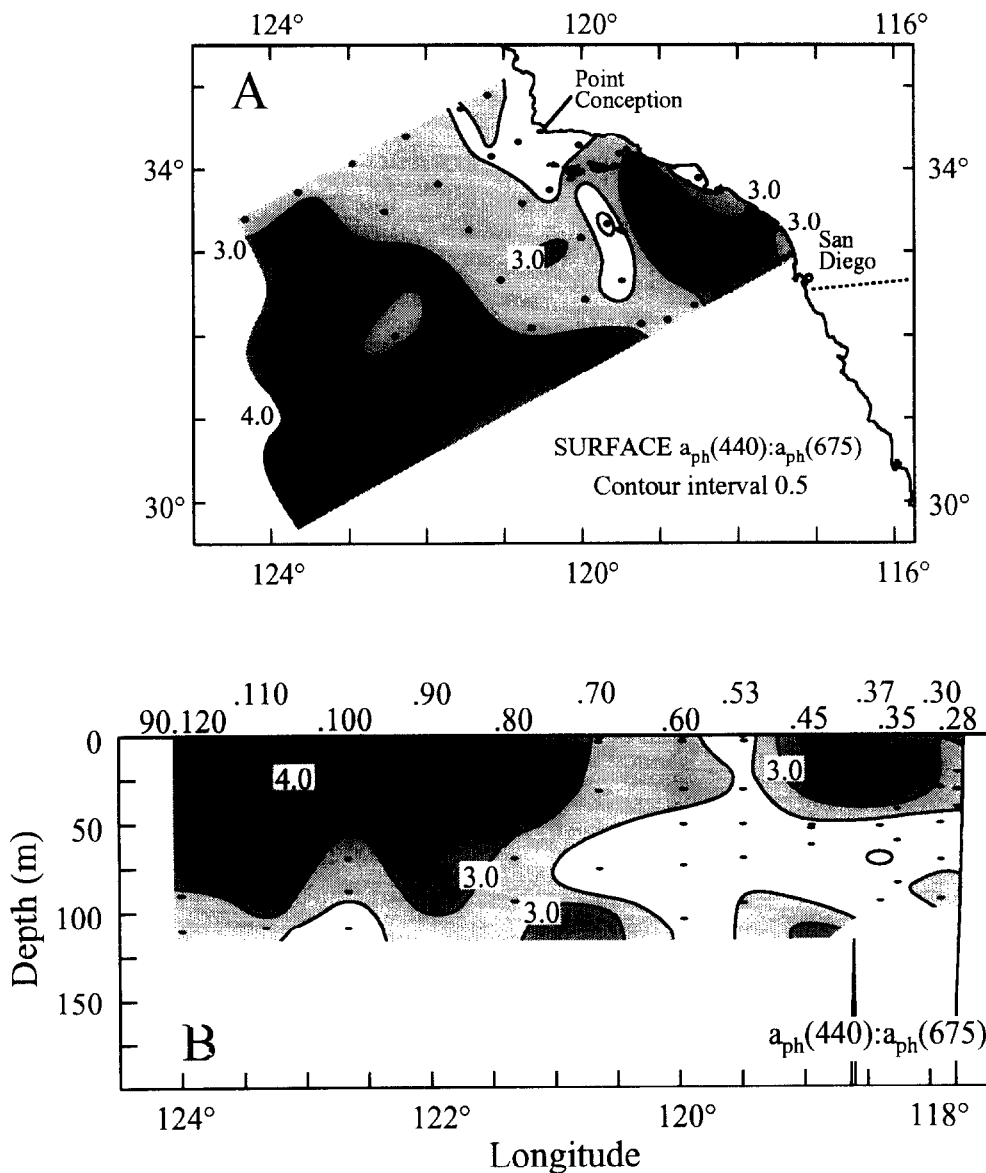
Fig. 16. Vertical and horizontal patterns of variability in the blue–red peak ratio for phytoplankton absorption in January–February of 1992 (CalCOFI cruise 9202). (A) Surface map; (B) same vertical transect as in Fig. 11 (line 90).

depth, distance from the nitracline and *in situ* temperature from which the particulate samples were collected as indices of the growth conditions for the phytoplankton. These indices are imperfect, since the absolute rate of supply of photons and inorganic nutrients are more relevant measures of the light and nutrient environment and, perhaps more importantly, since the photophysiological state of the phytoplankton is a function, not only of current conditions, but also of past exposure. The indices do, however, have some

obvious advantages since they can be readily estimated for many samples in a survey and, particularly for the case of light, the use of optical depth allows us to control for time of day and other factors such as short-term fluctuations in sky conditions.

While it is difficult to separate the roles of various environmental factors in a descriptive field study such as this, our results suggest that direct effects of light and nutrient conditions deserve further attention as sources of mesoscale variability in phytoplankton optical physiology. Photoacclimation is commonly invoked as a source of natural variability in specific absorption and our results are generally consistent with this idea. However, we also have evidence that the light regime may not always be a primary source of variability in $a_{ph}^*(\lambda)$. Particularly on the CalCOFI cruise 9110, distance from the nitracline is a better predictor of $a_{ph}^*(440)$ than optical depth (Fig. 13). In addition, on this cruise, the frequency distribution of surface $a_{ph}^*(\lambda)$ values is skewed toward high values in contrast to the broad distribution found on CalCOFI 9202 (Fig. 8). When these cruises are further compared, we find that the nitracline rarely outcropped on CalCOFI 9110 (1 station), whereas CalCOFI 9202 nearly 25% of the stations had nitrate $\geq 0.5\ \mu M$ at the surface. We hypothesize that the availability of inorganic nutrients plays an important role in determining the magnitude of $a_{ph}^*(\lambda)$ in this region. This hypothesis is consistent with results from laboratory studies (Herzig and Falkowski, 1989; Chalup and Laws, 1990; Sosik and Mitchell, 1991) and from other field investigations (Yentsch and Phinney, 1989).

Physiological acclimation vs changing community structure

The trends observed as a function of optical depth and distance from the nitracline (Fig. 13) are consistent with observations on physiology from controlled laboratory experiments. Higher values of $a_{ph}^*(\lambda)$ are found when cells of the same species are grown at high light or under nutrient-limited conditions. The trends with temperature (Fig. 15) are opposite to those observed in the laboratory, where low growth temperatures are associated with higher $a_{ph}^*(\lambda)$. This suggests that the relationships observed with temperature either are related to a change in species composition along the observed temperature gradient or, more likely, are the result of a covariance between temperature and some other more important factor (such as nutrients or light).

The role of changes in phytoplankton community structure as a source of variability in $a_{ph}^*(\lambda)$ must also be considered. To our knowledge, the highest values of $a_{ph}^*(\lambda)$ at blue–green wavelengths, which were typically found in offshore surface waters, have not been documented to occur in cultures of eukaryotic algae in the laboratory (e.g., Dubinsky *et al.*, 1986; Bricaud *et al.*, 1988; Mitchell and Kiefer, 1988a). We also routinely observed $a_{ph}(440){:}a_{ph}(675)$ values of 3 or greater, while eukaryotic phytoplankton studied in the laboratory have not been found with peak ratios in excess of 2.5 (reviewed by Cleveland *et al.*, 1989). Recent work on cyanobacteria (Stramski and Morel, 1990) and marine prochlorophytes (Partensky *et al.*, 1993; Moore *et al.*, 1995) has shown that these small prokaryotic cells can exhibit very high values of $a_{ph}^*(\lambda)$ at blue–green wavelengths and blue–red ratios which are typically greater than 2.5 (and even > 8 for very high light intensities). As expected from work with eukaryotes, these parameters have also been found to vary as a function of growth conditions in prokaryotes, with generally higher $a_{ph}^*(\lambda)$ and greater $a_{ph}(440){:}a_{ph}(675)$ at high light intensities. These characteristics arise from very low pigment packaging associated with small cell size combined with high abundances of carotenoid pigments such as zeaxanthin and α- and β-carotene. The effects

of nutrients and temperature on the photophysiology of these cells remain to be investigated.

Based on these laboratory studies, we conclude that the regions with the highest $a_{ph}^*(\lambda)$ and $a_{ph}(440):a_{ph}(675)$ are areas where prokaryotes are a significant component of the phytoplankton community. Both *Synechococcus* and *Prochlorococcus* have been shown to be abundant in various open ocean regions (Chisholm *et al.*, 1988; Olson *et al.*, 1990a,b). This conclusion is consistent with the results of Hoepffner and Sathyendranath (1992) showing higher values of $a_{ph}^*(\lambda)$ for oceanic stations in the Gulf of Maine region where HPLC pigment analysis suggests the presence of *Prochlorococcus*. More detailed studies of the taxonomic composition of the California Current phytoplankton are required to test this hypothesis.

Photosynthetically active absorption

As expected, for the blue–green region of the spectrum, values of $a_{ps}^*(\lambda)$ were found to be lower than the corresponding $a_{ph}^*(\lambda)$ which includes some absorption that is not active in photosynthesis [i.e. absorption by photoprotective accessory pigments, see equation (4)]. As for $a_{ph}^*(\lambda)$, $a_{ps}^*(\lambda)$ is more variable within a cruise than between cruises, however, the overall range of variability is lower (Figs 7 and 8). Furthermore, for the case of $a_{ps}(\lambda)$ determinations, the variability associated with the measurement itself is relatively high when compared with the particulate absorption techniques. Since the fluorescence measurements were made on unconcentrated seawater samples, the spectra are noisy, particularly when chlorophyll *a* concentrations are low. For this reason, we feel that the natural variability in $a_{ps}^*(\lambda)$ is probably substantially less than that observed with the present method. Other work in the Southern California Bight has demonstrated large changes in the relative absorption by photoprotective pigments which are correlated with hydrographic features (Bidigare *et al.*, 1992) and are probably related to changes in species composition as well as acclimation to changing light and nutrient environment. We suspect that these factors are responsible for the different patterns of variability observed for $a_{ph}^*(\lambda)$ and $a_{ps}^*(\lambda)$.

Implications for modeling of primary production

There are important implications for modeling of primary production if $a_{ps}^*(\lambda)$ is relatively invariant. While quantifying and understanding sources of variability in $a_{ph}^*(\lambda)$ is critical for many optical applications, our results suggest that $a_{ps}^*(\lambda)$ is a better choice for parameterizing the light absorption process in photosynthesis models. While $a_{ph}^*(440)$ shows strong vertical gradients (Fig. 11D) and horizontal patterns (Fig. 10D), $a_{ps}^*(440)$ does not (Fig. 12). This is most likely due to the fact that $a_{ps}^*(\lambda)$ values do not reflect absorption by photoprotective carotenoids which may be responsible for the high values of $a_{ph}^*(440)$ observed in many areas. Since this absorption by photoprotective pigments is not photosynthetically active, and since it introduces larger variance in $a_{ph}^*(\lambda)$, we propose that parameterizations based on $a_{ps}^*(\lambda)$ would improve bio-optical models of primary production. Using $a_{ps}^*(\lambda)$ instead of $a_{ph}^*(\lambda)$ in a modified version of the model introduced by Kiefer and Mitchell (1983):

$$P(z,t) = \mathrm{Chl}(z,t) \cdot \int \phi_{ps}(z,t,\lambda) \cdot a_{ps}^*(z,t,\lambda) \cdot E(z,t,\lambda) \, d\lambda, \qquad (9)$$

where $P(z,t)$ is the gross primary production at a given depth (z) and time (t), $\mathrm{Chl}(z,t)$ is the concentration of chlorophyll a, $\phi_{\mathrm{ps}}(z,t,\lambda)$ is the quantum yield (carbon fixed per active light absorbed) and $E(z,t,\lambda)$ is the scalar irradiance. It is important to emphasize that this model representation differs not only in the use of $a_{\mathrm{ps}}^*(\lambda)$ rather than $a_{\mathrm{ph}}^*(\lambda)$, but also that a new definition of the quantum yield must be introduced. The quantum yield ϕ_{ps} is based on only absorbed quanta which actually reach the photosynthetic reaction centers rather than the classical definition (e.g., Rabinowitch and Govindjee, 1969) based on all quanta absorbed by the cell regardless of fate. Just as $a_{\mathrm{ps}}^*(\lambda)$ is less variable than $a_{\mathrm{ph}}^*(\lambda)$, because it is based only on absorption by active pigments, ϕ_{ps} may be less variable than quantum yield based on total phytoplankton absorption.

The results of this field study suggest that this revised model has the potential to improve the accuracy with which primary production can be estimated; it must be tested, however, and compared to a similar formulation using $a_{\mathrm{ph}}^*(\lambda)$ in a variety of conditions before it is possible to make a definitive recommendation regarding model choice. Unfortunately, the ability to measure chlorophyll a fluorescence excitation spectra with far-red emission and thus derive $a_{\mathrm{ps}}(\lambda)$ is not widely available. In addition, the present method is more difficult compared to particulate absorption (low sensitivity can result in noisy data, samples can not be preserved and are more sensitive to handing prior to analysis). Despite these problems, if the observation of relatively low variability in $a_{\mathrm{ps}}^*(\lambda)$ can be verified for a variety of seasons and regions, ultimately fewer measurements will be necessary to characterize $a_{\mathrm{ps}}^*(\lambda)$ than would be required for $a_{\mathrm{ph}}^*(\lambda)$.

Even during this period of rather low physical forcing in the California Current System, we have documented high variability at the mesoscale in the pigment-specific absorption of the various components of the particulate pool. For $a_{\mathrm{ph}}^*(\lambda)$, this variability is as great as has been previously observed across a broad range of natural water types and for a wide range of phytoplankton culture conditions. Despite vertical and horizontal variability, cruise mean specific absorption coefficients are quite similar and the observed variance has predictable patterns associated with the physical forcing. If these conclusions stand up to further study under different conditions in this region, it should be possible to parameterize light absorption for models of large-scale processes in this system. As sources of the observed mesoscale variability, factors such as light environment and nutrient availability appear important while it is unlikely that temperature changes play a direct role in regulating the specific absorption properties of phytoplankton in this system. Changes in the composition of the phytoplankton population also play a role. Specific absorption for the photosynthetically active component of phytoplankton absorption did not vary between cruises and varied over a much more narrow range than total $a_{\mathrm{ph}}^*(\lambda)$ within a cruise. Based on these results, we recommend that bio-optical primary production models utilize $a_{\mathrm{ps}}^*(\lambda)$ and $\phi_{\mathrm{ps}}(\lambda)$ rather than the more traditional $a_{\mathrm{ph}}^*(\lambda)$ and $\phi_{\mathrm{ph}}(\lambda)$. This recommendation must be tested against traditional methods under a variety of conditions; however, the results presented here suggest that using $a_{\mathrm{ps}}^*(\lambda)$ should significantly reduce errors in primary productivity calculated from these models.

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