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Maximal quantum yield of photosynthesis in the northwestern Sargasso Sea

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ABSTRACT

The magnitude and variability of the maximal quantum yield of photosynthesis were examined in the northwestern Sargasso Sea in April 1985. Maximal quantum yield was calculated from light-limited photosynthetic rates and spectrally-weighted absorption coefficients. The absorption by total particulates collected on a glass fiber filter was partitioned into two components, one associated with living phytoplankton and one associated with other absorbing particles. Two types of maximal quantum yield were calculated: one from the absorption by total particulates and one from the absorption by the phytoplanktonic component alone. Maximal quantum yield calculated from absorption by total particulates was low [0.014 to 0.071 mol C (mol photons)$^{-1}$] and decreased as the proportion of absorption due to the nonphytoplanktonic particles increased. The phytoplanktonic maximal quantum yield was higher [0.033 to 0.102 mol C (mol photons)$^{-1}$] and varied by a factor of two over a period of two weeks during and following a spring bloom. Use of the phytoplanktonic component of absorption to calculate maximal quantum yield allowed analysis of changes in maximal quantum yield as a function of changes in phytoplankton physiology rather than changes in the amount of absorption by particulate detritus. The pattern of variation in quantum yield was related to nitrogen flux; these data suggest that maximal quantum yield can be predicted from environmental conditions on a regional or seasonal basis.

1. Introduction

Photosynthetic rates in the ocean are dependent on the absorption of incident irradiance by phytoplankton and the efficiency with which phytoplankton use this absorbed energy. By simplifying the control of the photosynthetic process to only these processes, primary production can be modelled as a function of irradiance, chlorophyll *a* concentration, the chlorophyll *a*-specific absorption coefficient, maximal quantum yield of photosynthesis, and a light-saturation parameter (Bannister, 1974; 1979; Smith, 1980; Kiefer and Mitchell, 1983; Collins *et al.*, 1986; Bidigare *et al.*, 1987). In

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this study, we measured two of these parameters, the chlorophyll *a*-specific absorption coefficient and the maximal quantum yield for phytoplankton populations in the northwestern Sargasso Sea.

Maximal quantum yield (ϕ_{max}) is defined as the maximal moles of carbon dioxide fixed or oxygen evolved per mole of photons absorbed at irradiances which are subsaturating to photosynthesis (Rabinowitch and Govindjee, 1969; Bannister, 1974). Maximal quantum yield represents the efficiency with which the photosynthetic apparatus converts absorbed electromagnetic energy to chemical energy. It is generally accepted that ϕ_{max} is 0.125 or 0.100 mol O_2 (mol photons)$^{-1}$, indicating that 8 or 10 quanta are required to produce one O_2 molecule (Kok, 1960; Radmer and Kok, 1977). Reduction of nitrate to ammonium competes with CO_2 fixation for photochemically produced reductant, so that ϕ_{max} for carbon fixation is lower than ϕ_{max} for oxygen evolution when phytoplankton are grown on nitrate. As a consequence, the ratio of O_2 evolved to CO_2 fixed varies with the redox state of the nitrogen source (Williams *et al.*, 1979; Megard *et al.*, 1985). For an algal cell with an elemental composition of 7 carbon atoms for each nitrogen atom, carbon-based quantum yield will be approximately 25% lower for growth on nitrate compared to ammonium. In the ocean, the redox state of available nitrogen can be expected to affect ϕ_{max}. In the laboratory, other factors which cause variation in ϕ_{max} include cellular nitrogen quota (Cleveland and Perry, 1987), growth rate (Chalup, 1987), growth stage of the culture (Welschmeyer and Lorenzen, 1981), and the phase of the cell-division cycle (Senger and Bishop, 1967); these factors may also be important in the field.

In order to model primary production from physiological and optical relationships, the magnitude and variability of ϕ_{max} in the ocean must be known; the present study examined the natural variability of ϕ_{max} as a function of depth and time for phytoplankton in the northwestern Sargasso Sea. Because phytoplankton biomass in the open ocean is low, ϕ_{max} cannot be measured with simultaneous ^{14}C uptake and light absorption measurements, as is done in the laboratory (e.g., Welschmeyer and Lorenzen, 1981). Instead, ϕ_{max} was calculated from the light-limited slope of photosynthetic rate as a function of irradiance (P vs. I) and a spectrally-weighted phytoplanktonic absorption coefficient. Direct measurement of absorption was necessary (rather than the use of measured chlorophyll *a* concentrations and an assumed chlorophyll *a*-specific absorption coefficient) because the chlorophyll *a*-specific absorption coefficient of phytoplankton has been shown, in laboratory experiments, to vary from three- to six-fold as a function of pigment packaging within algal cells (Morel and Bricaud, 1981; Sathyendranath *et al.*, 1987; Bricaud *et al.*, 1988). Furthermore, particulate matter in the ocean consists of living phytoplankton as well as other living and nonliving particles which absorb light. We partitioned light absorption by particles into two components, one due to phytoplankton and one due to nonphotosynthetic light-absorbing particles. The phytoplanktonic portion of the particulate absorption was used to calculate ϕ_{max}(phyt). When calculated in this way, ϕ_{max}(phyt) reflects the

efficiency of photosynthesis and differs from previously published field estimates of ϕ_{max} that may have been influenced by the detrital component of particulate absorption.

2. Materials and methods

a. Sample collection and routine measurements. Measurements were made during the Biowatt 1 cruise to the Sargasso Sea on the R/V *Knorr* in April 1985. The sampling site at 35N,70W was occupied from 3 to 7 April (Station 4) and again from 19 to 25 April (Station 19). Niskin bottles mounted in a rosette with either BOPS (Bio-optical Profiling System; Smith *et al.*, 1984) or a CTD were used to collect water. Samples for chlorophyll *a* and pheopigment measurements were filtered through Millipore HA (pore size 0.45 μm) membrane filters; filters were placed in 90% acetone and extracted for 24 h in the freezer. Chlorophyll *a* (chl *a*) and pheopigments were measured fluorometrically (Smith *et al.*, 1981). Other pigments were measured by high performance liquid chromatography (HPLC; Bidigare *et al.*, 1987); only chlorophyll *b* values are used here. Pheopigments were not measured by HPLC. Fluorometrically-measured pheopigment concentrations were corrected for interference from chlorophyll *b* using the relationship published by Vernet and Lorenzen (1987). Nutrient concentrations were measured immediately after sampling with an Alpkem autoanalyzer (Whitledge *et al.*, 1981).

b. Photosynthesis vs. irradiance curves. Photosynthesis as a function of irradiance (*P* vs. *I*) was measured at 24 irradiance levels ranging from 1 to 1500 μmol photons m^{-2} s^{-1} in miniaturized *P* vs. *I* incubators (Talbot *et al.*, 1985). The light source for each incubator was a 500W quartz-iodide bulb; the light passed through a water bath, a heat reflecting mirror, 1/8 inch light blue plexiglass (#2069), and nickel neutral density filters. Total visible irradiance incident on the samples was measured with a Biospherical Instruments QSL100 4π light meter. The irradiance spectrum (Fig. 1) was measured, at 3-nm resolution, using a Spectron spectral radiometer. Buffered $NaH^{14}CO_3$ stock solution, prepared according to Fitzwater *et al.* (1982), was added to 200 ml of sample to give a final activity of 0.90 μCi ml^{-1}. Aliquots (7 ml each) were distributed into 24 scintillation vials (vial capacity was 20 ml) and incubated for 1.0 h at *in situ* temperature (±0.20°C). Photosynthetic uptake of ^{14}C was stopped by freezing the vials containing the samples.

Processing was done in the laboratory within four months of the cruise. Vials were thawed and 5.0 ml of sample transferred to a new scintillation vial containing 1 drop of 6 N HCl. Vials were shaken for 30 min to allow unincorporated CO_2 to escape. Beckman MP scintillation cocktail (9 ml) was added; radioactivity was counted in a Beckman LS2800 liquid scintillation counter. *P* vs. *I* parameters were calculated, after subtraction of the carbon uptake at the lowest light level as the background correction,

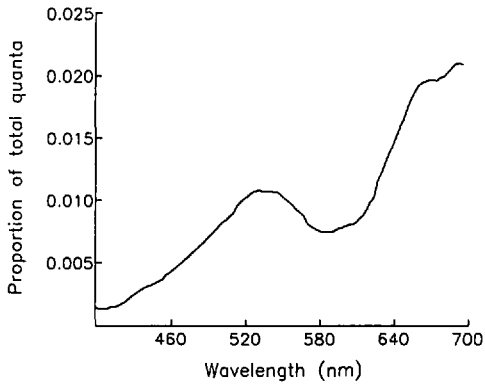

Figure 1. Spectrum of available irradiance for photosynthesis vs. irradiance (P vs. I) incubations.

using the nonlinear exponential equation presented by Peterson *et al.* (1987):

$$P_N = P_{N\max} - P_{G\max}\, e^{(-\gamma I)} \tag{1}$$

$$LL = P_{N\max}\gamma \tag{2}$$

$$\alpha = \frac{LL}{[\text{chl } a]} \tag{3}$$

where P_N is the net photosynthetic rate, $P_{N\max}$ is the net maximal photosynthetic rate, $P_{G\max}$ is the gross maximal photosynthetic rate, γ (this term is called ß in Peterson *et al.*, 1987) is an empirical parameter derived for each set of data, and I is the incident irradiance. The P vs. I parameters of interest (Fig. 2) were the light-limited slope [LL; mg C m^{-3} h^{-1} (μmol photons m^{-2} s^{-1})$^{-1}$] and the light-limited slope normalized to chlorophyll a concentration [α; mg C (mg chl a)$^{-1}$ h^{-1} (μmol photons m^{-2} s^{-1})$^{-1}$].

c. Specific absorption coefficients. Particulate matter was collected by filtering 1 to 4 l of seawater through a GF/F glass fiber filter (nominal pore size 0.7 μm) at low pressure (<5 mm Hg). Immediately after filtration, absorption spectra (400 to 700 nm) were measured in a dual beam spectrophotometer, using a GF/F filter dampened with filtered seawater as a blank. Diffuse absorption coefficients for total particulates [$a_{\text{part}}(\lambda)$; m^{-1}] were calculated using the equations and corrections described by Mitchell and Kiefer (1984; 1988a).

Using the partitioning technique described by Cleveland and Perry (1989), the absorption spectra were mathematically partitioned into two components which represent absorption by living phytoplankton [$a_{\text{phyt}}(\lambda)$] and by nonphotosynthetic [$a_{\text{det}}(\lambda)$] particles. The detrital component includes absorption by all nonphotosynthetic particles such as nonliving organic material, bacteria, inorganics, and pigment break-down

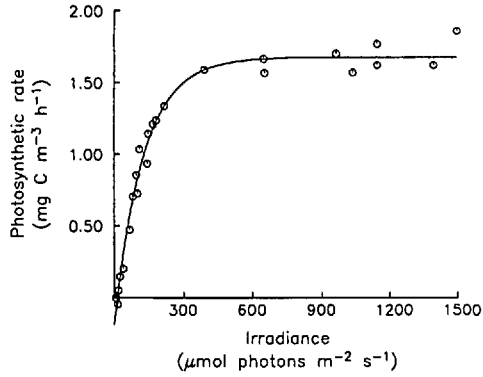

Figure 2. Photosynthetic rate as a function of irradiance for Station 4, cast 34, 3 m. The curve was fit using the exponential equation of Peterson *et al.* (1987). Maximal quantum yield was calculated using the light-limited region of the *P* vs. *I* relationship.

products. The model reconstructs the phytoplanktonic absorption spectrum [$a_{phyt}(\lambda)$] from the total particulate absorption spectrum, and is based on absorption at the red peak, chlorophyll *a* and pheopigment concentrations, and mean ratios of $a(\lambda)$:$a(676)$ for laboratory-grown phytoplankton cultures. This approach assumes that the spectral shapes of absorption by phytoplankton are conservative and that mean $a(\lambda)$:$a(676)$ spectra measured in the laboratory represent spectral shapes of absorption for natural populations. The model was developed in two stages for two types of phytoplankton assemblages. The first stage of the model is based on mean $a(\lambda)$:$a(676)$ spectra for chromophytes (chlorophyll *c*-containing species) and chlorophytes (chlorophyll *b*-containing species) and is appropriate for ocean waters dominated by eukaryotic phytoplankton. Other pigment groups, such as cyanobacteria and prochlorophytes, are accounted for in the second stage of the model which, in addition to mean spectra for chromophytes and chlorophytes, also employs the spectral characteristics of non-pigmented detrital particles.

For determination of ϕ_{max}, we calculated the light absorbed during the incubation by spectrally-weighting the total particulate and the phytoplanktonic absorption spectra by the available irradiance spectrum of the *P* vs. *I* incubator. This absorbed irradiance is similar to PUR (photosynthetically usable radiation; Morel, 1978). Spectrally-weighted mean absorption coefficients for total particulates (weighted $\bar{a}_{part}$) and phytoplankton alone (weighted $\bar{a}_{phyt}$) were determined by averaging between 400 and 700 nm.

d. Quantum yield. Maximal quantum yield [mol C (mol photons)$^{-1}$] was calculated from the slope of the *P* vs. *I* relationship [LL, in units of mg C m^{-3} h^{-1} (μmol photons m^{-2} s^{-1})$^{-1}$] and the spectrally-weighted mean absorption coefficient (m^{-1}) for either the total particulate absorption (weighted $\bar{a}_{part}$) or the phytoplanktonic absorption

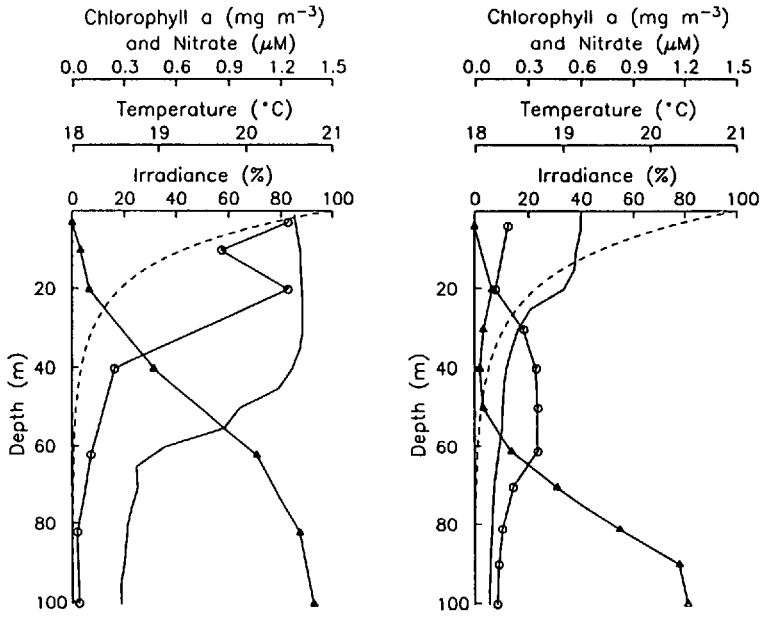

Figure 3. Vertical profiles of temperature (_____), irradiance as percent of surface irradiance (----), chlorophyll *a* concentration (O), and nitrate concentration (Δ) for (a) Station 4, cast 11; and (b) Station 19, cast 89.

(weighted $\bar{a}_{phyt}$):

$$\phi_{max}(\text{part}) = \frac{0.0231\ LL}{(\text{weighted}\ \bar{a}_{part})} \tag{4}$$

and

$$\phi_{max}(\text{phyt}) = \frac{0.0231\ LL}{(\text{weighted}\ \bar{a}_{phyt})} \tag{5}$$

where the constant, 0.0231, converts grams to moles and hours to seconds.

3. Results

Depth profiles of chlorophyll *a*, nitrate, temperature, and irradiance for one cast from each station are shown in Figure 3. The mean values reported below are specific only to the samples for which ϕ_{max} was calculated. At Station 4, chlorophyll *a* concentrations were high (0.82 mg m^{-3} ± 0.33; mean ± one standard deviation) and varied little with depth in the mixed layer. The proportion of pheopigments to chlorophyll *a* plus pheopigments was 0.20 (±0.08). The euphotic depth (1% of surface irradiance) was 55 m, and diatoms dominated the phytoplankton community (Marra, personal communication). Ammonium was detectable for all these samples but was

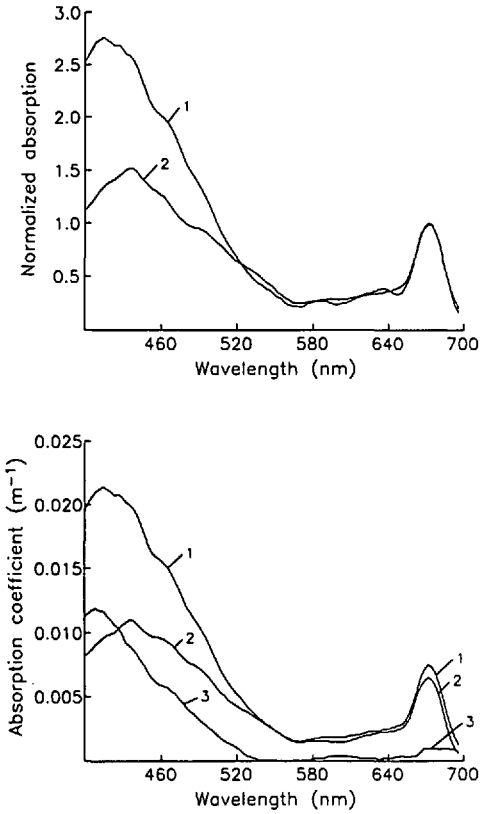

Figure 4. (a) Absorption spectra for Biowatt Station 4, cast 34, 3 m (curve 1) and *Chaetoceros gracilis* grown at 100 μmol photons m^{-2} s^{-1} (curve 2). The two spectra are normalized at the red absorption peak. (b) Absorption spectra for total particles (curve 1), the phytoplanktonic component (curve 2), and the other absorbing particles component (curve 3) for Biowatt Station 4, cast 34, 3 m.

less than 0.13 μM. Nitrate was low in the upper 30 m. Coastal Zone Color Scanner images indicate that a phytoplankton bloom occurred in the northern Sargasso Sea from about 30 March to 9 April 1985, coincident with our occupation of Station 4. The bloom ended before our occupation of Station 19 (Siegel *et al.*, 1989). At Station 19 (the same location as Station 4, two weeks later), the mean chlorophyll *a* concentration was 0.45 mg m^{-3} ($\pm$0.27) and the proportion of pheopigments to total pigments was 0.44 ($\pm$0.19). The euphotic depth was 63 m, similar to Station 4. Cyanobacteria were numerically more abundant than at Station 4 (Iturriaga and Marra, 1988), and the size of phytoplankton cells was smaller (Marra, personal communication). The nitracline was deeper, and ammonium was undetectable or less than 0.08 μM.

An example of a total particulate absorption spectrum for Station 4 and a spectrum for a laboratory-grown diatom (*Chaetoceros gracilis*) are shown in Figure 4a. The two

Table 1. Light-limited rate of photosynthesis normalized to chlorophyll *a* concentration (α), maximal quantum yield for total particulates [ϕ_{max}(part)], and maximal quantum yield for phytoplankton [ϕ_{max}(phyt)].

Station	Cast	Depth*	α**	ϕ_{max}(part)***	ϕ_{max}(phyt)***
04	11	7	0.0117	0.038	0.062
04	11	20	0.0122	0.059	0.091
04	24	14	0.0200	0.044	0.086
04	24	20	0.0193	0.051	0.080
04	24	60	0.0146	0.027	0.059
04	34	3	0.0180	0.065	0.089
04	34	10	0.0204	0.071	0.102
04	34	20	0.0177	0.049	0.075
04	34	40	0.0201	0.049	0.081
04	49	24	0.0148	0.060	0.081
19	19	3	0.0105	0.021	0.033
19	19	52	0.0144	0.040	0.068
19	89	20	0.0220	0.014	0.044
19	89	61	0.0188	0.024	0.046

*m
**mg C (mg chl *a*)$^{-1}$ h^{-1} (μmol photons m^{-2} s^{-1})$^{-1}$
***mol C (mol photons)$^{-1}$

spectra are normalized at the red absorption peak, where absorption is primarily due to chl *a*. For the healthy diatom, the blue absorption maximum was at the chlorophyll *a* Soret peak, 436 nm. In the Biowatt spectrum, the absorption peak was shifted to a lower wavelength, indicating a contribution by pheopigments which have a blue absorption peak at 416 nm. In addition, absorption at blue wavelengths normalized to the red peak was higher for the Biowatt sample compared to the diatom, suggesting the presence of nonphytoplanktonic particles with high absorption at blue wavelengths. Similar differences between field and laboratory samples are seen when absorption spectra are normalized to absorption integrated from 400 to 700 nm (not shown); normalized blue absorption remains higher for the field sample while normalized red absorption is lower, implying that absorption by chlorophyll *a* and pheopigments contributed a smaller proportion of the total absorption. The total particulate absorption and the partitioned absorption spectra for phytoplankton and other particles are shown in Figure 4b for the same sample. The spectrum for the nonphytoplanktonic particles exhibited high absorption in the blue and a small red peak associated with pheopigment absorption.

The light-limited rates of photosynthesis normalized to chlorophyll *a* (α) showed no trend with depth, time, or station. Values ranged from 0.011 to 0.022 mg C (mg chl *a*)$^{-1}$ h^{-1} (μmol photons m^{-2} s^{-1})$^{-1}$ (Table 1). Mean values for the two stations were essentially the same: 0.017 ($\pm$0.003) at Station 4 and 0.016 ($\pm$0.005) at Station 19.

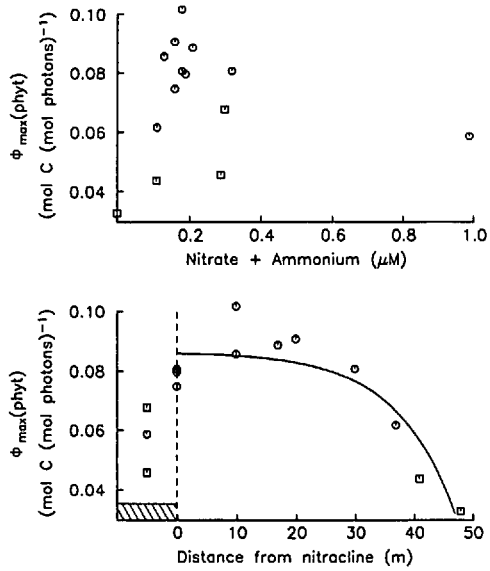

Figure 5. Maximal quantum yield for phytoplankton as a function of (a) nitrate plus ammonium concentration for Station 4 (○) and Station 19 (□); and (b) distance from the top of the nitracline for Station 4 (○) and Station 19 (□). Samples with nitrate concentration greater than 0.2 μM are shown in the hatched area. The curve was fit using linear regression after an exponential transform of distance from the nitracline.

Maximal quantum yields based on total particulate absorption [ϕ_{max}(part)] ranged from 0.027 to 0.071 mol C (mol photons)$^{-1}$ (mean 0.051 ± 0.013) at Station 4. At Station 19, the values were lower, ranging from 0.014 to 0.040 (mean 0.025 ± 0.011).

In contrast, ϕ_{max}(phyt) was higher than ϕ_{max}(part) at both stations, ranging from 0.059 to 0.102 mol C (mol photons)$^{-1}$ (mean 0.081 ± 0.013) at Station 4, and from 0.033 to 0.068 (mean 0.048 ± 0.015) at Station 19. The means for the two stations were significantly different ($p < 0.05$; t test). Values of ϕ_{max}(phyt) exhibited no trend with either depth or concentration of nitrate plus ammonium (Fig. 5a). However, lower values of ϕ_{max}(phyt) were correlated with greater distances from the top of the nitracline (z_n; Fig. 5b), where the top of the nitracline was defined as the depth at which the vertical gradient in nitrate concentration was largest. Samples with nitrate concentration greater than 0.2 μM are shown in the hatched region of Figure 5b and were excluded from the regression analysis because these lower quantum yields may have been the result of growth on nitrate rather than limited nitrogen availability. The exponential relationship,

$$\phi_{max}(\text{phyt}) = 0.0873 - 0.00050\, e^{(z_n)}, \tag{6}$$

was highly significant ($r_2 = 0.81$; $p < 0.001$; analysis of variance).

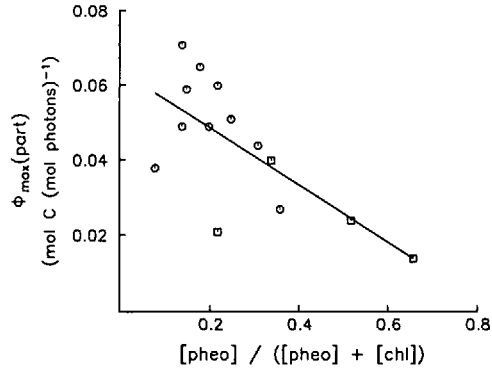

Figure 6. Maximal quantum yield for total particles as a function of the proportion of pheopigments to pheopigments plus chlorophyll for Station 4 (O) and Station 19 (□). The line was fit using linear regression.

4. Discussion

A current direction of biological oceanography is the development and testing of models for estimating primary production rates from *in situ* or remotely sensed optical measurements. One approach is to model primary production from physiological parameters such as the chlorophyll *a*-specific absorption coefficient and the maximal quantum yield of photosynthesis (Bannister, 1974; 1979; Smith, 1980; Kiefer and Mitchell, 1983; Collins *et al.*, 1986; Bidigare *et al.*, 1987; Platt and Sathyendranath, 1988). However, we have little field data on either true phytoplanktonic absorption or true maximal quantum yield (i.e., independent of absorption by nonphotosynthetic particles). By examining the magnitude and variability of both parameters, as in the present study, we can increase our understanding of the relationships between total particulate light absorption, phytoplanktonic light absorption, and light-limited photosynthetic rates in the ocean and ultimately improve primary production models which use *in situ* or remotely sensed data.

a. Absorption coefficients. Before we could properly determine ϕ_{max} in the field, the true absorption by phytoplankton had to be separated from the total particulate absorption. Field methods for measuring chlorophyll *a*-specific absorption coefficients generally do not separate phytoplanktonic absorption from detrital absorption. As a result, the absorption coefficients measured in other field studies often overestimate the light absorbed by phytoplankton, and, consequently, underestimate phytoplanktonic ϕ_{max}. To demonstrate this type of underestimate, ϕ_{max}(part) was calculated from the total particulate absorption coefficient as well as the phytoplanktonic component alone (Table 1). A negative trend was seen between ϕ_{max}(part) and the proportion of pheopigments to total chlorophyll plus pheopigments (Fig. 6). Since pheopigments constitute one type of nonphotosynthetic particle, this inverse relationship suggested that nonphotosynthetic particles contributed significantly to the absorption of photosyn-

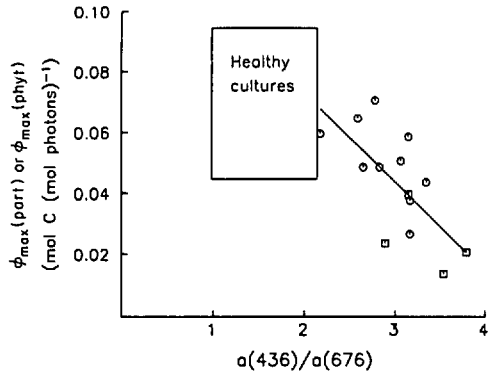

Figure 7. Maximal quantum yield for total particles as a function of the ratio of absorption at 436 nm to absorption at 676 nm for Station 4 (O) and Station 19 (□). The line was fit using linear regression. The box delineates the range observed in laboratory studies of phytoplanktonic maximal quantum yield (Welschmeyer and Lorenzen, 1981; Dubinsky *et al.*, 1986; Cleveland and Perry, 1987; Chalup, 1987) and the range in the ratio of $a(436)$:$a(676)$ (Senger and Fleischhacker, 1978; Davies-Colley *et al.*, 1986; SooHoo *et al.*, 1986; Maske and Haardt, 1987; Owens *et al.*, 1987; Sathyendranath *et al.*, 1987; Cleveland and Perry, 1989).

thetically active radiation. Because light absorbed by these particles cannot be transferred to the photosynthetic reaction centers, the presence of these particles caused an apparent decrease in quantum yield.

Examination of published absorption spectra for laboratory-grown algal cultures shows that ratios of absorption at the blue (436 nm) to red (near 676 nm) chl *a* peaks lie in a narrow range, about 1.1 to 2.5 (Senger and Fleischhacker, 1978; Mitchell *et al.*, 1984; SooHoo *et al.*, 1986; Davies-Colley *et al.*, 1986; Maske and Haardt, 1987; Owens *et al.*, 1987; Sathyendranath *et al.*, 1987; Bricaud *et al.*, 1988; Cleveland and Perry, 1989). High values of $a(436)$:$a(676)$ for field samples, as seen for Biowatt total particulate absorption spectra (e.g., Fig. 4a), indicate the presence of nonphytoplanktonic, blue-absorbing particles. The decrease in ϕ_{max}(part) with increasing $a(436)$:$a(676)$, shown in Figure 7, suggested that the enhanced blue absorption by nonphotosynthetic particles "diluted" the true phytoplanktonic absorption and lowered the apparent quantum yield. For laboratory-grown cultures, where absorption measurements represent true phytoplanktonic absorption, ϕ_{max}(phyt) is higher and $a(436)$:$a(676)$ is lower (Fig. 7). The box delimiting this range (Fig. 7) lies on a continuum with the field values of ϕ_{max}(part), supporting our suggestion that enhanced blue-absorption indicates the presence of nonphotosynthetic particles and lowers apparent quantum yield. Both $a(436)$:$a(676)$ and the proportion of pheopigments can be used as indicators of relative detrital concentration. The inverse trends observed for ϕ_{max}(part) vs. the proportion of pheopigments (Fig. 6) and $a(436)$:$a(676)$ (Fig. 7) indicated that the measured total particulate absorption included a variable amount of absorption by particles other than phytoplankton.

b. Phytoplanktonic quantum yield. By calculating ϕ_{max}(phyt) from the phytoplanktonic component of absorption instead of total particulate absorption, we were able to examine changes in ϕ_{max} that were related to phytoplankton physiology rather than changes related to absorption by nonphytoplanktonic particulates. During the period that Station 4 was occupied, the phytoplankton were in a bloom condition. Concentrations of nitrate and ammonium were generally detectable, chlorophyll *a* was high, and pheopigments were low. Under bloom conditions and for short photosynthetic incubations which minimize respiration of newly fixed carbon, quantum yield for nitrogen-replete cells can be expected to approach maximal values, as suggested by the generally high values at Station 4 (Table 1). Our highest observed value for ϕ_{max}(phyt), 0.102 mol C (mol photons)$^{-1}$, approached the theoretical maximum, and eight of the ten values calculated at Station 4 exceeded 0.070 mol C (mol photons)$^{-1}$. In contrast, when the location was revisited two weeks later (Station 19), the nitracline was deeper and the phytoplankton appeared to be in a post-bloom condition. Chlorophyll *a* was lower, pheopigments were slightly higher, $a(436):a(676)$ was higher, and ϕ_{max}(phyt) was lower (Table 1).

Two potential causes of the low values of ϕ_{max}(phyt) that we observed are related to the opposing effects of nitrogen availability and nitrogen redox state. Laboratory studies of both batch and chemostat cultures have shown that ϕ_{max} decreases when nitrogen availability is limited (Welschmeyer and Lorenzen, 1981; Cleveland and Perry, 1987; Chalup, 1987). This decrease may be caused by a reduction in photosynthetic reaction center activity without a concurrent decrease in light-harvesting ability, i.e., light energy is absorbed that cannot be converted to chemical energy. For example, Kolber *et al.* (1988) observed a decrease in the ratio of photosystem II reaction centers to light-harvesting complexes when algal cultures became nitrogen limited. Although no direct relationship between ϕ_{max}(phyt) and the concentration of nitrate plus ammonium was observed for Biowatt samples (Fig. 5a), variations in ϕ_{max}(phyt) may been a consequence of variations in the flux of nitrogen. Nitrogen flux is a function of the concentration gradient and the vertical diffusion coefficient. By assuming a constant vertical diffusion coefficient for our sample location and time, nitrogen flux can be represented as a function of only the concentration gradient. When nitrogen concentration is low at the sample depth, nitrogen flux will be inversely proportional to the distance between the sample depth and the nitracline (z_n). We considered this to be nitrogen rather than nitrate flux because nitrite production and ammonium regeneration may be enhanced near the base of the euphotic zone. Samples with the highest z_n, i.e., the lowest nitrogen flux, had the lowest values of ϕ_{max}(phyt) (Fig. 5b). Samples which had nitrate concentration greater than 0.2 μM (shown in the hatched region of Fig. 5b) were not included in the exponential regression because of the potential effect of nitrate reduction on ϕ_{max}(phyt) (see below). If distance from the nitracline is indeed proportional to nitrogen flux, the relationship shown in Figure 5b indicates that nitrogen availability affected ϕ_{max}(phyt). The exponential nature of the relationship

suggested that there was a range of z_n (0 to 30 m, in this case) where nitrogen flux was great enough to allow high ϕ_{max}(phyt), despite low concentrations of nitrate and ammonium.

The second set of samples with low values of ϕ_{max}(phyt) (4-24 60 m; 19-19 52 m; and 19-89 61 m) was associated with relatively high nitrate concentrations (0.91 μM; 0.30 μM; and 0.21 μM, respectively). Based on the relationship between new production and measured nitrate and ammonium concentrations proposed by Harrison *et al.* (1987; their Fig. 7), nitrate could have contributed more than 60% of the phytoplankton's nitrogen requirement in these three samples. The low values of ϕ_{max}(phyt) for these samples were not a result of nitrogen limitation, since nitrate concentration was high, but were most likely the result of competition between nitrate reduction and carbon fixation for photochemically-produced reductant (Thomas *et al.*, 1976; Williams *et al.*, 1979; Larsson *et al.*, 1985; Megard *et al.*, 1985).

c. Comparison to other measurements. Two important differences in methodology exist between the present study and most other published field reports of quantum yield. First, the method used to measure phytoplanktonic absorption differs. We used the glass fiber filter method with a correction for absorption by nonphytoplanktonic particles rather than an assumed spectrally averaged specific absorption coefficient (as in Dubinsky and Berman, 1976; Platt and Jassby, 1976; Morel, 1978) or regression of total attenuation on chlorophyll *a* (as in Tyler, 1975; Seaburg *et al.*, 1983; Priscu, 1984). Second, previous field estimates of quantum yield have often used photosynthetic rates measured at *in situ* irradiance ($\phi_{in\ situ}$), instead of at irradiances subsaturating to photosynthesis (ϕ_{max}). As a consequence, $\phi_{in\ situ}$ varies inversely with irradiance, and physiological variations in quantum yield are overwhelmed by the light-dependence of $\phi_{in\ situ}$, except when *in situ* irradiance is subsaturating and $\phi_{in\ situ}$ equals ϕ_{max}.

It was implicitly assumed that ϕ_{max} is independent of wavelength for comparison of our ϕ_{max}(phyt) to ϕ_{max} and $\phi_{in\ situ}$ from other studies, since the irradiance spectra were not the same for the various incubations. This implicit assumption is justified because ϕ_{max} varies little with wavelength, except when concentrations of photoprotective pigments are very high. For example, for the diatom *Navicula minima*, ϕ_{max} was essentially constant with wavelength except for a slight minimum at 475 nm, where nonphotosynthetic carotenoids absorb (Tanada, 1951). Field measurements by Lewis *et al.* (1985) also showed ϕ_{max} to be independent of wavelength.

Bannister and Weidemann (1984) evaluated the different studies of quantum yield done prior to 1984. They selected data from both laboratory and field studies where photosynthetic rate was proportional to irradiance, i.e., light-limited photosynthetic rates which assure measurement of ϕ_{max}, and where they believed that specific absorption coefficients were reliable. From their summary, Bannister and Weidemann (1984) concluded that ϕ_{max} in the field should lie between 0.04 and 0.08 mol C (mol

photons)$^{-1}$. The range of ϕ_{max}(phyt) values from Biowatt (0.033 to 0.102) encompassed the range predicted by Bannister and Weidemann (1984). Subsequent to Bannister and Weidemann's (1984) review, several studies (discussed below) have been published which use modified methods for calculating quantum yield. Dubinsky *et al.* (1984) calculated $\phi_{in\ situ}$ in Lake Constance using *in situ* photosynthetic rates and an ingenious modification of the glass fiber filter technique to account for spectral narrowing of the irradiance field with depth. In their study, $\phi_{in\ situ}$ increased with depth, reaching a maximal value of 0.061 mol C (mol photons)$^{-1}$ for their deepest sample, 15 m. At this depth, irradiance was less than 1% of surface irradiance and $\phi_{in\ situ}$ was equal to ϕ_{max}. The lower maximal value in Lake Constance, relative to the Biowatt area, may be due to a physiological effect related to nitrogen or to an overestimate of the phytoplanktonic component of absorption. We cannot distinguish between these alternatives. Dubinsky *et al.* (1984) measured mean absorption over the visible light region and did not publish spectral values of absorption, hence we cannot examine their absorption spectra or $a(436):a(676)$ to evaluate the contribution of particulate detritus to absorption. Additionally, Dubinsky *et al.* (1984) did not describe a correction for pathlength amplification within the glass fiber filter. Inclusion of a correction factor (cf. Kiefer and SooHoo, 1982; Mitchell and Kiefer, 1984; 1988a, b) would decrease their absorption coefficients and increase their quantum yields.

In April 1983, Lewis *et al.* (1985) calculated ϕ_{max}(part) (Lewis *et al.* use $\phi_{apparent}$ for this term) in the Sargasso Sea at a location close to the Biowatt sampling site. They used light-limited photosynthetic rates measured under various spectral qualities in *P* vs. *I* incubators [i.e., $\alpha(\lambda)$] and specific absorption coefficients [$a^*_{chl}(\lambda)$] measured for particles concentrated on glass fiber filters. Their values of ϕ_{max}(part), calculated by regression of $\alpha(\lambda)$ on $a^*_{chl}(\lambda)$, were all below 0.016 mol C (mol photons)$^{-1}$. Lewis *et al.* (1985) suggested that their low ϕ_{max}(part) values were due to absorption by spectrally covarying detrital material and to decreased carbon-based photosynthetic rate caused by nitrate reduction. The difference between $a^*_{chl}(\lambda)$ and $\alpha(\lambda)$ in the blue region compared to other spectral regions suggested the presence of blue-absorbing detritus. The shape of their absorption spectra (their Fig. 5) indicated that more detritus was present than in Biowatt samples (our Fig. 4). This comparison suggests interannual variability in the timing of the spring bloom and accumulation of detritus.

Kishino *et al.* (1986) calculated $\phi_{in\ situ}$ off Shikoku Island using photosynthetic rates measured with *in situ* and simulated *in situ* stable-isotope ^{13}C-bicarbonate incubations. They measured absorption spectra for particles collected on glass fiber filters and applied a pathlength amplification factor specific to local waters. Phytoplanktonic absorption was derived from the difference between absorption by total particles and absorption after extraction of pigments with methanol. They found that $\phi_{in\ situ}$ increased with depth, reaching a maximum value of 0.09 mol C (mol photons)$^{-1}$ at a depth where irradiance was 1.5% of surface irradiance. At this irradiance $\phi_{in\ situ}$ equalled ϕ_{max}. This ϕ_{max} is similar to the highest value reported in the present paper for

Biowatt samples. Both Kishino *et al.*'s (1986) and our results suggest that ϕ_{max} in the field can indeed approach the theoretical maximum value, particularly when the phytoplankton are growing rapidly and when the incubation period is short enough to keep respiration of newly incorporated carbon to a minimum (Kishino *et al.* 6 h; our study 1 h).

SooHoo *et al.* (1987) calculated ϕ_{max} using absorption coefficients measured for particles collected on glass fiber filters and photosynthetic rates determined from either incubations at 6 μmol photons m^{-2} s^{-1} or α from P vs. I incubations. For these Antarctic samples, ϕ_{max} ranged from 0.013 to 0.055 mol C (mol photons)$^{-1}$. SooHoo *et al.* (1987) suggested that these values of ϕ_{max} may be overestimated by 10 to 30% due to measurement of irradiance with a cosine collector rather than a 4π detector. The ratio of absorption at the blue to red peaks for spectra shown in their paper ranges from 1.62 to 2.22. This is within the range for healthy phytoplankton cultures (1.1 to 2.5), suggesting that blue-absorbing detrital particles were not present in their samples and a correction for absorption by detrital particles was not necessary.

5. Conclusions

The phytoplanktonic component of total particulate absorption was obtained using a partitioning model based on the shapes of absorption spectra for laboratory-grown algal cultures (Cleveland and Perry, 1989). Phytoplanktonic quantum yield computed from the modelled values of spectrally-weighted phytoplanktonic absorption varied from 0.033 to 0.102 mol C (mol photons)$^{-1}$. The difference between mean values of ϕ_{max}(phyt) at Station 4 (bloom conditions) compared to Station 19 (post-bloom) was significant at $p < 0.05$. Nitrogen flux, represented by the distance from the sample depth to the nitracline, was correlated with ϕ_{max}(phyt) in an exponential relationship for quantum yield samples where nitrate concentration was less than 0.2 μM. This suggests that nitrogen availability can control ϕ_{max}(phyt) in the field, as previously shown for algal cultures in the laboratory. Higher nitrate concentrations may lower ϕ_{max}(phyt) because of competition between nitrate reductase and the Calvin cycle enzymes for photosynthetically-produced reductant. From the variations observed in ϕ_{max}(phyt) as a function of nitrogen availability and redox state, we suggest the following patterns. In areas where ammonium regeneration rates are high and phytoplankton are growing rapidly, ϕ_{max}(phyt) should approach theoretical maximal values, as in the upper euphotic zone at Station 4. In areas where less nitrogen is available, as in post-bloom conditions with deeper nitraclines, ϕ_{max}(phyt) should be lower [e.g., 0.04 to 0.06 mol C (mol photons)$^{-1}$, as at Station 19], reflecting the effect of nitrogen deficiency on quantum yield. In upwelling areas where nitrate is the major nitrogen source, ϕ_{max}(phyt) should be intermediate between these two extreme cases [e.g., 0.07 mol C (mol photons)$^{-1}$], reflecting the combined effects of nitrogen-sufficient growth (higher ϕ_{max}) and diversion of photosynthetically-produced reductant from carbon fixation to nitrate reduction (lower ϕ_{max}). General information about the predominant

nitrogen source and the flux of nitrogen for a specific region should permit us to select appropriate values of ϕ_{max} for modelling primary production. The ability to measure phytoplanktonic absorption in the ocean will allow more extensive measurements of ϕ_{max} and further evaluation of the variability of ϕ_{max} with environmental conditions.

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