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Biological processes and optical measurements near the sea surface: Some issues relevant to remote sensing

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Abstract. The advent of remote sensing, the development of new optical instrumentation, and the associated advances in hydrological optics have transformed oceanography: it is now feasible to describe ocean-scale biogeochemical dynamics from satellite observations, verified and complemented by measurements from optical sensors on profilers, moorings, and drifters. Only near-surface observations are common to both remote sensing and in situ observation, so it is critical to understand processes in the upper euphotic zone. Unfortunately, the biological principles that must be used to interpret optical variability near the sea surface are weaker than we would like, because relatively few experiments and analyses have examined bio-optical relationships under high irradiance characteristic of the upper optical depth. Special consideration of this stratum is justified, because there is good evidence that bio-optical relationships are altered near the surface: (1) the fluorescence yield from chlorophyll declines, leading to bias in the estimation of pigment from fluorometry; (2) the modeled relationship between solar-stimulated fluorescence and photosynthesis seems to deviate significantly from that presented for the lower euphotic zone; and (3) carbon-specific and cellular attenuation cross sections of phytoplankton change substantially during exposures to bright light. Even the measurement of primary productivity is problematic near the sea surface, because vertical mixing is not simulated and artifactual inhibition of photosynthesis can result. These problems can be addressed by focusing more sampling effort, experimental simulation, and analytical consideration on the upper optical depth and by shortening timescales for the measurement of marine photosynthesis. Special efforts to study near-surface processes are justified, because new bio-optical algorithms will require quantitative descriptions of the responses of phytoplankton to bright light.

Introduction

Optical measurements are a window for observing biological dynamics in the ocean. A prime example is the coastal zone color scanner (CZCS), whose images of ocean color have transformed perceptions of biological variability in the sea and have established the feasibility of using satellites for estimating marine primary productivity and biogeochemical fluxes [e.g., *Dugdale et al.*, 1989; *Platt et al.*, 1991; *Lewis*, 1992]. Descriptions of oceanic processes from satellite observations are evaluated and complemented by measurements from optical sensors on profilers, moorings, and drifters. Already, in situ optical instruments are providing unprecedented records of bio-optical variability at sea [*Dickey*, 1991; *Abbott et al.*, this issue]. Development of new instruments and accelerating collection of data virtually assure that hydrological optics will figure prominently in the future of aquatic studies.

Appropriate validation and accurate biological interpretations are crucial to effective use of optical measurements for describing oceanic properties. Because only near-surface observations are common to both remote sensing and in situ observation, processes in the upper euphotic zone merit special attention. Unfortunately, near surface conditions (high irradiance, often with chronically low concentrations of nutrients) are rarely reproduced in the laboratory; the biological principles that must be used for interpreting bio-optical variability near the sea surface are therefore weaker than we would like, in large part because they rely heavily on observations of phytoplankton grown at lower irradiance.

There is good reason to expect bio-optical relationships to be different near the surface as compared to the lower euphotic zone. For example, bright light induces a quenching of stimulated fluorescence that can bias in vivo estimates of chlorophyll; backscatter and poorly understood changes in fluorescence yield complicate the estimation of near-surface chlorophyll and productivity from upwelling radiance at 683 nm (natural fluorescence); bright light and the cell division cycle cause changes in the optical characteristics of phytoplankton, affecting both beam attenuation as a measure of particle dynamics and the fundamental relationships that result in satellite-sensed water-leaving radiance; and artifactual inhibition of photosynthesis during conventional ^{14}C incubations can compromise attempts to calibrate optical estimates of near-surface productivity. In what follows, we review these processes and suggest strategies for considering them during the development of models relating optical properties of the upper ocean to biogeochemical processes.

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Characterizing the Near-Surface Environment

Only near-surface measurements are appropriate for direct comparisons with passive optical observations from aircraft or

satellites. The bio-optical models and parameterizations that can be used to interpret these observations (for a review see *Bidigare et al.*, [1992]) are, however, seldom based exclusively on data representative of near-surface conditions. This is not necessarily a problem, and, in fact, it represents a strength, unless the underlying generalizations fail under conditions encountered in the upper optical depth. It is therefore important to know if bio-optical relationships change near the surface. This requires appropriate sampling and experimentation.

Sampling Effort at Sea

When the distributions and activities of marine phytoplankton are studied, sampling is generally concentrated in the lower euphotic zone. For a typical cruise (Figure 1), only 10% of the observations come from depths that contribute 88% of the water-leaving signal. Potentially important near-surface processes or relationships are thus easily overlooked in models or calibrations. Clearly, sampling strategies should be modified if we are to improve biological interpretations of optical measurements near the sea surface. For the present, analyses can be focused on bio-optical relationships that might be peculiar to near-surface waters.

Conditions in the Laboratory

The transmission of light in oceanic waters is strongly influenced by phytoplankton [*Morel*, 1988], so it is important to understand the optical properties of these living particles. A key objective is to describe the influence of biological processes on the apparent [e.g., *Smith and Baker*, 1978] and inherent [e.g. *Gordon et al.*, 1988] optical properties of the ocean; the inverse problem is to characterize variations of phytoplankton pigment or perhaps microbial biomass on the basis of optical observations [*Gordon et al.*, 1988; *Siegel et al.*, 1989; *Stramski and Reynolds*, 1993]. Variability in bulk optical properties of phytoplankton assemblages, normalized to pigment concentration, might reflect changes in community structure and physiological status. An integrated view of these relationships forms the "bridge between ocean optics and microbial ecology" [*Yentsch and Phinney*, 1989, p. 1694].

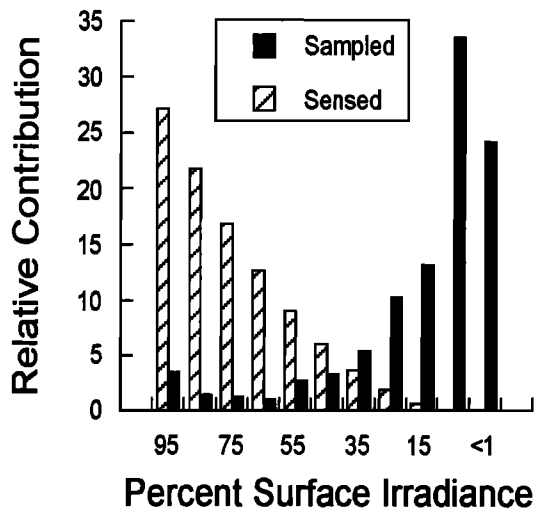

Figure 1. Sampling effort for a biological oceanographic cruise (relative proportion of samples, solid bars) as a function of relative irradiance (downwelling quantum irradiance, 400 - 700 nm, calculated from spectral irradiance and normalized to a deck reference), compared to the importance of each stratum to remote sensing, indicated by a weighting for water-leaving radiance (hatched bars). The weighting for remote sensing is approximated roughly as e^{-2kz}, where k (m^{-1}) is the attenuation coefficient for downwelling irradiance and z (meters) is depth [*Gordon*, 1979]. This example is from the WEC88 cruise in the equatorial Pacific Ocean [*Cullen et al.*, 1992a].

The optical properties of planktonic particles are functions of size, shape, pigmentation, and the concentration of intracellular materials that contribute to refractive index [*Morel*, 1990]. These properties can vary between taxonomic groups [*Sathyendranath et al.*, 1987; *Stramski and Kiefer*, 1991; *Johnsen et al.*, 1994] and with growth conditions for individual species [*Stramski and Morel*, 1990; *Ackleson et al.*, 1993; *Stramski et al.*, this issue]. Likewise, pigment fluorescence characteristics are a function of taxonomic grouping [*Yentsch and Phinney*, 1985] and physiological state [*Falkowski et al.*, 1992]. It is thus feasible to characterize microbial community structure, rate processes, or the physiological status of phytoplankton on the basis of optical measurements. In this context, progress has been made with active optical measurements, such as beam attenuation [*Denman and Gargett*, 1988; *Siegel et al.*, 1989; *Mitchell and Holm-Hansen*, 1991; *Cullen et al.*, 1992a], stimulated fluorescence [*Kiefer*, 1973b; *Cullen*, 1982], manipulative fluorescence techniques [*Demers et al.*, 1985; *Falkowski et al.*, 1992; *Kolber and Falkowski*, 1993] and flow cytometry [*Yentsch and Pomponi*, 1986; *Neale et al.*, 1989; *Perry and Porter*, 1989; *Olson et al.*, 1990; *Li et al.*, 1993]. Passive measurements of spectral reflectance and diffuse attenuation should also be useful, because they are differentially affected by variations in particulate scatter and absorption [*Gordon et al.*, 1988; *Roesler and Perry*, this issue], which change with community structure and physiological state of phytoplankton [*Mitchell and Holm-Hansen*, 1991; *Hoepffner and Sathyendranath*, 1992]. Another passive measurement, solar-stimulated fluorescence of chlorophyll [*Neville and Gower*, 1977; *Kiefer et al.*, 1989; *Chamberlin et al.*, 1990; *Kiefer and Reynolds*, 1992; *Gitelson et al.*, 1994], is closely (but not necessarily simply) related to biomass and photosynthesis. All these optical measurements, interpreted effectively, can enhance the utility of ocean color observations, which, up to now, have been used principally to estimate the concentration of chlorophyll-like pigment.

Laboratory studies of cultured phytoplankton are crucial to the interpretation of optical measurements. Studies on cultures describe the influence of light, temperature, and nutrition on growth rates [*Langdon*, 1988], pigment content [*Geider*, 1987; *Chalup and Laws*, 1990], and photosynthetic performance [*Li and Morris*, 1982; *Prézelin and Matlick*, 1983; *Kolber et al.*, 1988] of phytoplankton. Some strong generalizations can be made, even though a coherent and comprehensive description of these interacting environmental effects is not yet possible [*Cullen et al.*, 1993]. For example, increased light leads to reduced cellular pigmentation. It can be useful to consider "increased" as a relative term, referring to the absorption of photons by the cell (source), relative to its capacity to process those photons through photosynthesis and the anabolic processes that depend on it (sink). With respect to pigment content, a decrease of temperature (which would reduce enzymatic rates but not light absorption efficiency) or a reduction in nitrogen availability (which would reduce the rate of protein synthesis relative to the rate of light absorption) are both equivalent to increases in light intensity in that the ratio of source to sink increases. Balance is

restored by a reduction of pigment content [*Geider et al.*, 1986; *Cullen and Lewis*, 1988] and shifts in physiological and light-absorption efficiencies [*Geider*, 1987; *Chalup and Laws*, 1990; *Falkowski and LaRoche*, 1991]. Because these changes alter the quantitative relationships between light absorption, photosynthesis, and the specific growth rates of phytoplankton, they must be appreciated and quantified to describe biogeochemical dynamics on the basis of ocean color.

Here we encounter a problem. Generalizations about physiological limitation of phytoplankton productivity in the upper ocean [e.g., *Cleveland et al.*, 1989; *Kolber et al.*, 1990; *Geider et al.*, 1993] are made on the basis of field measurements compared with laboratory data on photosynthesis, growth, and light absorption of phytoplankton under a broad range of conditions. Few laboratory studies have been representative of the upper optical depth, however (i.e., irradiance greater than approximately 1000 μmol m^{-2} s^{-1} over a range of nutrient-limited growth rates). Also, sets of observations at lower irradiance (reviewed by *Cullen et al.* [1992b]) are contradictory for unknown reasons. Although present interpretations are generally consistent with available information, it is prudent to keep in mind that they might be altered as more data are obtained. As reliance on observations of near-surface processes increases and as large research programs are developed, it is essential, though not necessarily obvious, to include relevant laboratory research in the plans.

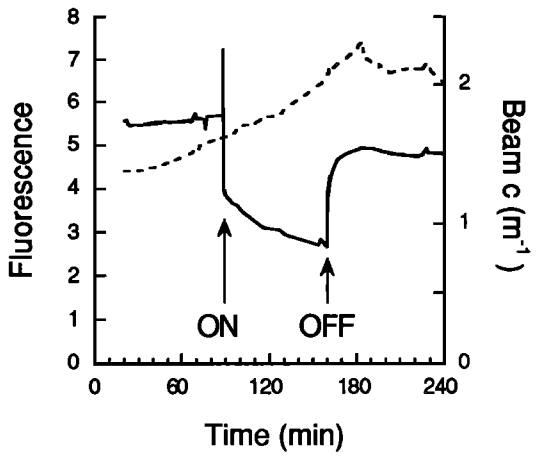

Figure 2. Inhibition of chlorophyll fluorescence (solid line) by bright light approximating near-surface conditions [*Cullen et al.*, 1988]. This experiment was done with a SeaTech fluorometer (solid line) and transmissometer (beam c, dashed line) immersed in a dilute culture of a marine diatom. "On" and "off" refer to the bright lights. Similar reductions of fluorescence relative to beam attenuation have been observed in near-surface waters and related to excess irradiance [*Denman and Gargett*, 1988; *Abbott et al.*, 1990].

Special Consideration of Near-Surface Observations

Although we need to know much more about near-surface biological processes and their optical consequences, a great deal of information can be obtained by examining available data for patterns peculiar to the upper optical depth.

Stimulated Fluorescence as a Measure of Chlorophyll

The concentration of chlorophyll *a* (chl*a*) near the surface should be accurately determined for validation of remote-sensing algorithms. Fluorometry, particularly in situ stimulated fluorometry, is especially important for estimating chl*a* [*Strass and Woods*, 1988; *Dickey*, 1991]. Techniques for continuous underway transects of fluorescence have been reviewed [*Smith et al.*, 1981], but some principles bear repeating in this context. Many studies have shown that fluorescence per unit chl*a* declines rapidly in bright light [*Kiefer*, 1973a, b; *Loftus and Seliger*, 1975; *Harris*, 1980; *Vincent*, 1980; *Abbott et al.*, 1982; *Denman and Gargett*, 1988; *Demers et al.*, 1991], an expression of nonphotochemical quenching and other physiological processes [*Kiefer and Reynolds*, 1992]. This response has been observed experimentally with modern in situ fluorometers (e.g., Figure 2), so it would seem reasonable to consider irradiance explicitly when calibrating fluorometers used in surveys or moorings, particularly because irradiance-dependent underestimates of near-surface chlorophyll could seriously compromise efforts to relate in situ observations to estimates of ocean color from satellites. However, because samples from near the surface generally represent only a small proportion of the data for field calibration or validation (Figure 1), commonly used regression analyses (Figure 3a) will not detect an influence of irradiance, and underestimates of near-surface chl*a* of about 40% can result (Figure 3b). The relationships in Figure 3 show that near-surface effects are not important if calibrations are intended for the entire euphotic zone, but they should be explicitly quantified if accuracy is desired for near-surface estimates of chl*a* from in situ fluorometry.

Solar-Stimulated Fluorescence

Because solar irradiance stimulates the fluorescence of chl*a* near 683 nm, "natural fluorescence" can be detected passively in situ [*Kiefer et al.*, 1989; *Chamberlin et al.*, 1990; *Stegmann et al.*, 1992] and sensed remotely in water-leaving radiance [*Neville and Gower*, 1977; *Gordon*, 1979; *Kishino et al.*, 1984a,b; *Roesler and Perry*, this issue]. Natural fluorescence, estimated from in situ measurements of upwelling radiance at 683 nm (L_u683), has been related to both the concentration of chl*a* and the instantaneous rate of photosynthesis P using functions of local photosynthetically active radiation (PAR) [*Kiefer et al.*, 1989; *Chamberlin et al.*, 1990; *Chamberlin and Marra*, 1992]. Principally because backscattered solar radiation at 683 nm would be detected near the surface, but also because the physiological consequences of excess irradiance are hard to assess, these functions were developed and evaluated for depths below several meters. However, commercially available instruments (e.g., Biospherical Instruments, San Diego, California) use an algorithm to report photosynthesis solely on the basis of L_u683, with no explicit rejection of near-surface measurements contaminated by backscatter.

Let us consider measurements close to the surface, where both in situ and remote instruments can detect the fluorescence of chl*a*. Accepting that published functions [*Chamberlin et al.*, 1990; *Chamberlin and Marra*, 1992] adequately describe the relationship between L_u683 and P in deeper strata, we can ask if the relationship is the same for the upper optical depth, once the data are corrected for backscattered solar irradiance.

The measurement of the fluorescence band and the correction for backscatter are naturally a concern, and sources of error have been identified [see *Roesler and Perry*, this issue]. When

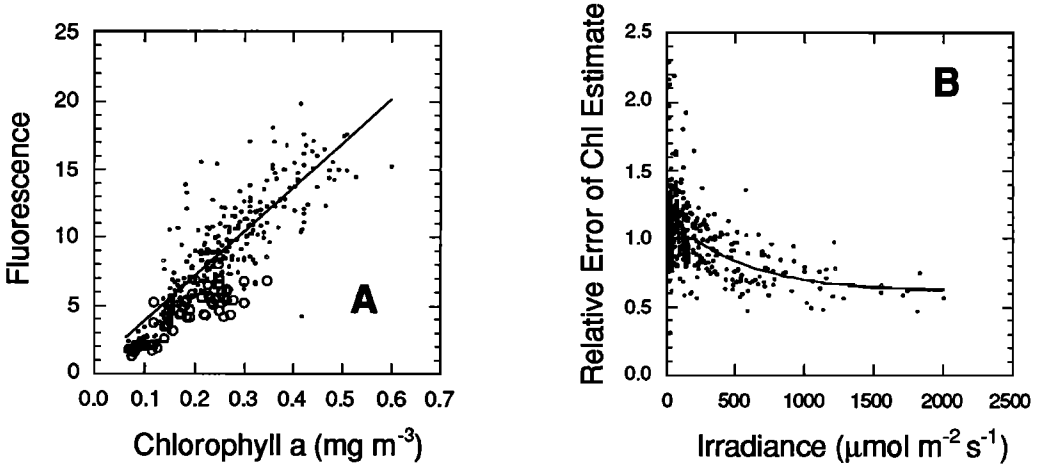

Figure 3. (a) Linear-regression calibration of a SeaTech fluorometer for a cruise in the equatorial Pacific Ocean (data from F. Chavez and C.O. Davis [see *Cullen et al.* 1992a]). Fluorescence is in arbitrary units. Downwelling quantum irradiance (photosynthetically available radiation (PAR) 400 - 700 nm) was calculated from downwelling spectral irradiance. Depths below the 1% light level, which commonly show anomalous fluorescence:chl*a*, have been excluded. Samples corresponding to high irradiance (> 500 μmol m^{-2} s^{-1}) are represented with open circles. Number of samples is 357, proportion of variance explained r^2 is 0.74. (b) Apparent effect of in situ irradiance E_d on the estimation of chl*a* from SeaTech fluorescence: the ratio of measured versus estimated chl*a* (from Figure 3a) as a function of E_d in situ. The line is a best fit to a simple exponential model of estimated chl*a*, relative to measured, as a function of irradiance greater than a threshold: estimated / measured = 0.61 + 0.39{exp[-(E_d - 199) / E_k]}, where E_k = 542 μmol m^{-2} s^{-1}. The threshold (199 μmol m^{-2} s^{-1}) was determined by the curve-fitting process. Application of this correction to the calibration algorithm in (Figure 3a) left the r^2 nearly unchanged at 0.76. This is not a significant improvement if the criterion is variance explained for the entire data set. The effect was negligible, because relatively few near-surface samples contribute to total variance. The pattern in Figure 3b is very similar to that presented by Marra [1992] for a moored fluorometer, except that he plotted fluorescence relative to the morning maximum at that depth.

radiance is measured at appropriate wavelengths above and below the emission band of chl*a* fluorescence, an imperfect [*Roesler and Perry*, this issue], but useful baseline correction can be applied [*Neville and Gower*, 1977; *Gordon*, 1979; *Gitelson et al.*, 1994]. A less accurate method requiring fewer sensors is to measure downwelling irradiance at 683 nm (E_d683) and to correct L_u683 by applying a reflectance ratio [*Stegmann et al.*, 1992]. If only L_u683 and quantum scalar irradiance (PAR) are measured, as with commercially available natural fluorometers, near-surface observations must be discarded. Without additional information on the irradiance field, however, it is difficult to know exactly the depth at which the influence of scattered solar irradiance becomes significant. *Kiefer et al.* [1989] suggested that 6 m was a cutoff, but this would depend on water type.

The relationship between natural fluorescence and PAR at high irradiance can be examined using data from the equatorial Pacific ocean at 150°W, where bio-optical studies were conducted in February 1988 [*Cullen et al.*, 1992a; *Stegmann et al.*, 1992]. Both P^B (normalized photosynthesis; g C g chl*a*$^{-1}$ h^{-1}) and natural fluorescence yield (as approximated by backscatter-corrected L_u683 normalized to chl*a*) can be described as functions of irradiance, showing similar saturation phenomena at 500 - 1000 μmol m^{-2} s^{-1} (Figure 4a).

A critical parameter for modeling purposes is the ratio of natural fluorescence to photosynthesis [*Kiefer et al.*, 1989], approximated here by the ratio of backscatter-corrected L_u683 to modeled P. The ratio is a positive function of PAR at low irradiance and varies little between about 300 and 1600 μmol m^{-2} s^{-1} (Figure 4b). In contrast, the empirical function of *Chamberlin et al.* [1990], when plotted in this parameter space, describes the ratio of yields as a direct, linear function of irradiance.

We have purposely presented our L_u683:P ratio in arbitrary units to quell any thoughts of using data from only one station for an empirical algorithm relating photosynthesis to fluorescence. Only shapes of the two relationships in Figure 4b should be compared. Given the variability in measurements presented to date, it would be difficult to distinguish between the shape of the equatorial relationship and that of the *Chamberlin et al.* [1990] model for irradiance less than about 800 μmol m^{-2} s^{-1} (i.e., the range of irradiance for which the algorithm was originally intended). We conclude from this comparison that (1) the empirical function presented by *Chamberlin et al.* [1990] for deeper strata should not be extrapolated to near-surface irradiance, even if backscatter-corrected measurements are available and (2) if measurements of near-surface L_u683 are to be used for estimating P, then new algorithms must be developed and validated using measurements of P near the surface.

The exact shape of the saturating fluorescence-versus-photosynthesis function for equatorial phytoplankton in Figure 4b cannot be known, because it is so dependent on the backscatter correction, but it is clearly different from the linear relationship presented by *Chamberlin et al.* [1990]. The linear function is consistent with a model of fluorescence and photosynthesis that predicts nearly all photosynthetic reaction centers to be open (i.e., immediately functional) in dim light, declining to zero as irradiance approaches near-surface intensities [*Kiefer and Reynolds*, 1992, Figures 2 and 3]. However, data presented by *Kiefer and Reynolds* [1992, Figure 8]) show that about 30% of

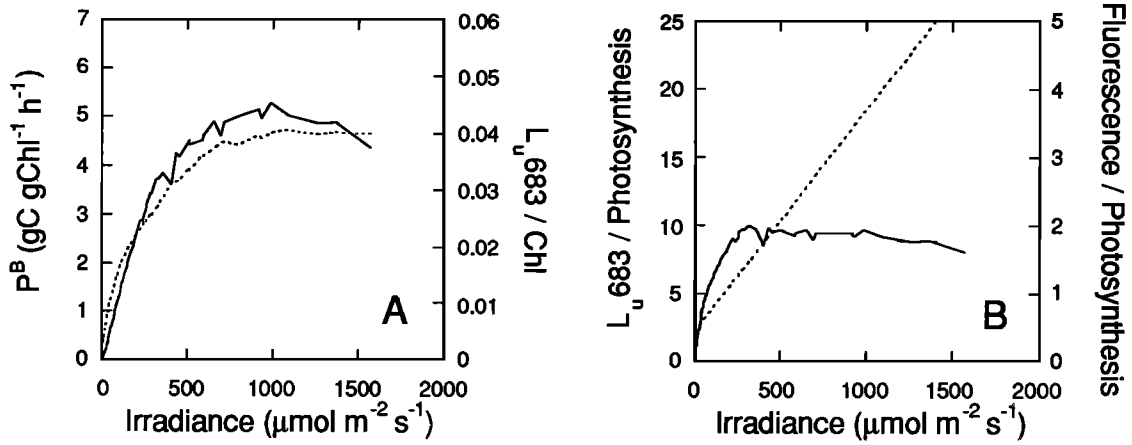

Figure 4. (a) Chlorophyll *a*-specific photosynthetic rate P^B (dotted line) and backscatter-corrected L_u683 / chl*a* (relative units, solid line) versus quantum scalar PAR I (μmol m^{-2} s^{-1}) at a station on the equator in the Pacific (150°W). Conditions varied little over 6 days at the station [*Cullen et al.*, 1992a], so midday observations were averaged. Measurements of short-term P versus I (1-hour photosynthetron incubations with 24 subsamples of 1 mL each) and chl*a*, at 4 depths, along with continuous profiles of stimulated fluorescence and PAR, were used to model P^B versus I in the euphotic zone [*Cullen et al.*, 1992a]. Because of small sample sizes, the contribution of large cells and aggregates to measurements of P was underestimated, but this should affect magnitude of P^B much more than the shape of P^B versus I. Midday profiles of L_u683 were corrected for backscatter as described by *Stegmann et al.* [1992], averaged, and normalized to chl*a*. (b) The ratio of natural fluorescence:P (from Figure 4a), plotted versus irradiance at the equatorial station (solid line), compared to the empirical relationship presented by *Chamberlin et al.* [1990; equation 15], extrapolated beyond its intended upper limit for illustrative purposes (dotted line). Caution: the equatorial L_u683:P ratio is in arbitrary units, and only the shapes of the two relationships should be compared. The shape of the equatorial relationship is sensitive to the choice of reflectance ratio for the backscatter correction. A value of 0.00026 sr^{-1} was used, as mentioned by *Chamberlin et al.* [1990].

reaction centers remain open for irradiance greater than about 200 μmol m^{-2} s^{-1} PAR. This unexplained phenomenon should be explored in the context of fluorescence-versus-photosynthesis models. A first-order effect (calculations not shown) would be to bend the linear relationship in Figure 3b toward the shape of the saturating function for the equatorial Pacific phytoplankton.

Incubations to Measure Productivity

A balanced evaluation of near-surface observations and interpretations requires critical examination of the biological as well as the optical measurements. Modern analytical methods (high-performance liquid chromatography (HPLC)) should accurately measure particulate pigments [*Mantoura and Llewellyn*, 1983], so the measurement of chl*a* will not be discussed, except to mention that some commonly used solvents, such as 90% acetone, do not efficiently extract all marine samples and that passage of particulate pigment through filters can be a concern [*Phinney and Yentsch*, 1985; *Dickson and Wheeler*, 1993]. More aggressive extraction (e.g., dimethyl sulfoxide, with or without acetone [*Shoaf and Lium*, 1976; *Stramski and Morel*, 1990]) should be used periodically to check for problems, and different filters should be compared to ensure convincing results.

Measurements of near-surface photosynthesis, essential to the calibration and validation of bio-optical estimates of productivity in the upper optical depth, are much more problematic. The potential for error has been described many times [*Harris*, 1978; *Marra*, 1978; *Legendre and Demers*, 1984; *Gallegos and Platt*, 1985; *Neale*, 1987; *Cullen and Neale*, 1993]. A major problem is that conventional measurements of photosynthesis near the surface require incubation of samples in bottles for hours to a day at constant irradiance relative to the surface. Such long incubations mimic natural irradiance if the water column is strongly stratified, but if the water mixes vertically, average rates of photosynthesis in near-surface incubations will underestimate natural rates due to artifactual photoinhibition. This is because phytoplankton in nature can tolerate and exploit brief exposures to supersaturating irradiance near the surface associated with vertical mixing, but during prolonged exposures (greater than approximately 30 min), photosynthetic rates decline [*Neale*, 1987].

An example from the equatorial Pacific (Figure 5) shows how the artifact of static incubation can be quantified. Vertical mixing extended to at least 50 m at 10°N on the day of sampling. This was indicated not only by constant temperature, but also by vertically uniform chl*a* and short-term photosynthesis versus quantum-scalar PAR (P versus I) curves for phytoplankton assemblages within the upper 40 m near dawn, midday, and dusk (data not shown). If the water had not been mixing more rapidly than the adaptation time of phytoplankton (scale of hours [*Cullen and Lewis*, 1988]), then P versus I would have differentiated with depth during the course of the day. To quantify the potential responses of phytoplankton to the light gradient near the surface, we incubated samples in conventional on-deck incubators from early morning until 1530 LT. The incubated samples showed profound responses to the light gradient. In particular, they experienced cataclysmic photoinhibition (reduction of photosynthetic capacity and destruction of chl*a*) during the incubation designed to simulate near-surface conditions. If the incubations had been done in UV-transparent containers, even more destruction would likely have been observed [*Cullen and Neale*, 1993]. Clearly, the incubations were a poor simulation of natural conditions: they indicated severe photoinhibition near the

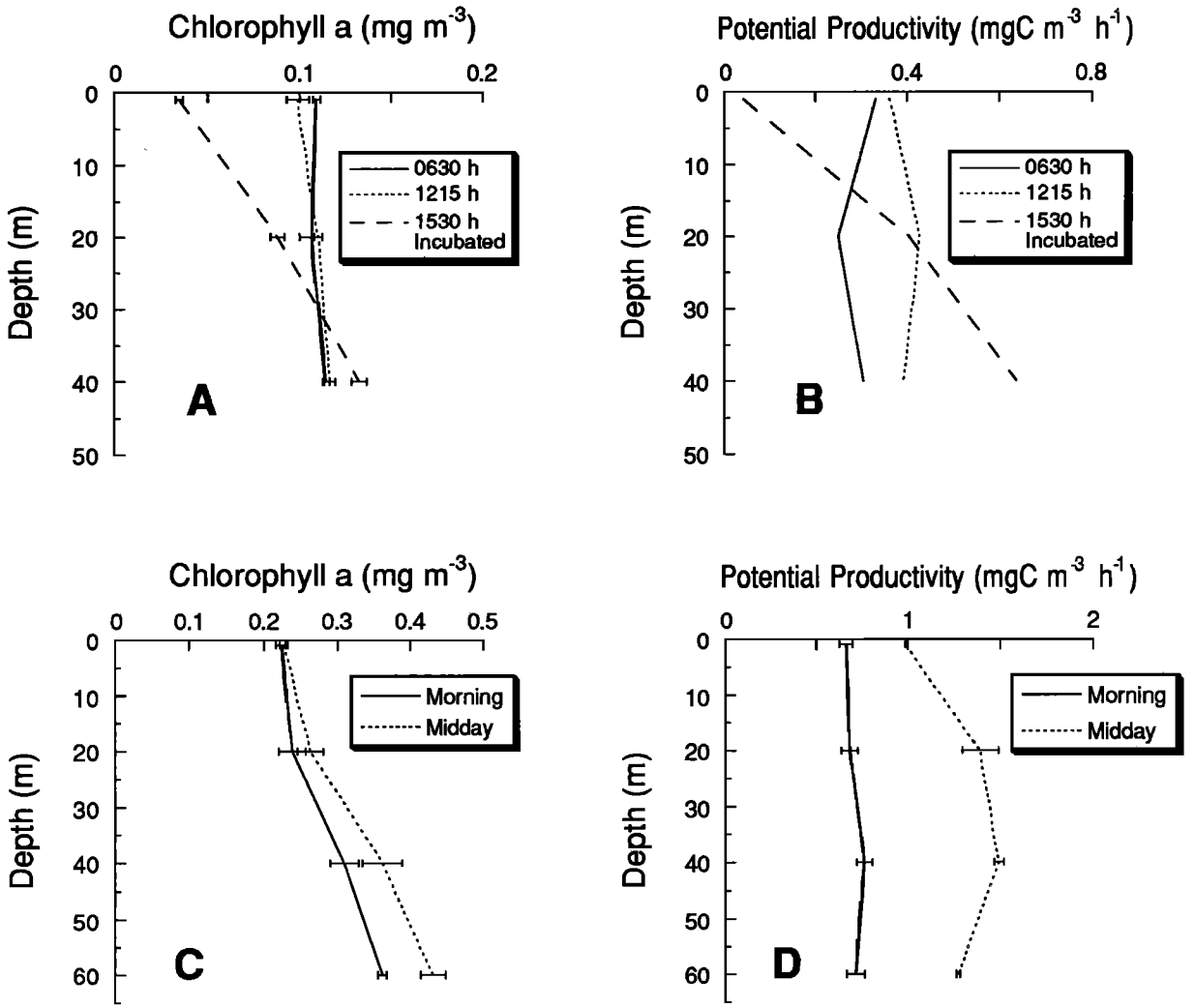

Figure 5. Vertical mixing and the artifacts associated with fixed-depth incubations. These data are from stations in the equatorial Pacific Ocean at (a)-(b) 10°N, 150°W where there was a well-developed mixed layer to about 50 m [from *Cullen and Neale,* 1993] and at (c)-(d) the equator (150°W), where nocturnal mixing extended below 20 m followed by stratification that was established each day by solar heating (data from *Cullen et al.,* [1992a]). Figures 5a and 5c show concentration of chl*a*; while Figures 5b and 5d show potential productivity. Error bars in Figure 5a are standard errors of triplicates; in Figures 5c and 5d they represent standard errors for the measurements averaged over 6 days. Potential productivity was determined from short-term P versus I measurements; it is maximal photosynthesis per unit chl*a* times the chl*a* concentration. When photoinhibition of photosynthesis occurs, potential productivity declines. Profiles labeled 0630 hours (solid lines) and 1215 hours (dotted lines) are measurements made on fresh samples from hydrocasts at the vertically mixed station (LT). Data labeled 1530 hours (dashed lines) are from 0630-hour samples incubated until 1530 hours in a conventional simulated in situ incubator, with UVB and some UVA radiation excluded by an acrylic incubator and polycarbonate containers. Assuming that the midday profile, when irradiance was maximal, is characteristic for the afternoon, we predict that if incubations mimicked nature, the incubated samples would show the same vertical patterns as the fresh samples. They don't. Instead, these data show severe photoinhibition during conventional incubations near the surface, resulting in massive net destruction of chl*a*, even though UVB and some UVA was excluded. Measurements on fresh samples at 1215 LT suggest that vertical mixing moved the phytoplankton through the light gradient fast enough to protect them from such damage. This inference is supported by a calculation of photosynthesis in the mixed layer from P versus I, chl*a* and vertical profiles of I. Modeled productivity for incubated samples was 35% lower than for fresh samples. At the equator (Figures 5c and 5d), samples from stratified surface waters showed evidence of photoinhibition in situ; potential productivity was depressed about 30% relative to 20 m, even though the two depths were similar in the morning. These experiments show the utility of the "fresh sample" approach [*Vincent et al.,* 1984; *Neale and Richerson,* 1987; *Cullen et al.,* 1989] and demonstrate that the results of near-surface incubations should be interpreted with caution if the water column is mixed vertically.

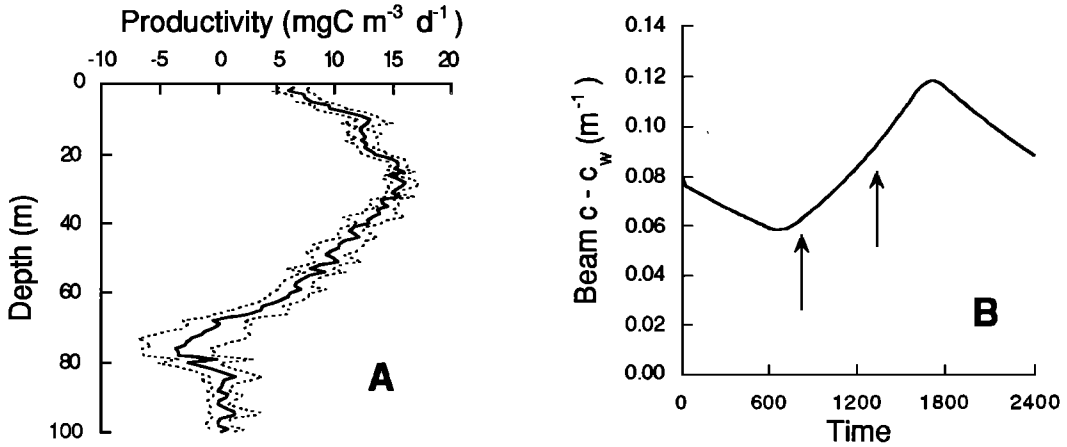

Figure 6. (a) Primary productivity (5-day mean plus/minus standard error) at a station in the equatorial Pacific, estimated from the average hourly change of beam attenuation between morning (about 0830 LT) and afternoon (about 1330 LT) observations. Estimated integral productivity was 702 mg C m^{-2} d^{-1}. The estimate from 24 hour ^{14}C incubations was 710 mg C m^{-2} d^{-1}. (b) Diel changes of beam attenuation (corrected for the contribution of water c_w) from a model of particle dynamics. The model equates beam c-c_w with particle concentration. Arrows indicate the times at which most measurements were made, constraining the model [from *Cullen et al.*, 1992a]. Data from moorings provide much better temporal resolution.

surface, whereas freshly sampled phytoplankton in nature showed no ill effects of being near the surface at midday. We cannot exclude the possibility that a part of the assemblage experienced irreversible damage near the surface which was obscured by vertical mixing, but we can assert that static incubations produced extreme artifacts, which demonstrate that conventional methods are inappropriate for estimating near-surface photosynthesis during vertical mixing. It should be noted that at the equator, where solar heating produced diurnal stratification of the water column [*Carr et al.*, 1991], the same types of experimental observations indicated measurable photoinhibition of photosynthesis in the natural water column (Figures 5c and 5d) as well as in bottles [*Cullen et al.*, 1992a, Figure 5a], similar to what was observed during diel stratification in the tropical alpine Lake Titicaca [*Vincent et al.*, 1984; *Neale and Richerson*, 1987].

These results reinforce a recommendation that has been made before: the timescale of the measurement should match the time scale of the process. Simply, conventional strategies are often inappropriate for measuring primary productivity near the surface. Short incubations and P versus I determinations may help, but these methods can have drawbacks, such as difficulties accounting for rare large cells or aggregates using small sample volumes [*Cullen et al.*, 1992a]. Perhaps independent methods of estimating instantaneous photosynthesis, such as manipulative fluorometry [*Kolber and Falkowski*, 1993] will provide the information necessary to determine relative photosynthetic rates near the surface during vertical mixing.

It should be remembered that, with respect to the modeling of primary productivity, proper evaluation of near-surface photoinhibition is essential only if near-surface processes figure prominently, e.g., when productivity is to be estimated from solar-stimulated fluorescence or changes in beam attenuation (see below), and when near-surface measurements are needed for algorithm development. Artifactual underestimation of near-surface photosynthesis has a smaller effect on integral water-column productivity, however [*Gallegos and Platt*, 1985], so it is not a big problem if the objective is to relate ocean color to areal rates of photosynthesis.

Particle Dynamics From Optical Measurements

Recently, *Siegel et al.* [1989] described yet another bio-optical approach to estimating primary productivity; they interpreted the diel variability of beam attenuation (beam c, m^{-1}) as a manifestation of particle dynamics (Figure 6). In their model, the observed increase of attenuation during the day is ascribed to light-dependent growth of autotrophs, balanced by a constant loss process which is responsible for the decline of c overnight. The assumptions and limitations of the model have been discussed at some length [*Siegel et al.*, 1989; *Cullen et al.*, 1992a] and have also been explored experimentally [*Ackleson et al.*, 1993; *Stramski and Reynolds*, 1993; *Stramski et al.*, this issue]. Here we examine the assumption that, on the diel timescale, beam attenuation, corrected for the contribution due to water, can be used as an accurate measure of particulate carbon, i.e., that the carbon-specific attenuation coefficient c_c^* (m^2 mg C^{-1}) remains constant. Because the organic carbon content of phytoplankton cannot be measured directly [*Eppley*, 1980], we evaluate the assumption by looking for consistency between predictions from beam c measurements and those from other oceanographic observations.

Cullen et al. [1992a] showed that if variation of beam c is used to describe particle dynamics, then the attenuation measurements, which must be converted to estimates of phytoplankton carbon, specify not only photosynthesis, but also the C:chl*a* ratio of phytoplankton (g g^{-1}) and their specific growth rate μ (d^{-1}). Critical assumptions include the chosen c_c^*, the proportional contribution of autotrophs to total attenuation [*Stramski and Kiefer*, 1991], and the nature of foodweb interactions between optically detectable components [*Siegel et al.*, 1989]. Predictable biases arise when some assumptions are violated. For example, growth rates and photosynthesis would be overestimated if grazing pressure were higher at night or if c_c^* was elevated in direct response to increased irradiance [*Ackleson et al.*, 1993] or as part of the cell division cycle [*Olson et al.*, 1990; *Stramski and Reynolds*, 1993; *Stramski et al.*, this issue].

Calculations show that a simple model treating beam attenuation as a measure of particulate C (Table 1) fails to

Table 1. The Use of Changes in Beam Attenuation to Estimate Primary Productivity, Growth Rate, and Chemical Composition of Phytoplankton at a Station in the Equatorial Pacific (30 m, Figure 6)

Parameter	Units	Independent Estimate	Simple Optical Model	Physiological-Optical Model
f_p	dimensionless		0.5	0.5
f_c	dimensionless		0.7	0.7
c_c^*	m^2 mg C^{-1}		0.004	0.002
Δc_c^*	dimensionless		0	+30%
P	mg C m^{-3} d^{-1}	12.3	22.7	13.5
μ	d^{-1}	0.7	1.85	0.67
C:chl*a*	g g^{-1}	58	27	53

The parameters f_p (proportion of total attenuation attributable to autotrophs), f_c (proportion of total ^{14}C uptake expected to be measurable in the small particles as opposed to the grazers, which are assumed to contribute insignificantly to attenuation), c_c^* (specific attenuation coefficient for C), and Δc_c^* (the proportional change in c_c^* assumed to occur in the 5 hours between the morning and afternoon profiles, due to physiological processes and changes in the particle-size spectrum) must be specified to interpret beam c in this context. The independent estimate of rate of photosynthesis P is from 24-hour ^{14}C incubations, specific growth rate μ comes from several estimates based on incubations, and carbon-to-chlorophyll *a* (C:chl*a*) was estimated from chemical measurements. Once the parameters are chosen, μ, P, and C:chl*a* are specified as a function of beam c and its diel variation [*Cullen et al., 1992* a]. The simple optical model uses reasonable guesses for these parameters. The physiological-optical model was tuned for better agreement between optical estimates and independent estimates. Diel variability in grazing pressure would influence predictions in a manner that would be difficult to distinguish from Δc_c^*. See text for details and references.

produce reasonable estimates of productivity P, growth rate μ, and also chemical composition of phytoplankton (C:chl*a*) at a station in the equatorial Pacific (30 m, Figure 6). Independent estimates were obtained by more established procedures: productivity from 24-hour ^{14}C incubations, growth rate from several estimates based on incubations [*Chavez et al.*, 1991; *Cullen et al.*, 1992a], and C:chl*a* from chemical measurements [*Eppley et al.*, 1992]. The parameters f_p (proportion of total attenuation attributable to autotrophs), f_c (proportion of total ^{14}C uptake expected to be measurable in the small particles as opposed to the grazers [cf. *Smith et al.*, 1984]), c_c^* (specific attenuation coefficient for C), and Δc_c^* (the proportional change in c_c^* assumed to occur in the 5 hours between the morning and afternoon profiles, due to physiological processes and changes in the particle-size spectrum) must be specified to interpret beam c in this context [*Cullen et al.*, 1992a]. Once the parameters are chosen, μ, P, and C:chl*a* are specified. The simple optical model in Table 1 uses reasonable guesses for these parameters, including c_c^* from *Siegel et al.*, [1989], but it excludes the possibility of a change in c_c^* and thus overestimates μ and underestimates C:chl*a*. Consequently, we developed a physiological-optical model to give reasonable agreement between estimates; by halving c_c^* and setting Δc_c^* to +30%, the parameterized variability of beam attenuation was brought into conformity with our understanding of productivity, chemical composition, and particle dynamics of the equatorial assemblage (Table 1). We do not know if these two fairly arbitrary assumptions about cellular optics accurately represent conditions in the equatorial Pacific, but they are closely consistent with direct measurements from a recent laboratory study [*Stramski et al.*, this issue], and the resulting calculated growth rate is consistent with our initial estimate [*Cullen et al.*, 1992a] and what has been subsequently reported for the region [*Murray et al.*, 1994]. Diel variability in grazing pressure would influence predictions in a manner that would be difficult to distinguish from Δc_c^*. The point of this presentation (supported by other calculations not shown here) is that a simple optical model, excluding changes in c_c^* or diel variability in grazing, cannot produce internally consistent estimates of P, μ, and also C:chl*a*. It is reasonable to look for processes that cause c_c^* to change [*Ackleson et al.*, 1993; *Stramski and Reynolds*, 1993; *Stramski et al.*, this issue].

A simplified model ("anomalous diffraction approximation" of cellular optical properties as presented by *Morel and Bricaud* [1986] and *Ackleson et al.* [1990], among others) was constructed to illustrate some of the changes in beam attenuation that might occur in response to short-term physiological changes in phytoplankton (Figure 7). Calculations were made for attenuation of light at 660 nm, as measured by conventional transmissometers. Three alterations of cellular characteristics are simulated. We represent "growth" as a 10% increase in cellular diameter with no change in refractive index or in the intracellular absorption coefficient (cellular C increases 33%). "Swelling" is modeled as a 10% increase in diameter, but not in C per particle (i.e., cells take on water); refractive index and intracellular absorption coefficients are reduced according to the appropriate dilution factor. "Storage" represents the net accumulation of cellular material but no increase in size (refractive index and intracellular absorption coefficients increase 33%). These idealized results for suspensions of particles with uniform size and optical properties demonstrate that fairly small changes in size and chemical composition of particles can correspond to rather large changes of attenuation, independent of changes in particulate C [see *Ackleson et al.*, 1993] but strongly dependent on initial refractive index (data not shown) and cell diameter. This could confound efforts to use beam c as a measure of particulate carbon. We suggest that if beam attenuation is to be used to measure particle dynamics as a complement to remote sensing, more attention should be focused on the possible causes of variable carbon-specific attenuation in nature.

Conclusions

The unique nature of the light environment of the upper euphotic zone has significant implications for the remote sensing of both the pigment concentration and the rate of primary productivity in the ocean. Future space-based ocean color missions and the increased attention being paid to autonomous

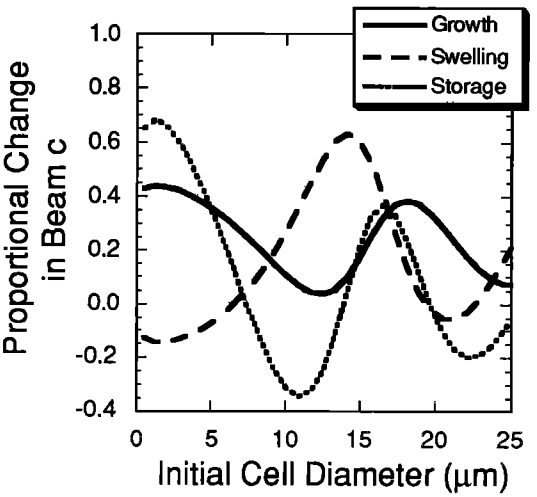

Figure 7. Changes of beam attenuation in a suspension of spherical particles, modeled as a function of initial diameter. These are results of the "anomalous diffraction approximation" (see text). Growth is represented as a 10% increase in diameter with no change in refractive index or in the intracellular absorption coefficient (cellular C increases 33%). Swelling is modeled as a 10% increase in diameter, but not in C per particle (i.e., cells take on water). Storage is represented as a 33% increase in the concentration of cellular constituents, including C. with no change in cell diameter. Calculations for each initial diameter are for attenuation of light at 660 nm by suspensions of particles homogeneous with respect to size and optical properties. Initial settings are refractive index (real part) = 1.05; concentration of intracellular C = 150 kg m^{-3}; and specific absorption coefficient for C = 0.2 m^2 g C^{-1}. In a heterogeneous population of particles the oscillations as a function of wavelength would tend to cancel out, thereby reducing the variability of beam c as a function of cell diameter [*Morel and Bricaud*, 1986].

buoy observations will depend in large part on the success of so-called bio-optical algorithms relating optical signals to properties and processes of interest in a biogeochemical context. Here we have argued that physiological adaptation to high irradiance in the surface waters results in strong variations in the optical properties of the phytoplankton which must be understood and parameterized in future bio-optical algorithms.

For example, assuming that satellite radiance observations can be perfectly corrected for atmospheric contributions, the observed water-leaving radiances must be related to pigment concentration and perhaps the productivity of the upper euphotic zone. Ignoring processes such as fluorescence or Raman scattering for now, the radiances can be cast directly from first principles in terms of the inherent optical properties, suitably integrated with respect to depth, and the local surface spectral irradiance. Variations in these inherent optical properties can then, in principle, be explicitly decomposed into contributions from dissolved and particulate constituents, and the seawater itself [e.g. *Gordon et al.*, 1988; *Morel*, 1988]. The accuracy of the decomposition depends on empirical observations relating biological to optical properties; we have seen in the above that these relationships have a high degree of variability, in particular as a result of the high irradiance conditions experienced in the upper ocean. While most of the laboratory experiments to date have been instructive in evaluating physiological responses at low intensities, they are insufficient for the robust development of semiempirical algorithms for remote sensing of biological processes from measurements of the ocean surface layer. It is our contention that these physiological variations can be a dominant term in error budgets for the retrieval of pigment concentration and, in particular, primary productivity, from such remote observations.

Nowhere is this more true than the estimation of pigment and productivity from remote measurement of solar-stimulated fluorescence. Several upcoming satellite missions (NASA's moderate-resolution imaging spectrometer, MODIS, and the European Space Agency's medium-resolution imaging spectrometer, MERIS) will attempt to measure water-leaving radiances near 683 nm with a view toward evaluating the contribution by fluorescent phytoplankton. Apart from the not insurmountable technical difficulties of making the measurement with sufficient signal to noise ratio, there is an extremely scant body of evidence that makes the link between the measured signal and the biological properties at high irradiance levels (e.g., Figure 4). Much work remains to be done.

This is not to say that the situation is bleak, more that there has been insufficient attention paid to the relationships between optical and biological properties in the near-surface region. It is a difficult and optically complicated environment to work in, and lessons learned in the interior do not translate well to the surface environment. The development of new bio-optical algorithms with a high degree of accuracy and precision will require significant effort, both in the field and in the laboratory, to describe quantitatively the responses of phytoplankton to high light. As work progresses, particularly in the laboratory, where artificial sources of irradiance are used, the potential influences of wave-induced variability [*Stramski and Legendre*, 1992; *Stramski et al.*, 1993] and ultraviolet radiation [*Smith et al.*, 1992; *Cullen and Neale*, 1993; *Vincent and Roy*, 1993] should be considered.

The measurements that we have discussed, stimulated fluorescence, natural fluorescence, beam attenuation, and near-surface photosynthesis, will be used to relate remotely sensed information to biological processes in the sea. We have identified problems in making or interpreting these measurements near the sea surface. Although we can not fully explain or quantify the processes that cause errors in our measurements, we can make reasonable corrections or modifications to methods, thereby obtaining better information for developing and validating bio-optical models for remote sensing.

Notation

μ	specific growth rate, d^{-1}.
c	beam attenuation coefficient, m^{-1}.
c_w	beam attenuation coefficient for pure seawater (0.364 m^{-1}), m^{-1}.
c_c^*	specific attenuation coefficient for C, m^2 mg C^{-1}.
Δc_c^*	proportional change in c_c^*, dimensionless.
chl*a*	chlorophyll *a* concentration, mg m^{-3}.
C:chl*a*	carbon-to-chl*a* ratio of phytoplankton, g C g chl a^{-1}.
E_d	downwelling quantum irradiance (PAR), μmol m^{-2} s^{-1}
E_d683	downwelling irradiance at 683 nm, W m^{-2} nm^{-1}.
f_p	proportion of total attenuation attributable to autotrophs, dimensionless.

f_c	proportion of total ^{14}C uptake expected to be measurable in the small particles as opposed to the grazers, dimensionless.
I	quantum scalar irradiance (PAR) μmol m^{-2} s^{-1}.
k	diffuse attenuation coefficient, m^{-1}.
L_u683	upwelling radiance at 683 nm, W m^{-2} nm^{-1} sr^{-1}.
P	rate of photosynthesis, mg C m^{-3} h^{-1}, mg C m^{-3} d^{-1}.
P^B	rate of photosynthesis, normalized to chl*a*, mg C mg chl a^{-1} h^{-1}.
PAR	photosynthetically available quantum radiation, μmol m^{-2} s^{-1}.
z	depth, m.

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