



ELSEVIER

Available online at www.sciencedirect.com

SCIENCE @ DIRECT®

Deep-Sea Research I 50 (2003) 1537–1549

DEEP-SEA RESEARCH
PART I

www.elsevier.com/locate/dsr

The beam attenuation to chlorophyll ratio: an optical index of phytoplankton physiology in the surface ocean?

Michael J. Behrenfeld^{a,*}, Emmanuel Boss^b

^a National Aeronautics and Space Administration, Goddard Space Flight Center, Code 971, Building 22, Greenbelt, MD 20771, USA

^b School of Marine Sciences, 209 Libby Hall, University of Maine, Orono, ME 04469-5741, USA

Received 27 February 2003; received in revised form 13 August 2003; accepted 4 September 2003

Abstract

The particulate beam attenuation coefficient (c_p) is proportional to the concentration of suspended particles in a size domain overlapping that of the phytoplankton assemblage. c_p is largely insensitive to changes in intracellular chlorophyll concentration, which varies with growth irradiance (a process termed ‘photoacclimation’). Earlier studies have shown that the ratio of c_p :chlorophyll (i.e., c_p^*) exhibits depth-dependent changes that are consistent with photoacclimation. Similar relationships may likewise be expected in the horizontal and temporal dimensions, reflecting changes in mixing depth, incident irradiance, and light attenuation. A link between c_p^* and more robust photoadaptive variables has never been explicitly tested in the field. Here we use five historical field data sets to directly compare spatial and temporal variability in c_p^* with two independent indices of photoacclimation: the light-saturated, chlorophyll-normalized photosynthetic rate, P_{opt}^b , and the light-saturation index, E_k . For the variety of oceanographic conditions considered, a first-order correlation emerged between c_p^* and P_{opt}^b or E_k . These simple empirical results suggest that a relationship exists between a bio-optical variable that can potentially be retrieved remotely (c_p^*) and physiological variables crucial for estimating primary productivity in the sea.

© 2003 Elsevier Ltd. All rights reserved.

Keywords: Beam Attenuation; Phytoplankton; Photosynthesis

1. Introduction

The particulate backscattering coefficient (b_{bp}), chlorophyll concentration (Chl), beam attenuation coefficient (c), particulate organic carbon (POC) concentration, and net primary production (NPP) are central variables of contemporary oceanographic research that share an important char-

acteristic: they all vary to first-order with the suspended particle load. Oceanic particle assemblages include detrital components of in situ or terrigenous origin, viruses, bacteria, phytoplankton, zooplankton, and inorganic compounds. Together, these constituents create continuous and relatively conserved particle size distributions, with Junge-like differential slopes of ~ 4 (e.g., Bader, 1970; Stramski and Kiefer, 1991). Deviations from this ‘typical’ size spectrum can be pronounced, though, such as in coastal waters and during bloom events.

The various measures related to particle concentration (b_{bp} , Chl, c , POC, NPP) are dominated

*Corresponding author. Tel.: +1-301-286-2742; fax: +1-301-286-5337.

E-mail address: mjb@neptune.gsfc.nasa.gov
(M.J. Behrenfeld).

by different components and size domains of the assemblage. For example, b_{bp} is strongly influenced by non-algal, submicron particles (Morel and Ahn, 1991; Stramski and Kiefer, 1991; Ulloha et al., 1994; Loisel et al., 2001), while particulate beam attenuation at 660 nm ($c_p = c - c_w$, where c_w is the attenuation coefficient for pure seawater) is dominated by the 0.5–20 μm fraction (Morel, 1973; Stramski and Kiefer, 1991; Boss et al., 2001). This range for c_p encompasses the lower portion of the size domain represented in Chl, POC, and NPP data. Chlorophyll concentration is selective for the phytoplankton crop, but its relation to algal cell number or carbon biomass varies widely with growth conditions (e.g., light and nutrient availability (MacIntyre et al., 2002)). Photosynthesis is also an algal-specific trait, but the measurement of NPP can be influenced by the heterotrophic community. Finally, POC measurements composite all constituent sources above a chosen filter pore size (or between a maximum and minimum size if a prefilter is used (e.g., Bishop, 1999; Bishop et al., 1999)) into a single carbon value.

The different biomass-dependent variables each offer beneficial attributes at different space and time scales. Consequently, significant efforts are being invested to interrelate b_{bp} , Chl, c_p , POC, and NPP, despite the dissimilarities identified above. Notable examples of such relationships include the estimation of global ocean NPP from remotely sensed surface chlorophyll fields (C_{sat}) (e.g., Longhurst, 1995; Antoine et al., 1996; Field et al., 1998; Behrenfeld et al., 2001) and satellite- and in situ-based estimates of POC from measurements of b_{bp} (Stramski et al., 1999; Loisel et al., 2001) and c_p (Gardner et al., 1993, 1995; Walsh et al., 1995; Loisel and Morel, 1998; Bishop, 1999; Bishop et al., 1999; Claustre et al., 1999). Success of these efforts stems from the conservative nature of ocean particle size distributions and the large dynamic range in particle concentrations relative to uncertainties in the conversion factors explicitly or implicitly employed.

The benefit of a large dynamic range in particle abundance is lost when the ratio of two biomass-dominated variables is used to investigate a characteristic of the particle assemblage. Specifically, each of the above variables can be expressed

as the product of an attribute per particle and the concentration of particles. Consequently, the concentration terms essentially cancel out in the ratio of any two variables, leaving a relation between particle-specific attributes. For example, the ratio of POC to c_p is not dependent on the concentration of particles, but on the particle size distribution (since c_p is sensitive to only a portion of the size domain represented by POC data) and the median attenuation coefficient per particle (c_c^*), itself a function of the index of refraction and particle size (Cullen and Lewis, 1995; DuRand and Olson, 1996). Similarly, chlorophyll-specific photosynthesis (P^b) is not explicitly dependent on the concentration of phytoplankton, since both NPP and Chl vary with the abundance of algae.

Without the overpowering influence of variability in particle abundance, observed changes in the ratio of ‘biomass-variables’ can be difficult to interpret. For example, c_p provides a robust index of variability in particle concentration (e.g., Bishop, 1999) but, when measurements are made on a particular water mass at two different times, the ratio of the two c_p values does not necessarily provide a robust measure of changes in particle abundance. This is precisely the problem that has been encountered in c_p -based estimates of particle growth rates in the field (Siegel et al., 1989; Cullen et al., 1992). Changes in c_p that originally were interpreted as changes in cell number now appear largely to reflect diel variability in c_c^* (DuRand and Olson, 1996). With such dangers in mind, we endeavored here to investigate the relationship between a ratio of two ‘biomass-variables’ and a particular characteristics of the particle assemblage. Namely, we compared the c_p to Chl ratio (c_p^*) with independent measures of phytoplankton photoacclimation (i.e., the physiological response of algae to variable growth irradiance).

Our motivation stems from the repeated observation that depth-dependent changes in c_p^* are consistent with expected changes from photoacclimation (Kitchen and Zaneveld, 1990; Mitchell and Kiefer, 1988; Mitchell and Holm-Hansen, 1991; Fennel and Boss, 2003). The link between c_p^* and photoacclimation has never been directly tested, but if the relationship holds in the vertical dimension, it could very well also hold in the

horizontal and temporal dimensions (which are of particular interest to us). The preferred metric of photoacclimation is the light-saturation index, E_k , calculated from photosynthesis–irradiance relationships as the intersection of the light-limited slope (α^b) and the light-saturated rate (P_{\max}^b) (Talling, 1957). Unfortunately, for the historical data sets employed here, only one involved simultaneous measurements of E_k and c_p^* . In the remaining data sets, productivity was measured by prolonged (12–24 h) incubations that yield a single light-saturation rate for the water column (P_{opt}^b —which is similar to but slightly less than P_{\max}^b (Behrenfeld and Falkowski, 1997a,b; and see footnote in Table 1)). Nevertheless, P_{opt}^b has been demonstrated in certain cases to be a useful index of photoacclimation (Behrenfeld et al., 2002a,b).

With the many complications involved in relating c_p^* to phytoplankton photoacclimation, it is unlikely that the former will, at any time soon, replace more traditional measures of the latter (e.g., ^{14}C -uptake) at the local-scale of field

observations. However, accessibility of c_p^* to optical measurements alone does permit autonomous or mooring applications and bestows a potential for remote sensing retrievals at the regional to global scale over seasonal to inter-annual periods. At these scales, extrapolations based on sparse in situ data sets are accompanied by exceptionally large uncertainties, making alternative approaches appealing. Thus, the significance of unveiling a relationship between c_p^* and photoacclimation is that it may provide a new tool for investigating broad-scale changes in algal physiology and for gaining insights into the causative environmental forcings for this variability.

2. Methods

Field data were assembled from five oceanographic studies (Fig. 1). For each study, light-saturated photosynthesis was measured as ^{14}C -uptake, chlorophyll concentration (chl: mg m^{-3}) was measured by high-performance liquid chromatography (HPLC) using samples filtered onto Whatman[®] GFF filters, and beam attenuation (c) was measured with a Sea Tech 25 cm pathlength transmissometer (660 nm). The attenuation coefficient at 660 nm is little influenced by dissolved material absorption (c_g) in the open ocean (Pak et al. 1988) and has a component of $\sim 0.41 \text{ m}^{-1}$ associated with pure seawater (Pope and Fry, 1997) that is little affected by variations in salinity or temperature (Pegau et al., 1997). However, practical determinations of c_p from c also require corrections for instrument calibration, fouling, and drift. These corrections were made by referencing all attenuation data to values of c measured at depths of ~ 200 – 400 m , where the particulate contribution to beam attenuation is presumably negligible compared to c_w and temporal variability in c is small. In other words, c_p at each depth was calculated as c minus the deep-water attenuation coefficient for each profile. In most cases, these deep-water values were close to or equal to 0.364 m^{-1} , which is the attenuation coefficient that Sea Tech transmissometers are factory calibrated to give in pure water (c_w). All

Table 1
Notation

c	Beam attenuation coefficient
c_w	Attenuation coefficient for pure seawater
c_p	Particulate attenuation coefficient
\bar{c}	Median attenuation coefficient per particle
c_p^*	c_p normalized to chlorophyll concentration
P_{\max}^b	Light-saturated, chlorophyll-normalized photosynthetic rate
P_{opt}^b	Maximum chlorophyll-specific photosynthetic rate measured within a water column ^a
α^b	Initial, light-limited slope of the chlorophyll-normalized photosynthesis–irradiance relationship
E_k	Light-saturation index, calculated as the ratio of P_{\max}^b to α^b
I_g	Light level to which phytoplankton are photoacclimated

^a P_{\max}^b is determined using artificial light and is a direct measure of the light-saturated carbon fixation capacity. P_{opt}^b is measured under ambient light conditions during in situ or simulated in situ incubations. Natural fluctuations in sunlight cause photosynthetic rates to vary over the course of such incubations. P_{opt}^b is generally observed close to the surface, where light levels maintain photosynthesis near P_{\max}^b for a bulk of the incubation period. Thus, unless photoinhibition is excessive or ambient PAR is very low, P_{opt}^b will vary in parallel with P_{\max}^b .

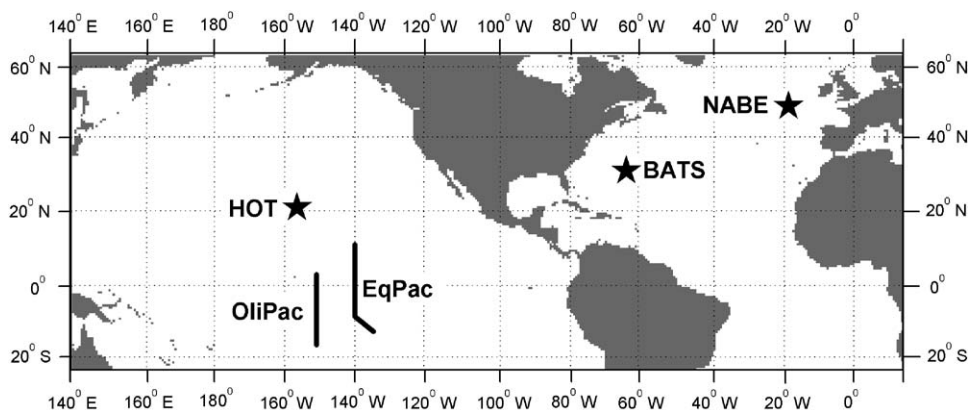


Fig. 1. Geographic location of the HOT, BATS, NABE, EqPac study, and OliPac study.

values of c_p reported here refer to particulate attenuation at 660 nm [i.e., $c_p(660)$].

2.1. Hawaii Ocean Time Series (HOT)

Depth profiles of c , chlorophyll, and photosynthesis at Station Aloha (22°45' N, 158°W) for the 1991–1996 period were obtained from the web site <http://hahana.soest.hawaii.edu/hot/>. Primary production measurements were conducted on samples collected from eight depths and incubated in situ from sunrise to sunset. For each productivity profile, the maximum photosynthetic rate measured in the upper four sampling depths was taken as P_{opt}^b . Beam attenuation was not measured during 1996. However, results from 1991 to 1995 indicated that monthly c_p values exhibited little interannual variability. To illustrate this, monthly average c_p values were used to calculate c_p^* during 1996 (gray symbols in Fig. 2A). HOT measurement protocols can be found at the above web site.

2.2. Bermuda Atlantic Time Series (BATS) and Bermuda Biooptics Program (BBOP)

Depth profiles of c , chlorophyll, and photosynthesis collected at the BATS/BBOP site (31°N, 64°W) during the 1992–1997 period were obtained from the web site <http://www.bbsr.edu/cintoo/bats/>. Primary production measurements were conducted on samples collected from eight depths and incubated in situ from sunrise to sunset. P_{opt}^b

values were determined according to Behrenfeld et al. (2002b). BATS and BBOP measurement protocols are described in Knap et al. (1993), Michaels and Knap (1996), and Siegel et al. (1995a, b).

2.3. North Atlantic Bloom Experiment (NABE)

c_p , chlorophyll, and photosynthesis data for Legs 4 and 5 of the NABE experiment on the R.V. *Atlantis* (April 25–June 6, 1989) (Gardner et al., 1993) were obtained from the web site <http://usjgofs.whoi.edu/jg/dir/jgofs/>. Primary production measurements were conducted on samples collected from six to eight depths and incubated for 24 h in situ (during Leg 4, samples were incubated onboard in the dark from sunset to sunrise). P_{opt}^b was taken as the maximum photosynthetic rate measured in the upper four sampling depths.

2.4. Equatorial Pacific (EqPac) study

EqPac c_p , chlorophyll, and P_{opt}^b data were obtained from the web site <http://usjgofs.whoi.edu/jg/dir/jgofs/eqpac/>. The 1992 EqPac study entailed four separate components: Transect TT007 (February 4–March 7; 12°N–12°S, ~140°W), Station TT008 (March 23–April 9; 0°, 140°W), Transect TT011 (August 10–September 14; 12°N–12°S, ~140°W), and Station TT012 (October 1–20; 0°, 140°W). Primary production measurements were conducted on samples collected from

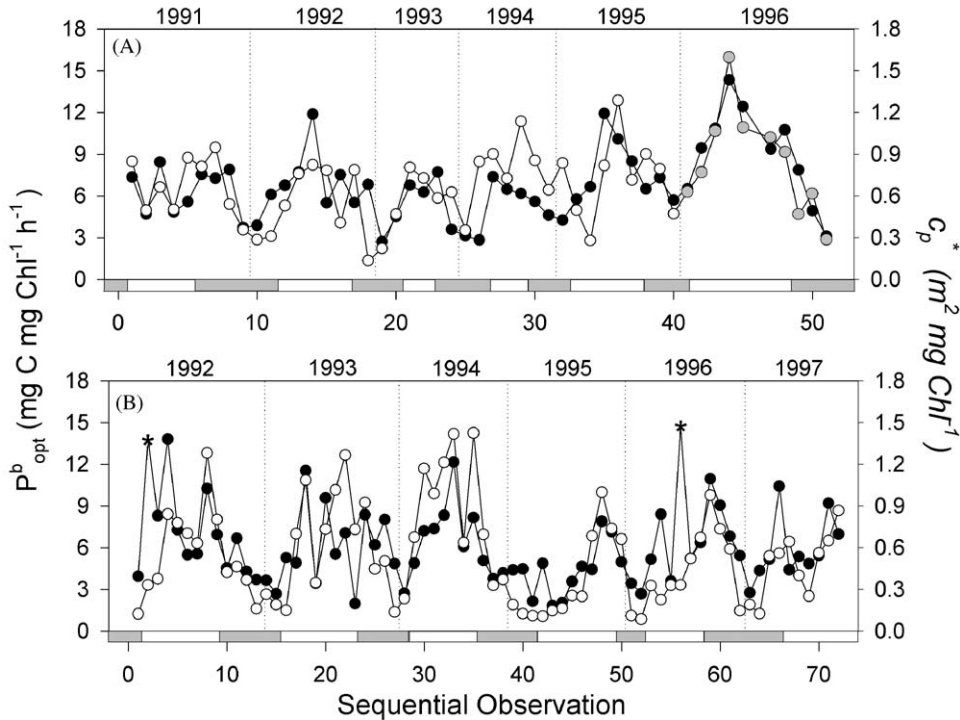


Fig. 2. Comparison of light-saturated photosynthesis ($P_{\text{opt}}^b = \bullet$) and the chlorophyll-normalized particulate attenuation coefficient ($c_p^* = \circ$) for (A) the HOT and (B) the BATS. Data are plotted by sequential observations during each time series. Observations are not equally spaced in time, so vertical dotted lines have been added to delineate years (labeled at the top). Shaded and unshaded bars are also shown along the x -axis to indicate winter (November–April) and summer (May–October), respectively. Gray circles in (A) identify c_p^* estimates based on climatological c_p values. Asterisks in (B) identify two extreme outliers in the BATS $P_{\text{opt}}^b - c_p^*$ relationship.

eight depths and incubated in situ for ~ 24 h. P_{opt}^b was taken as the maximum photosynthetic rate measured in the upper four sampling depths. Surface mixed layer depths (used in our analysis) were taken from Gardner et al. (1995). EqPac measurement protocols can be found on the above web site.

2.5. Oligotrophic Pacific (OliPac) study

OliPac data were collected in November 1994 between 16°S , 150°W and 1°N , 150°W (Dandonneau, 1999), which is close to the EqPac study area (140°W). Photosynthesis–irradiance measurements were conducted on samples collected from eight to ten depths between the surface and the 0.1% light depth (Behrenfeld et al., 1998). For each sampling depth, α^b and P_{max}^b were determined by fitting the model of Jassby and Platt (1976) to

carbon fixation rates measured at 12 light levels between 5 and $400 \mu\text{mol quanta m}^{-2} \text{s}^{-1}$ (Babin et al., 1994). E_k was calculated as $P_{\text{max}}^b / \alpha^b$.

3. Results

3.1. Ocean time series results (HOT and BATS)

Over the 6 year HOT record, P_{opt}^b fluctuated between 2.7 and $14.3 \text{ mg C mg Chl}^{-1} \text{ h}^{-1}$ (Fig. 2A), c_p varied from 0.01 to 0.15 m^{-1} , and chlorophyll ranged from 0.04 to 0.18 mg m^{-3} (Table 2). No correlation existed between c_p and chlorophyll concentration ($r^2 < 0.04$), suggesting that changes in chlorophyll were largely intracellular and independent of phytoplankton abundance. c_p^* ranged from 0.14 to $1.60 \text{ m}^2 \text{ mg Chl}^{-1}$ and, in accord with a prominent influence of photoacclimation, varied to

Table 2

Range in chlorophyll concentrations (Chl: mg m^{-3}), particulate beam attenuation coefficients (c_p : m^{-1}), c_p : Chl ratios (c_p^* : $\text{m}^2 \text{mg Chl}^{-1}$), and ^{14}C -based light-saturated photosynthesis ($P_{\text{opt}}^{\text{b}}$ or $P_{\text{max}}^{\text{b}}$: $\text{mg C (m}^3 \text{h)}^{-1}$) for the HOT (1991–1996), the BATS (1992–1997), the NABE (1989), the EqPac (1992) study, and the OliPac (1994) study. Also provided are coefficients of determination (r^2) for regressions of $P_{\text{opt}}^{\text{b}}$ or $P_{\text{max}}^{\text{b}}$ versus c_p^* and c_p

Study	Chl	c_p	c_p^*	$P_{\text{opt}}^{\text{b}}$ or $P_{\text{max}}^{\text{b}}$	r^2 for c_p^*	r^2 for c_p
HOT	0.04–0.18	0.01–0.15	0.14–1.60	1.6–14.3	0.39	0.02
BATS	0.03–0.42	0.01–0.07	0.08–1.42	1.8–14.7	0.47 ^a	< 0.01 ^a
NABE						
Leg 4	0.55–1.72	0.17–0.46	0.25–0.48	2.5–4.8	0.68	0.02
Leg 5	0.58–3.00	0.48–0.89	0.30–0.84	1.6–5.4	0.82	0.35
EqPac	0.06–0.37	0.03–0.14	0.22–0.70	2.6–15.3	<0.01	0.67
OliPac	0.04–0.40	<0.01–0.09	0.04–0.91	0.1–4.5 ^b	0.23	0.04

^a Outliers identified by asterisks in Fig. 2B were not included in this r^2 calculation.

^b $P_{\text{max}}^{\text{b}}$ was measured during the OliPac study, while $P_{\text{opt}}^{\text{b}}$ was determined for all other studies.

first order with $P_{\text{opt}}^{\text{b}}$ (Fig. 2A). c_p^* and $P_{\text{opt}}^{\text{b}}$ were well correlated during the 1996 period when climatological monthly average values for c_p were used, again emphasizing the prominent influence of photoacclimation on seasonal changes in chlorophyll. Extending this application of climatological c_p values to all data collected between 1989 and 1999, we found resultant c_p^* values to be well correlated with $P_{\text{opt}}^{\text{b}}$ ($r^2 = 0.49$) (data not shown), the simple point being that interannual variability in phytoplankton carbon biomass is relatively constrained at HOT and better estimated from c_p than chlorophyll concentration.

The seasonal cycle of deep winter mixing and summer stratification is much stronger at the BATS site than at the HOT site, resulting in larger amplitude changes in growth irradiance (I_g) and pronounced seasonal cycles in photoacclimation (Behrenfeld et al., 2002b). For the 1992–1997 period, $P_{\text{opt}}^{\text{b}}$ ranged from 1.8 to 14.7 $\text{mg C mg Chl}^{-1} \text{h}^{-1}$ (Fig. 2B), c_p ranged from 0.01 to 0.07 m^{-1} , chlorophyll varied from 0.03 to 0.42 mg m^{-3} , and c_p^* fluctuated between 0.08 and 1.42 $\text{m}^2 \text{mg Chl}^{-1}$ (Fig. 2B) (Table 2). Chlorophyll concentration and c_p were again uncorrelated in the BATS record, while c_p^* varied in parallel with $P_{\text{opt}}^{\text{b}}$ (Fig. 2B) (Table 2). Behrenfeld et al. (2002b) independently demonstrated that photoacclimation was a prominent source of $P_{\text{opt}}^{\text{b}}$ variability throughout much of the annual cycle at the BATS location.

3.2. North Atlantic Bloom Experiment

During the NABE, surface nitrate levels were elevated and an early shoaling of the mixed layer from $\sim 125 \text{ m}$ to $< 20 \text{ m}$ gave rise to a phytoplankton bloom that increased surface chlorophyll concentrations from 0.55 to 3.0 mg m^{-3} and increased c_p from 0.17 to 0.89 m^{-1} (Gardner et al., 1995). Unlike BATS and HOT, changes in chlorophyll during the NABE were generally dominated by changes in phytoplankton abundance, rather than photoacclimation, resulting in a strong correlation between c_p and chlorophyll ($r^2 = 0.73$). Nevertheless, c_p^* retained information on physiological variability during the bloom. During Leg 4, chlorophyll biomass increased steadily from 0.55 to 1.72 mg m^{-3} , while $P_{\text{opt}}^{\text{b}}$ exhibited only a modest increase from 2.5 to 4.8 $\text{mg C mg Chl}^{-1} \text{h}^{-1}$ that was paralleled by similar changes in c_p^* (Fig. 3) (Table 2). Chlorophyll biomass continued to increase during Leg 5 until May 25, then decreased to 0.58 mg m^{-3} by June 6. $P_{\text{opt}}^{\text{b}}$ varied inversely with chlorophyll concentration and was highly correlated with c_p^* (Fig. 3) (Table 2). A clear shift in the relationship between $P_{\text{opt}}^{\text{b}}$ and c_p^* occurred between Legs 4 and 5 (Fig. 3), corresponding to methodological changes in productivity measurements. Conceivably, a change in the particle assemblage during the 10-day gap separating the two data sets could also have contributed to this shift.

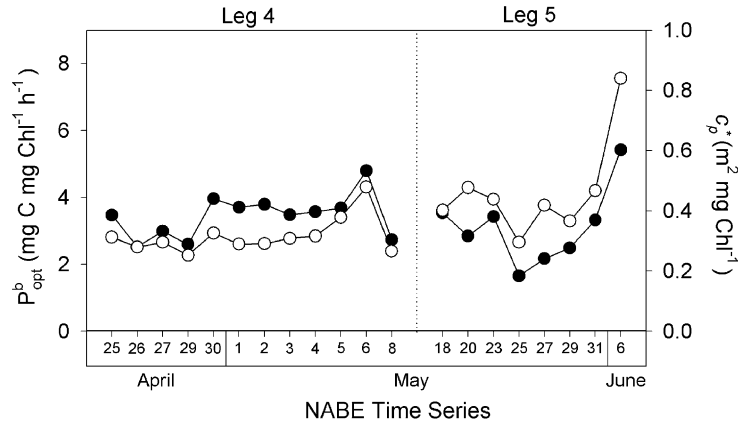


Fig. 3. Comparison of light-saturated photosynthesis ($P_{opt}^b = \bullet$) and the chlorophyll-normalized particulate attenuation coefficient ($c_p^* = \circ$) for Legs 4 and 5 (labeled at top) of the NABE.

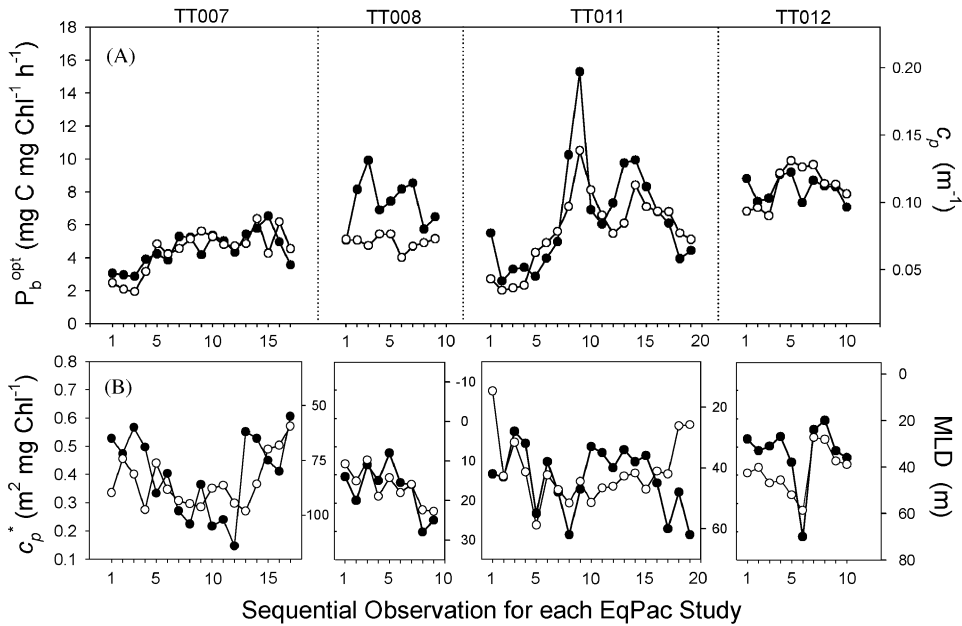


Fig. 4. (A) Comparison of light-saturated photosynthesis ($P_{opt}^b = \bullet$) and particulate beam attenuation ($c_p = \circ$) for the four studies (labeled at top) of the EqPac program. (B) Comparison of the chlorophyll-normalized particulate attenuation coefficient ($c_p^* = \circ$) and mixed layer depths (MLD = \bullet). MLD values are from Gardner et al. (1995). Data in (A) and (B) are plotted in sequential order for each study.

3.3. Equatorial Pacific results (EqPac and OliPac)

Conditions during the four EqPac studies varied widely, from an El Nino (TT007 and TT008) to a La Nina (TT011 and TT012) and from oligotrophic to equatorial upwelling systems

(Gardner et al., 1995; Walsh et al., 1995; Chung et al., 1996, 1998). P_{opt}^b varied from 2.7 to 9.9 mg C mg Chl⁻¹ h⁻¹ during the El Nino period and from 2.6 to 15.3 mg C mg Chl⁻¹ h⁻¹ during the La Nina (Fig. 4A). Chlorophyll ranged from 0.06 to 0.37 mg Chl m⁻³ and c_p varied from 0.03 to

0.14 m^{-1} during the four studies. Chlorophyll largely varied as a function of phytoplankton abundance and was well correlated with c_p ($r^2 = 0.67$). Unlike HOT, BATS, and NABE, c_p^* and P_{opt}^b were not correlated (Table 2). Interestingly, P_{opt}^b did covary with c_p (Table 2), particularly during TT007, TT011, and TT012 (Fig. 4A).

Two explanations exist for the lack of correspondence between c_p^* and P_{opt}^b during the EqPac studies: either c_p^* was an unreliable index of photoacclimation or variability in P_{opt}^b was dominated by factors other than photoacclimation. If the later were the case, then c_p^* should still exhibit a degree of correspondence with surface mixing depths (MLD), since MLD is an important determinant of growth irradiance in surface phytoplankton populations. Indeed, primary features in MLD profiles for each study were evident in c_p^* (Fig. 4B), suggesting that c_p^* was tracking changes in photoacclimation. Provoked by this result, we turned to the OliPac data for further insights.

EqPac and OliPac data were collected from a similar region of the Pacific Ocean (Fig. 1) and, like P_{opt}^b data for EqPac, P_{max}^b exhibited little correlation with c_p^* during OliPac (Fig. 5A) (Table 2). Photosynthesis–irradiance measurements conducted during OliPac, however, also allowed calculation of the light-saturation index, E_k . Comparison of c_p^* with E_k yielded a clear correlation (Fig. 5B) ($r^2 = 0.76$). This result again supports a functional link between c_p^* and phytoplankton photoacclimation and suggests that the uncoupling of c_p^* from P_{opt}^b and P_{max}^b during the two equatorial studies was due to physiological responses to environmental forcings that had a greater influence on carbon fixation than cellular carbon to chlorophyll ratios (i.e., c_p^*).

4. Discussion

The apparent consistency between spatio-temporal changes in c_p^* and our two indices of photoacclimation is intriguing, given the many dissimilarities in these variables. For example, while c_p is sensitive to all particles in the water, its variability is largely determined by particles in

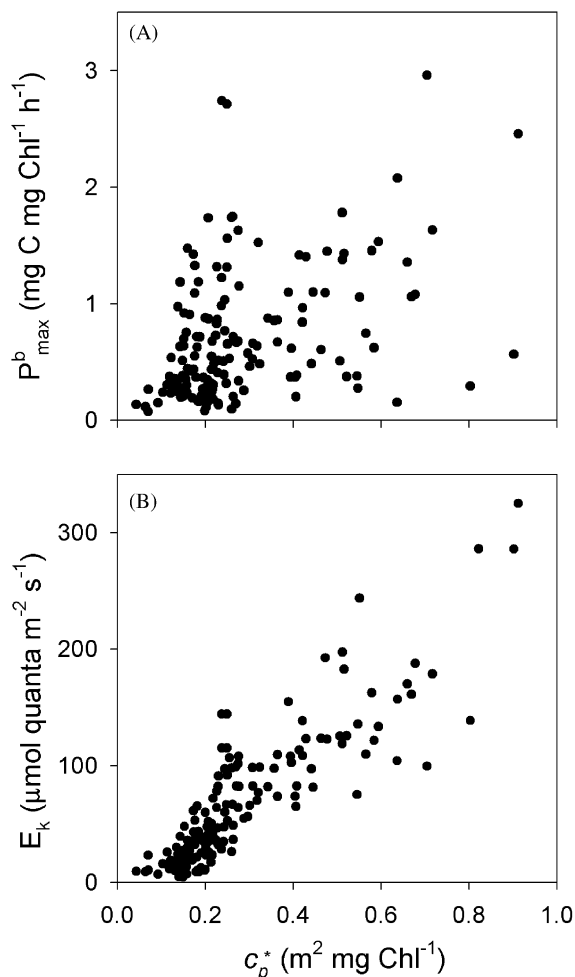


Fig. 5. The chlorophyll-normalized particulate attenuation coefficient (c_p^*) versus (A) light-saturated photosynthesis (P_{max}^b) ($r^2 = 0.23$; $n = 161$) and (B) the light saturation index, $E_k (= P_{\text{max}}^b/\alpha^b)$ ($r^2 = 0.76$; $n = 161$) for the OliPac study. The highest value for P_{max}^b has been omitted from (A) to better view the remaining data. The omitted variable pair is $P_{\text{max}}^b = 4.54\text{ mg C (m}^3\text{ h)}^{-1}$ and $c_p^* = 0.82\text{ m}^{-1}$.

~ 0.5 and $20\text{ }\mu\text{m}$ range (whether bacterial, detrital, or algal) for typical open ocean particle size distributions (Morel, 1973; Stramski and Kiefer, 1991; Boss et al. 2001). Consequently, even in the open ocean only a fraction (but often dominant) of c_p (or POC) can be attributed to phytoplankton (Letelier et al., 1996; DuRand et al., 2001; Gundersen et al., 2001; and see discussion in Fennel and Boss, 2003). In fact, c_p is not even

equally influenced by the different $<20\ \mu\text{m}$ algal groups, with ultraplankton ($1\text{--}2\ \mu\text{m}$) and nanoplankton ($2\text{--}20\ \mu\text{m}$, but particularly $2\text{--}3\ \mu\text{m}$) apparently having a greater influence on c_p than the picoplankton, *Prochlorococcus* and *Synechococcus* (DuRand and Olson, 1996). In addition, variability in c_p^* can arise from a change in the phytoplankton size distribution simply because normalization to chlorophyll involves the division of one size domain ($c_p \sim 0.5\text{--}20\ \mu\text{m}$) by another ($\text{Chl} > \text{filter pore size}$). Photosynthetic rates, on the other hand, are influenced (in a growth-rate dependent manner) by all taxonomic groups of algae collected on a filter and the derived photoacclimation variables reflect physiological changes in the phytoplankton fraction alone. These issues, among others (e.g., changes in c_c^* , influence of coccoliths (Balch et al., 2001)), compromise any potential for relating c_p^* to photoacclimation, particularly over large horizontal and temporal scales. It was somewhat surprising, therefore, that

our empirical analysis did reveal a first-order correspondence between c_p^* and P_{opt}^b (Fig. 6) or E_k (Fig. 5B). One interpretation of this result is that c_p^* , E_k , and P_{opt}^b are not causally linked, but simply covary under certain environmental conditions. An alternative interpretation, and the one we favor, is that the dynamic range of variability in cellular chlorophyll resulting from physiological responses to changing light and nutrient conditions is sufficient to overcome the formerly identified dissimilarities between c_p and phytoplankton carbon biomass.

The photosynthesis–irradiance relationship can exhibit a tremendous degree of flexibility, with two primary types of change: ‘ E_k -dependent’ and ‘ E_k -independent’ (Behrenfeld et al., 2003). Photoacclimation is the primary cause of the former and entails an order of magnitude (or more) variability in cellular pigmentation over ecologically relevant light levels (e.g., Geider et al., 1985, 1986; Behrenfeld et al., 2002b). Beam attenuation is

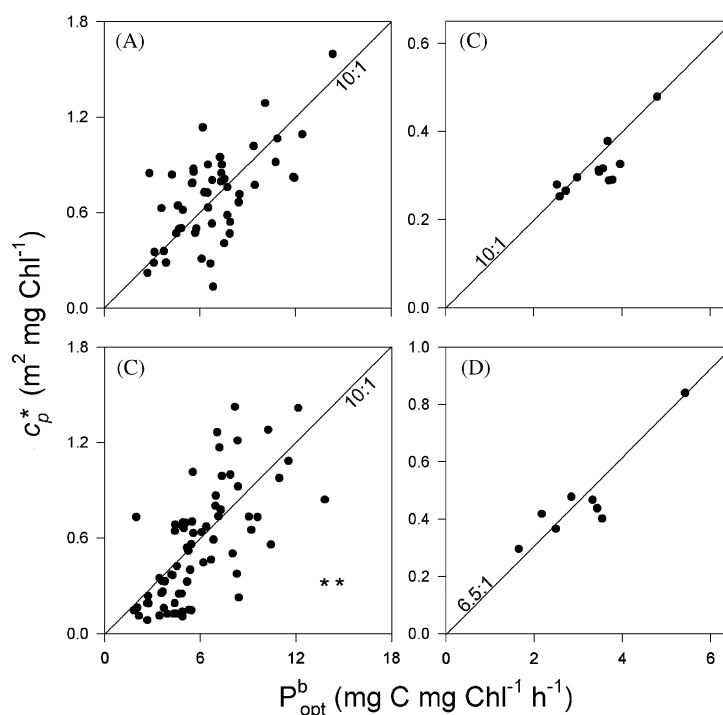


Fig. 6. The chlorophyll-normalized particulate attenuation coefficient (c_p^*) versus light-saturated photosynthesis (P_{opt}^b) for the (A) HOT and (B) BATS programs (data from Fig. 2) and for (C) Leg 4 and (D) Leg 5 of the NABE (data from Fig. 3). See Table 2 for statistics.

relatively insensitive to intracellular changes in pigmentation, thereby engendering c_p^* with a sensitivity to photoacclimation. This causal link was earlier proposed as the basis for depth-dependent changes in c_p^* (Kitchen and Zaneveld, 1990; Mitchell and Kiefer, 1988; Mitchell and Holm-Hansen, 1991; Fennel and Boss, 2003) and is here suggested as the dominant cause of the covariations in c_p^* , E_k , and P_{opt}^b illustrated in Figs. 2, 3 and 5B.

In the equatorial Pacific, we propose that the lack of correspondence between c_p^* and either P_{opt}^b or P_{max}^b (Fig. 4A and 5A) is due to ' E_k -independent' variability dominating over ' E_k -dependent' processes. The physiological basis for ' E_k -independent' change in photosynthesis–irradiance relationships appears to be growth rate-dependent alterations in the allocation of photosynthetic products to alternative metabolic pathways (Behrenfeld et al., 2003). Specifically, as growth rate decreases the demand for light harvesting decreases more slowly than the demand for newly fixed carbon, such that P_{max}^b decreases more rapidly with increasing nutrient stress than cellular carbon:chlorophyll (thus causing divergent behavior in P_{max}^b and c_p^*). As indicated by its name, ' E_k -independent' variability involves (often large) parallel changes in α^b and P_{max}^b that do not alter E_k , allowing E_k to remain a sensitive index of photoacclimation only. Accordingly, c_p^* covaried with E_k during OliPac (Fig. 5B) despite the prominence of ' E_k -independent' processes degrading the relationship between c_p^* and P_{max}^b (Fig. 5A).

Results presented here are tantalizing, but not definitive evidence of a relationship between an optically accessible variable (c_p^*) and algal physiology. Our analysis is clearly of an empirical nature, but we believe it is the first direct field-based comparison between c_p^* and independent measures of photoacclimation. While a single global relationship between c_p^* and P_{opt}^b is not proposed, we did find a relatively consistent conversion for the HOT, BATS, and NABE Leg 4 data sets: $P_{opt}^b = c_p^* \times 10 \text{ mg C m}^{-2} \text{ h}^{-1}$ (the scalar having units of a cross-sectional carbon-specific growth rate) (Figs. 6A–C). A conversion factor of $6.5 \text{ mg C m}^{-2} \text{ h}^{-1}$ provided a better fit for the NABE Leg 5 data set (Fig. 6D).

Morel and Prieur (1977) defined Case I waters as those in which scattering is dominated by phytoplankton. All of the data sets considered here fall into this category. Consequently, c_p was related to POC (at least regionally) and POC was related to phytoplankton carbon. The stability of these relationships is a chief determinant of whether c_p^* will reliably register changes in photoacclimation. We can expect such relationships to become weaker the more disparate the controlling size domains of any two 'biomass variables'. For example, the size domain dominating particulate backscattering (b_{bp}) overlaps even less with the algal population or practical POC data than c_p . Nevertheless, even b_{bp} can provide regional estimates of POC (e.g., Stramski et al., 1999; Loisel et al., 2001). This is an important result because it suggests that, at least regionally, phytoplankton carbon biomass may be related to global remote sensing retrievals of b_{bp} . Of course, such relationships will be far more complicated in regions where suspended inorganic particle loads are high (e.g., coastal regions or coccolithophore blooms). In such cases, strong relationships between c_p^* and photoacclimation are also unlikely.

Often, central science issues regarding ocean productivity require information on rates (e.g., 'Is ocean productivity changing?'), not simply standing stocks, yet there is no known quantitative optical signature of aquatic photosynthesis. A reliance has therefore developed on field-based empirical relationships that approximate the required rate terms, but the large uncertainties in these estimates translate directly into the confidence intervals placed on modeled productivity. The fundamental finding of the current study is that first-order correlations appear to exist between a bio-optical variable, c_p^* , and independent measures of phytoplankton physiology (E_k and P_{opt}^b). Implications of this result are that c_p may provide a better estimate of algal carbon biomass than chlorophyll concentration in Case I waters, that the c_p^* ratio may yield information on spatio-temporal variability in important rate terms (reflecting an association between cellular chlorophyll, incident light, and growth rate), and that relationships likely exist between near-surface c_p^* and physiological mixed layer depths. The optical

nature of the c_p^* ratio makes it accessible to autonomous or mooring measurements (e.g., Jones et al. 2001; Dickey, 2003) and a candidate for remote sensing retrievals, either through passive approaches involving relationships with b_{bp} (e.g., Stramski et al., 1999; Loisel et al., 2001) or c_p (Roesler and Boss, 2003) or through active approaches, such as a lidar system with multiple fields-of-view (Gordon, 1982).

Acknowledgements

We thank the HOT, BATS, NABE, EqPac, and OliPac programs for access to field data, Dr. Marcel Babin for OliPac photosynthesis–irradiance data, Dr. David Siegel for assistance with BATS data, Dr. Mary Jane Perry for helpful discussions, and three anonymous reviewers for constructive comments on the manuscript. This research was supported by the National Aeronautics and Space Administration (NAGS-12385, RTOP-622-52-58) and by the National Science Foundation (NSF-INT99-02240).

References

- Antoine, D., André, J.-M., Morel, A., 1996. Oceanic primary production 2. Estimation at global scale from satellite (coastal zone color scanner) chlorophyll. *Global Biogeochem Cycles* 10, 57–69.
- Babin, M., Morel, A., Gagnon, R., 1994. An incubator designed for extensive and sensitive measurements of phytoplankton photosynthetic parameters. *Limnology and Oceanography* 39, 694–702.
- Bader, H., 1970. The hyperbolic distribution of particle sizes. *Journal of Geophysical Research* 75, 2822–2830.
- Balch, W.M., Drapeau, D.T., Fritz, J.J., Bowler, B.C., Nolan, J., 2001. Optical backscattering in the Arabian Sea—continuous underway measurements of particulate inorganic and organic carbon. *Deep-Sea Research I* 48, 2423–2452.
- Behrenfeld, M.J., Falkowski, P.G., 1997a. Photosynthetic rates derived from satellite-based chlorophyll concentration. *Limnology and Oceanography* 42, 1–20.
- Behrenfeld, M.J., Falkowski, P.G., 1997b. A consumer's guide to phytoplankton primary productivity models. *Limnology and Oceanography* 42, 1479–1491.
- Behrenfeld, M.J., Prasil, O., Kolber, Z.S., Babin, M., Falkowski, P.G., 1998. Compensatory changes in photosystem II electron turnover rates protect photosynthesis from photo-inhibition. *Photosynthesis Research* 58, 259–268.
- Behrenfeld, M.J., Randerson, J., McClain, C., Feldman, G., Los, S., Tucker, C., Falkowski, P., Field, C., Frouin, R., Esaias, W., Kolber, D., Pollack, N., 2001. Biospheric primary production during an ENSO transition. *Science* 291, 2594–2597.
- Behrenfeld, M.J., Esaias, W.E., Turpie, K., 2002a. Assessment of primary production at the global scale. In: Williams, P.J., Thomas, D.N., Reynolds, C.S. (Eds.), *Phytoplankton Productivity: Carbon Assimilation in Marine and Freshwater Ecosystems*. Blackwell, Oxford, pp. 156–186 (Chapter 7).
- Behrenfeld, M.J., Marañón, E., Siegel, D.A., Hooker, S.B., 2002b. A photoacclimation and nutrient based model of light-saturated photosynthesis for quantifying oceanic primary production. *Marine Ecology—Progress Series* 228, 103–117.
- Behrenfeld, M.J., Prasil, O., Babin, M., Bruyant, F., 2003. In search of a physiological basis for covariations in light-limited and light-saturated photosynthesis. *Journal of Phycology*, in press.
- Bishop, J.K.B., 1999. Transmissometer measurements of POC. *Deep-Sea Research I* 46, 353–369.
- Bishop, J.K.B., Calvert, S.E., Soon, M.Y.S., 1999. Spatial and temporal variability of POC in the northeast Subarctic Pacific. *Deep-Sea Research II* 46, 2699–2733.
- Boss, E., Twardowski, M.S., Herring, S., 2001. Shape of the particulate beam attenuation spectrum and its inversion to obtain the shape of the particulate size distribution. *Applied Optics* 40, 4885–4893.
- Chung, S.P., Gardner, W.D., Richardson, M.J., Walsh, I.D., Landry, M.R., 1996. Beam attenuation and micro-organisms: spatial and temporal variations in small particles along 140°W during the 1992 JGOFS EqPac transects. *Deep-Sea Research II* 43, 1205–1226.
- Chung, S.P., Gardner, W.D., Landry, M.R., Richardson, M.J., Walsh, I.D., 1998. Beam attenuation by microorganisms and detrital particles in the equatorial Pacific. *Journal of Geophysical Research* 103, 12669–12681.
- Claustre, H., Morel, A., Babin, M., Cailliau, C., Marie, D., Marty, J.-C., Tailliez, D., Vaultot, D., 1999. Variability in particle attenuation and chlorophyll fluorescence in the tropical Pacific: scales, patterns, and biogeochemical implications. *Journal of Geophysical Research* 104, 3401–3422.
- Cullen, J.J., Lewis, M.R., 1995. Biological processes and optical measurements near the sea surface: some issues relevant to remote sensing. *Journal of Geophysical Research* 100, 13255–13266.
- Cullen, J.J., Lewis, M.R., Davis, C.O., Barber, R.T., 1992. Photosynthetic characteristics and estimated growth rates indicate grazing is the proximate control of primary production in the equatorial Pacific. *Journal of Geophysical Research* 97, 639–654.
- Dandonneau, Y., 1999. Introduction to special section: biogeochemical conditions in the equatorial Pacific in late. *Journal of Geophysical Research* 104, 3291–3295.
- Dickey, T., 2003. Emerging ocean observations for interdisciplinary data assimilation systems. *Journal of Marine Systems* 40–41, 5–48.

- DuRand, M.D., Olson, R.J., 1996. Contributions of phytoplankton light scattering and cell concentration changes to diel variations in beam attenuation in the equatorial Pacific from flow cytometric measurements of pico-, ultra-, and nanoplankton. *Deep-Sea Research II* 43, 891–906.
- DuRand, M.D., Olson, R.J., Chisholm, S.W., 2001. Phytoplankton population dynamics at the Bermuda Atlantic Time-Series station in the Sargasso Sea. *Deep-Sea Research II* 48, 1983–2003.
- Fennel, K., Boss, E., 2003. Subsurface maxima of phytoplankton and chlorophyll: steady state solutions from a simple model. *Limnology and Oceanography* 48, 1521–1534.
- Field, C.B., Behrenfeld, M.J., Randerson, J.T., Falkowski, P.G., 1998. Primary production of the biosphere: integrating terrestrial and oceanic components. *Science* 281, 237–240.
- Gardner, W.D., Walsh, I.D., Richardson, M.J., 1993. Biophysical forcing on particle production and distribution during a spring bloom in the North Atlantic. *Deep-Sea Research II* 40, 171–195.
- Gardner, W.D., Chung, S.P., Richardson, M.J., Walsh, I.D., 1995. The oceanic mixed-layer pump. *Deep-Sea Research II* 42, 757–775.
- Geider, R.J., Osborne, B.A., Raven, J.A., 1985. Light dependence of growth and photosynthesis in *Phaeodactylum tricorutum* (Bacillariophyceae). *Journal of Phycology* 21, 609–619.
- Geider, R.J., Osborne, B.A., Raven, J.A., 1986. Growth, photosynthesis and maintenance metabolic cost in the diatom *Phaeodactylum tricorutum* at very low light levels. *Journal of Phycology* 22, 39–48.
- Gordon, H.R., 1982. Interpretation of airborne oceanic lidar: effects of multiple scattering. *Applied Optics* 21, 2996–3001.
- Gundersen, K., Orcutt, K.M., Purdie, D.A., Michaels, A.F., Knap, A.H., 2001. Particulate organic carbon mass distribution at the Bermuda Atlantic Time-Series study (BATS) site. *Deep-Sea Research II* 48, 1697–1718.
- Jassby, A.D., Platt, T., 1976. Mathematical formulation of the relationship between photosynthesis and light for phytoplankton. *Limnology and Oceanography* 21, 540–547.
- Jones, B., Noble, M., Dickey, T., 2001. Hydrographic and particle distribution over the Palos Verdes continental shelf: spatial, seasonal, and diurnal variability. *Continental Shelf Research* 22, 945–965.
- Kitchen, J., Zaneveld, J.R., 1990. On the noncorrelation of the vertical structure of light scattering and chlorophyll a in case I waters. *Journal of Geophysical Research* 95, 20237–20246.
- Knap, A.H., et al., 1993. BATS Methods—March 1993, BATS Method Manual Version 3. US JGOFS Planning and Coordination Office, Woods Hole, MA.
- Letelier, R.M., Dore, J.E., Winn, C.D., Karl, D.M., 1996. Seasonal and interannual variations in photosynthetic carbon assimilation at station ALOHA. *Deep-Sea Research II* 43, 467–490.
- Loisel, H., Morel, A., 1998. Light scattering and chlorophyll concentration in case I waters: a reexamination. *Limnology and Oceanography* 43, 847–858.
- Loisel, H., Bosc, E., Stramski, D., Oubelkheir, K., Deschamps, P.-Y., 2001. Seasonal variability of the backscattering coefficient in the Mediterranean Sea on Satellite SeaWiFS imagery. *Geophysical Research Letters* 28, 4203–4206.
- Longhurst, A., 1995. Seasonal cycles of pelagic production and consumption. *Progress in Oceanography* 36, 77–167.
- MacIntyre, H.L., Kana, T.M., Anning, T., Geider, R.J., 2002. Photoacclimation of photosynthesis irradiance response curves and photosynthetic pigments in microalgae and cyanobacteria. *Journal of Phycology* 38, 17–38.
- Michaels, A.F., Knap, A.H., 1996. Overview of the U.S. JGOFS Bermuda Atlantic Time-series Study and the Hydrostation S program. *Deep-Sea Research II* 43, 157–198.
- Mitchell, B.G., Holm-Hansen, O., 1991. Bio-optical properties of Antarctic Peninsula waters: differentiation from temperature ocean models. *Deep-Sea Research* 38, 1009–1028.
- Mitchell, B.G., Kiefer, D.A., 1988. Variability in pigment specific particulate fluorescence and absorption spectra in the northeastern Pacific Ocean. *Deep-Sea Research* 35, 665–689.
- Morel, A., 1973. Diffusion de la lumière par les eaux de mer: Résultats expérimentaux et approche théorique. In: AGARD Lecture Series 61 on Optics of the Sea (Advisory Group for Aerospace Research and Development; NATO, London), pp. 3.1.1–3.1.76.
- Morel, A., Ahn, Y.-H., 1991. Optics of heterotrophic nanoflagellates and ciliates: a tentative assessment of their scattering role in oceanic waters compared to those of bacterial and algal cells. *Journal of Marine Research* 48, 1–26.
- Morel, A., Prieur, L., 1977. Analysis of variations in ocean color. *Limnology and Oceanography* 22, 709–722.
- Pak, H., Kiefer, D.A., Kitchen, J.C., 1988. Meridional variations in the concentration of chlorophyll and microparticles in the North Pacific Ocean. *Deep-Sea Research* 35, 1151–1171.
- Pegau, W.S., Gray, D., Zaneveld, J.R.V., 1997. Absorption of visible and near-infrared light in water: the dependence on temperature and salinity. *Applied Optics* 36, 6035–6046.
- Pope, R.M., Fry, E.S., 1997. Absorption spectrum (380–700 nm) of pure water. II. Integrating cavity measurements. *Applied Optics* 36, 8710–8723.
- Roesler, C., Boss, E., 2003. A novel ocean color inversion model: retrieval of beam attenuation and particle size distribution. *Geophysical Research Letters* 30(9), 10.1029/2002GL016366.
- Siegel, D.A., Dickey, T.D., Washburn, L., Hamilton, M.K., Mitchell, B.G., 1989. Optical determination of particulate abundance and production variations in the oligotrophic ocean. *Deep-Sea Research* 36, 211–222.
- Siegel, D.A., Michaels, A.F., Sorensen, J., O'Brien, M.C., Hammer, M.A., 1995a. Seasonal variability of light availability and its utilization in the sargasso sea. *Journal of Geophysical Research* 100, 8695–8713.

- Siegel, D.A., O'Brien, M.C., Sorensen, J.C., Konnoff, D., Fields, E., 1995b. BBOP Data Processing and Sampling Procedures. US JGOFS Planning Report Number 19, US JGOFS Planning and Coordination Office, 77pp.
- Stramski, D., Kiefer, D., 1991. Light scattering by microorganisms in the open ocean. *Progress in Oceanography* 28, 343–383.
- Stramski, D., Reynolds, R.A., Kahru, M., Mitchell, B.G., 1999. Estimation of particulate organic carbon in the ocean from satellite remote sensing. *Science* 285, 239–242.
- Talling, J.F., 1957. The phytoplankton population as a compound photosynthetic system. *New Phytologist* 56, 133–149.
- Ulloha, O., Sathyendranath, S., Platt, T., 1994. Effect of the particle-size distribution on the backscattering ratio in seawater. *Applied Optics* 33, 7070–7077.
- Walsh, I.D., Chung, S.P., Richardson, M.J., Gardner, W.D., 1995. The diel cycle in the integrated particle load in the equatorial Pacific: a comparison with primary production. *Deep-Sea Research II* 42, 465–477.