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## Calculated quantum yield of photosynthesis of phytoplankton in the Marine Light–Mixed Layers (59°N, 21°W)

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**Abstract.** The quantum yield  $\phi$  of photosynthesis ( $\text{mol C (mol photons)}^{-1}$ ) was calculated at six depths for the waters of the Marine Light–Mixed Layer (MLML) cruise of May 1991. As there were photosynthetically available radiation (PAR) but no spectral irradiance measurements for the primary production incubations, three ways are presented here for the calculation of the absorbed photons (AP) by phytoplankton for the purpose of calculating  $\phi$ . The first is based on a simple, nonspectral model; the second is based on a nonlinear regression using measured PAR values with depth; and the third is derived through remote sensing measurements. We show that the results of  $\phi$  calculated using the nonlinear regression method and those using remote sensing are in good agreement with each other, and are consistent with the reported values of other studies. In deep waters, however, the simple nonspectral model may cause quantum yield values much higher than theoretically possible.

### Introduction

Traditional methods for estimating the light absorbed by phytoplankton at depth in the ocean have often used nonspectral photosynthetically available radiation (PAR) measurements or calculations, and spectrally averaged (without light-field weighting) phytoplankton specific-absorption coefficients. Two alternative spectral methods are presented here for use with remotely sensed data: one for use with remote floating or moored arrays equipped with nonspectral PAR sensors, and one for use with satellite or aircraft-derived remote sensing reflectance data. Both alternatives utilize spectrally dependent total absorption coefficients to model the depth dependent, spectral light field. These light fields are then spectrally integrated at depth for comparison with PAR measurements.

Primary production (PP) in the ocean is dependent on the absorption of incident photons by phytoplankton and on the efficiency with which phytoplankton use this absorbed energy. At depth  $z$  for a time period of  $T$ , PP is

$$PP(z) = \phi(z) \int_T \int_\lambda E_q(z, \lambda, t) \cdot [\text{chl } a(z)] a_{\text{ph}}^*(z, \lambda, t) d\lambda dt. \quad (1)$$

(Symbols are defined in the notation section. To be brief, the functionality of one quantity to another might not be explicitly expressed in the remaining text.) The symbol  $\phi$  on the right side of (1) describes the energy-conversion efficiency for photosynthesis and is defined as quantum yield of photosynthesis [Bannister, 1974; Tyler, 1975; Kiefer and Mitch-

ell, 1983; Bannister and Weidemann, 1984; Dubinsky *et al.*, 1984; Cleveland *et al.*, 1989]. The rest of the right side of (1),

$$AP(z) = \int_T \int_\lambda E_q(z, \lambda, t) [\text{chl } a(z)] a_{\text{ph}}^*(z, \lambda, t) d\lambda dt, \quad (2)$$

describes the absorbed photons by phytoplankton at that depth for the time period. Equations (1) and (2) are usually integrated over hours or a day, and over a wavelength range from 400 to 700 nm. So quantum yield  $\phi$ , a time average, is

$$\phi(z) = \frac{PP(z)}{AP(z)}. \quad (3)$$

In order to estimate primary production through optical properties, using either moored sensors [Marra *et al.*, 1992] or remote measurements [Cullen, 1990; Platt *et al.*, 1991; Balch *et al.*, 1992], the magnitude and variability of the quantum yield of photosynthesis ( $\phi$ ) in the ocean must be known. Laboratory studies have been carried out [Kiefer and Mitchell, 1983; Langdon, 1988 and references cited therein], but there is a paucity of in situ  $\phi$  measurements in the field. Shipboard incubations have been used to simulate in situ studies, but most have used white light, which can cause errors as large as a factor of 2 [Laws *et al.*, 1990]. Also, in many cases, nonspectral models have been used to calculate  $\phi$  at depth [Tyler, 1975; Bannister, 1979; Marra *et al.*, 1992]. However, due to the filtration effect of the overlying water column, nonspectral models do not accurately describe the light field available for phytoplankton absorption at depth [Morel, 1978; Kishino *et al.*, 1986]. For more accurate in situ  $\phi$  measurements, the spectral character of the light at depth needs to be considered.

Bannister and Weidemann [1984] and Kishino *et al.* [1986] presented approaches to derive in situ  $\phi$ . However, these approaches require obtaining knowledge of the spectral character of  $E_q(\lambda, z)$ , which can be a rather expensive proposition: either (1) a ship must remain near a PP array to measure the spectral light field at each incubation depth, or (2) a spectral, scalar-irradiance meter must be attached to a floating array at each incubation depth.

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Neither of these alternatives were feasible for the Marine Light-Mixed Layers (MLML) study, although spectrally integrated PAR measurements (inexpensive) were made at four depths from a floating array. For the calculation of  $\phi$ , AP at the incubation depths (different from the depths of PAR measurements) were calculated by three simplified methods. The first is a typical nonspectral method [e.g., Marra *et al.*, 1992] to show how the results differ from spectral model results. The second is through use of a nonlinear regression method for interpolating PAR values between and below PAR measurements. The third, based upon surface PAR and absorption coefficients derived from surface remote sensing measurements, is applicable to ocean color data collected from spacecraft or aircraft. These methods were tested at four MLML sites, and the differences among the results are discussed and evaluated.

## Measurements

Data of PAR( $z$ ), PP( $z$ ),  $a_{ph}(\lambda)$  (absorption coefficient of phytoplankton), and  $R_{rs}(\lambda)$  (remote sensing reflectance) were collected on an MLML cruise from May 17 to May 24, 1991, in the waters south of Iceland. The water depths where PAR and PP were measured were not the same (see below), although they were carried out on the same floating array for four days: May 17, 20, 22, and 24. The sampling site, conditions, wind, mixing, and nutrients are presented by Marra *et al.* [this issue] (also, B. Jones *et al.*, Spatial variability and physical and bio-optical properties in the sub-Arctic North Atlantic during MLML 1991, submitted to *Journal of Geophysical Research*, 1994; hereinafter referred to as submitted manuscript).

### Photosynthetically Available Radiation

Photosynthetically available radiation, PAR( $z$ ), at four depths (0, 2, 12.5, and 25 m) was monitored and averaged for every 10-min. interval throughout the day with a Biospherical PAR sensor attached to each incubation array [see Marra *et al.*, this issue].

### Primary Production

Dawn-to-dusk (17 hours) incubations with four replicates were carried out in situ at each of six depths (5, 10, 15, 20, 30, and 40 m) chosen to span the euphotic zone. Primary production measurements, PP( $z$ ), were made using the  $^{14}\text{C}$  technique [see Marra *et al.*, this issue].

### Absorption Coefficient of Phytoplankton Pigments

Measurements of  $a_{ph}(\lambda)$  for replicates of the incubation samples were obtained in the following manner. The method described by Mitchell and Kiefer [1988] was used to measure the particulate absorption coefficients, with a Lambertian diffuser added between the light source and the filter pad to minimize any dependence of the diffuse transmittance on the optical geometry of the light which is incident on the pad. This arrangement is very similar to that of Bricaud and Stramski [1990], who illuminated a pad in front of a diffusing window which was adjacent to an end-on photomultiplier tube. Our collector was a Spectron Engineering spectroradiometer with  $10^\circ$  acceptance angle. We filtered about 300-mL water samples onto Whatman GF/F pads, the transmission spectra (380–780 nm) of these pads were ratioed against that of wetted blank pads to obtain the optical density of the particles, and this optical density was corrected for large-

particle scattering. The particulate absorption coefficient was calculated, using (2) from Bricaud and Stramski [1990] to correct for optical pathlength elongation due to scattering in the pad (" $\beta$  factor"). After this measurement, each sample was soaked in hot methanol [Kishino *et al.*, 1985; Roesler *et al.*, 1989] for about 15 min to remove pigments, and its transmission spectra was again measured and ratioed against a methanol wetted blank to obtain the detrital absorption coefficient  $a_d(\lambda)$ . The difference between the particle and detrital absorption coefficients provided the absorption coefficient for phytoplankton,  $a_{ph}(\lambda)$ .

Gelbstoff absorption coefficients for surface waters were reported by Walsh *et al.* [1992], who filtered seawater through 0.2- $\mu\text{m}$  Gelman Supor 200 filters and measured the absorption on a Cary model 2200 spectrophotometer with a 10-cm cell. The approach followed that of Bricaud *et al.* [1981], where absorption at 370 nm was extrapolated to 440 nm as  $a_g(440) = a_g(370)e^{-0.014(440-370)}$  with an average semilog spectral slope of  $-0.014 \text{ nm}^{-1}$ .

### Remote Sensing Reflectance

Hyperspectral remote sensing reflectance  $R_{rs}(\lambda)$  (the ratio of water leaving radiance to the downwelling irradiance above the sea surface) was measured for the noon site by the method developed by Carder and Steward [1985], using the Spectron Engineering spectroradiometer. It has 253 channels and covers the wavelength range from 370 to 1100 nm. With this instrument the water-leaving radiance and downwelling sky radiance were directly measured, and downwelling irradiance was measured by viewing a standard diffuse reflector (Spectralon,  $\sim 8.5\%$ ). Sky radiance reflected from the sea surface was removed by the method of Carder and Steward [1985] when calculating  $R_{rs}(\lambda)$ .

## AP and $\phi$ Calculation

### Simple Nonspectral Model

Due to the expense of obtaining the spectral light field  $E_q(\lambda)$  with depth, a simplified model for PP is usually used [Tyler, 1975; Bannister, 1979; Morel, 1991; Marra *et al.*, 1992],

$$\text{PP}(z) = \phi(z)[\text{chl } a(z)]\bar{a}_{ph}^*(z)\text{PAR}(z), \quad (4)$$

where  $\bar{a}_{ph}^*$  ( $\text{m}^2 (\text{mg chl } a)^{-1}$ ) is the spectrally averaged chlorophyll-specific absorption coefficient:

$$\bar{a}_{ph}^* = \frac{\int_{400}^{700} a_{ph}(\lambda) d\lambda}{[\text{chl } a](700-400)}, \quad (5)$$

and

$$\text{PAR}(z) = \int_T \int_{400}^{700} E_q(\lambda, t, z) d\lambda dt. \quad (6)$$

For the calculation of PAR at incubation depths,  $K_{\text{PAR}}$  was calculated first according to

$$K_{\text{PAR}} = \frac{\ln [\text{PAR}(z_1)] - \ln [\text{PAR}(z_2)]}{z_2 - z_1}, \quad (7)$$

**Table 1.** Summary of Results

Day	PAR(0), mol photons/m <sup>2</sup> /d	Integrated [chl <i>a</i> ], mg/m <sup>2</sup>	Integrated PP, g C/m <sup>2</sup> /d	<i>a<sub>g</sub></i> (440)	
				Nonlinear	<i>R<sub>rs</sub></i>
May 17	38.27	162.2	2.3	0.013	0.026
May 20	16.25	108.2	1.2	0.024	0.021
May 22	65.72	56.0	1.1	0.018	0.029
May 24	28.73	50.6	1.2	0.017	0.028

and then the  $K_{\text{PAR}}$  value between 2 and 12.5 m is used to calculate PAR(5) and PAR(10), and the value between 12.5 and 25 m is used to calculate PAR(15), PAR(20), PAR(30), and PAR(40).

Thus, from (1) and (2), we have

$$\phi(z) = \frac{\text{PP}(z)}{[\text{chl } a(z)]\bar{a}_{\text{ph}}^* \text{PAR}(z)}. \quad (8)$$

Since PP, [chl *a*], and  $\bar{a}_{\text{ph}}^*$  were measured, it is easy to calculate  $\phi$  this way. However, as has been pointed out by Morel [1978] and Kishino *et al.* [1986], a simple average for  $\bar{a}_{\text{ph}}^*$  (5) does not accurately describe the phytoplankton absorption at depth, and a light-field-weighted average needs to be applied to  $\bar{a}_{\text{ph}}^*$ . Thus a better approximation that includes the character of light at depth is necessary. The following two sections describe two ways to model the spectral character of the light field at depth when only PAR(*z*), or  $R_{\text{rs}}(\lambda)$  and  $a_p(\lambda, z)$  are available.

### Nonlinear Regression

At depth *z*, daily PAR can be expressed as

$$\text{PAR}(z) \approx \int_{\text{Day}} \int_{\lambda} E_q(0, \lambda, t) e^{-\{K(\lambda, t)\}z} d\lambda dt, \quad (9)$$

where  $E_q(0, \lambda, t)$  is the subsurface scalar irradiance at time *t* in units of mol quanta m<sup>-2</sup> s<sup>-1</sup> nm<sup>-1</sup>, {*K*} is the vertically averaged diffuse attenuation coefficient, and {*K*} is approximated by {*K*} = 1.08(*a* + *b<sub>b</sub>*)/ $\mu_0$  [Kirk, 1984; Gordon, 1989]. In (9), since most of the stations were cloudy,  $E_q$  from the Sun and from the sky are combined. For clear-sky situations, separation of these two may be necessary, since the average cosine values for sunlight and skylight are generally different [Platt *et al.*, 1991]. Since there were no time series of  $E_q(0, \lambda)$  and  $a_p(\lambda)$ , some assumptions have to be made in order to calculate the spectral light field at depth.

1. The Gelbstoff absorption was constant for all depths.
2. The average of  $a_p$  for dawn and noon measurements was considered to represent the particle absorption coefficient for the whole day.
3. Due to the presence of clouds, it is difficult to estimate  $\mu_0$  for any given time. Thus an average subsurface cosine of  $\mu_0 = 0.77$  was used for these high-latitude sites for the whole day, including sunny, cloudy, and overcast conditions.
4. The condition holds that  $b_b \ll a$  [Morel and Prieur, 1977].

Then we have

$$\text{PAR}(z) \approx \int_{\lambda} E_q(0) e^{-1.4[(a_w + a_p)z + \sum a_p \Delta z]} d\lambda, \quad (10)$$

where 1.4 in the exponent is  $\approx 1.08/0.77$  and integration over time is implicitly combined into  $E_q(0)$ , and  $\sum \Delta z = z$ , and  $\sum a_p \Delta z = \sum_i a_p(z_i)(z_{i+1} - z_i)$ .

In (10), vertical stratification of  $a_p$  is considered, although most of the stations were quite well mixed [see Marra *et al.*, this issue]. Also for (10), PAR(*z*) and  $a_p(z)$  were measured,  $a_w$  is known [Smith and Baker, 1981], and  $E_q(0)$  and  $a_g$  must be derived.

Parameter  $a_g(\lambda)$  can be expressed as  $a_g(\lambda) = a_g(440) e^{-0.014(\lambda - 440)}$  [Bricaud *et al.*, 1981]. Since this variable is very difficult to measure at visible wavelengths for open-ocean waters [Bricaud *et al.*, 1981], Walsh *et al.* [1992] measured  $a_g(370)$  and used the above expression to extrapolate to  $a_g(440)$  for waters at the MLML site. The spectral slope 0.014 nm<sup>-1</sup> for  $a_g$  is assumed and kept as constant for all stations.

$E_q(0)$  is expressed as  $E_q(0) = \text{PAR}(0)_{\text{der}} E_q^*(0)$ , where PAR(0)<sub>der</sub> is the derived surface PAR in order to correct possible errors in measured PAR(*z*) due to sea surface roughness, and  $E_q^*(0) = E_q(0)/\text{PAR}(0)$ .  $E_q(0)$  and PAR(0) are computed using the model of Gregg and Carder [1990]. There were typically four (three for May 22) PAR measurements for each day, so PAR(0)<sub>der</sub> and  $a_g(440)$  for each day can be derived by nonlinear regression, i.e., minimize the variance between the modeled and measured PAR. The derived  $a_g(440)$  values are shown in Table 1.

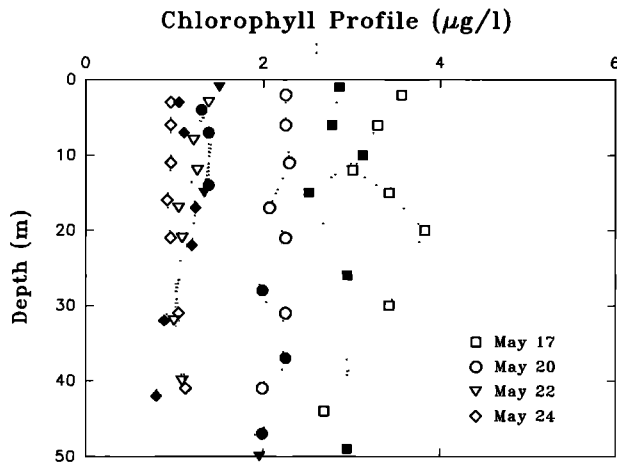
After the derivation of PAR(0)<sub>der</sub> and  $a_g(440)$ , quantum yield can be calculated for each depth through

$$\phi(z) = \frac{\text{PP}(z)}{\text{PAR}(0)_{\text{der}} \int_{\lambda} E_q^*(0) e^{-1.4[(a_w + a_p)z + \sum a_p \Delta z]} a_{\text{ph}} d\lambda}. \quad (11)$$

### Remote Sensing Reflectance

With recent measurement techniques [e.g., Carder and Steward, 1985] and models for interpreting hyperspectral remote sensing reflectance ( $R_{\text{rs}}$ ) data [Carder and Steward, 1985; Peacock *et al.*, 1990; Lee *et al.*, 1992, 1994a, b], it has been shown that by inversion of the measured  $R_{\text{rs}}$ , the total absorption coefficient for the surface layer can be derived [Lee *et al.*, 1994a, b]. This measurement approach avoids the inherent problems of in-water reflectance measurements such as instrument self-shading [Gordon and Ding, 1992] and ship shadows [Gordon, 1985].

To use this approach, i.e., deriving the total absorption coefficient and then calculating the photons absorbed by phytoplankton at depth for a day, we still need most of those assumptions made for the nonlinear regression method. However, PAR(0)<sub>der</sub> is set to equal the measured surface PAR, and the total absorption  $a(\lambda)$  is derived by inverting



**Figure 1.** Depth profiles of chlorophyll values. open symbols, predawn measured values; solid symbols, noon measured values.

$R_{rs}(\lambda)$  data [see Lee *et al.*, 1994a]. One approach for deriving  $a(\lambda)$  from  $R_{rs}$  is suggested by Gordon *et al.* [1988], Morel [1988], and Sathyendranath and Platt [1988]. They empirically derive the chlorophyll concentration first and use an empirical specific-absorption coefficient to calculate the particle absorption coefficient. The Gelbstoff absorption coefficient is assumed to covary with [chl  $a$ ]. This method only works well for "case 1" waters [Morel and Prieur, 1977].

Recent studies [Gordon *et al.*, 1988; Morel and Gentili, 1993; Lee *et al.*, 1992, 1994a] show that  $R_{rs}$  can be expressed as

$$R_{rs} = \frac{G}{a_w + a_p + a_g} \left[ b_{bw} + X \left( \frac{400}{\lambda} \right)^Y \right], \quad (12)$$

where  $G \approx 0.093(\pi/n)^2$ , the air-sea interface transmittance  $\tau \approx 0.97$  for most of the ocean [Austin, 1974], and  $n \approx 1.341$  is the refractive index of seawater. The two terms in brackets consist of scattering contributions due to water molecules and particles, respectively. The backscattering coefficient of pure water,  $b_{bw}$ , is given by Smith and Baker [1981], and  $X$  and  $Y$  are site specific and can be derived from  $R_{rs}$  [Lee *et al.*, 1994a, b].

By adjusting parameters affecting the modeled  $R_{rs}$  curve to achieve a close fit with the measured  $R_{rs}$  curve,  $a_g(\lambda)$  of the surface layer was derived. The derived  $a_g(440)$  values are shown in Table 1. In the derivation of  $a_g$  using  $R_{rs}$ , a multiplication factor  $f$  was applied to the surface  $a_p$  as in the work by Lee *et al.* [1994a]. For the MLML waters,  $f$  varied from 1.0 to 1.2. This factor accounts for possible errors in particle absorption due to plankton patchiness, vertical stratification, and the "β factor."

After the inversion of  $R_{rs}$ , the sum  $a_w + fa_p + a_g$  was used as the average total absorption coefficient for the water column to calculate PAR and AP at depth using measured profiles of  $a_{ph}(z)$ . Quantum yield values were then calculated based upon measured values of primary production.

## Results and Discussion

Figure 1 shows the predawn (open symbols) and noon (solid symbols) values of measured chlorophyll for the

cruise. Notice that there was no strong vertical structure in the water column if the averages of the predawn and noon profiles are considered. The differences between predawn and noon chlorophyll values were larger for May 17 and 20, but much smaller for May 22 and 24.

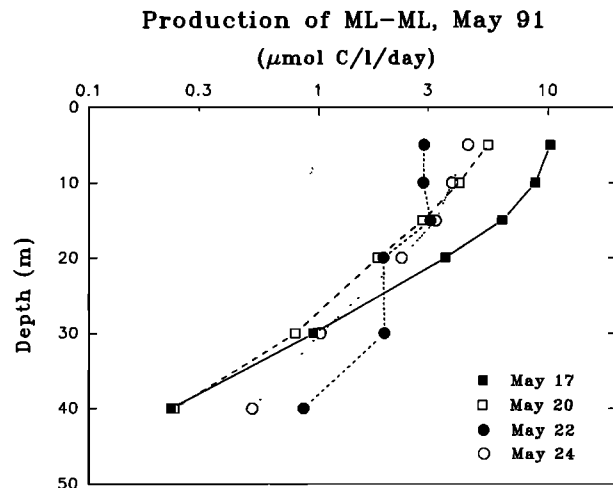
Figure 2 shows the measured primary production for each of the four days. The surface production decreased from day 1 to day 4. This might be due in part to the progressive reduction in chlorophyll with time, but the variation in PAR(0) values in Table 2 suggests a more complicated explanation.

Figures 3a and 3b show the measured spectra of remote sensing reflectance and the predawn particle absorption coefficients for the upper water column, respectively. May 17 had the lowest  $R_{rs}$  values around 440 nm, consistent with the highest noon chlorophyll concentration among the four days (Figure 1). Also notice the high  $R_{rs}(685)$  values for May 17, likely resulting from the contribution of chlorophyll  $a$  fluorescence. For the following three stations, the  $R_{rs}$  values were similar, as their surface noon chlorophyll concentrations did not vary much (Figure 1).

The detritus-to-pigment ratio for absorption at 440 nm was in the range of 15–20%, with an average of about 18%. The spectral curves were simulated using exponential functions with an average semilog spectral slope for  $a_d$  of about  $-0.010 \text{ nm}^{-1}$ , similar to that found by Roesler *et al.* [1989].

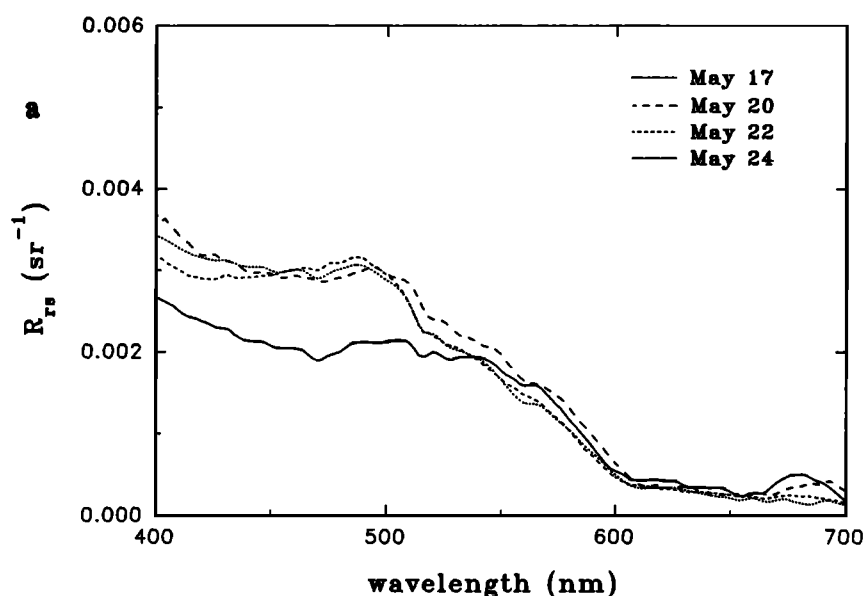
Figures 4a–4d show the measured and calculated PAR for the four days. In general, PAR values at greater depths calculated by the simple, nonspectral model were lower than those determined by nonlinear regression and by  $R_{rs}$  methods. One reason why PAR estimates at greater depths were lower using the nonspectral model is that Beer's law does not hold for  $K_{PAR}$ . The PAR values determined by nonlinear regression and  $R_{rs}$  methods were quite close (average difference of 9%). Compared with the PAR values at 2, 12.5, and 25 m, the average difference between the measured and the  $R_{rs}$ -method calculations was 19%. Most of the difference was found at 2 m (see Figure 4), where the measured values appeared to be low, especially on May 24. However, it is not clear what caused this result.

Figures 5a–5d show the calculated quantum yield  $\phi$  values for the four days. The simple, nonspectral model generates



**Figure 2.** Depth profiles of measured production values.

## Remote-sensing Reflectance of ML-ML May 91



## Particle Absorption Coefficient of ML-ML May 91

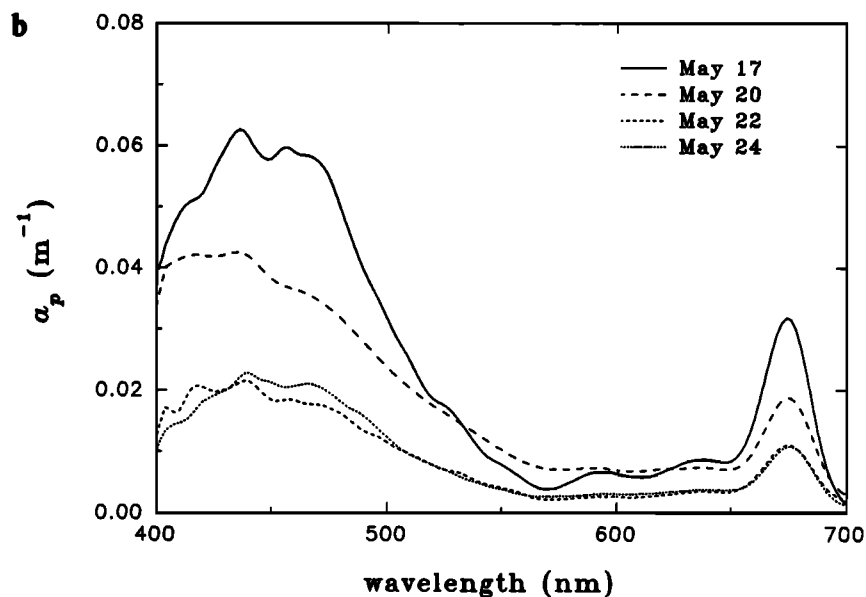


Figure 3. Measured spectra of water properties for (a) remote sensing reflectance and (b) particle absorption coefficients.

the highest  $\phi$  values at 30 and 40 m, some of which are much higher than the  $0.12 \text{ mol C (mol photons)}^{-1}$  theoretical maximum [Kok, 1960]. Possible reasons for these overestimates include (1) nonconsideration of the spectral character of the light field [Morel, 1978; Kishino *et al.*, 1986] and (2) PAR(30) and PAR(40) were derived by extrapolation using  $K_{\text{PAR}}$ , which does not follow Beer's law.

The differences in derived  $\phi$  values for the nonlinear regression and  $R_{\text{rs}}$  methods are 2–28% (average 11%), with most of the differences occurring at 40 m near the bottom of the euphotic zone. This difference is largely due to the

different derived  $a_g$  values. As there were no PAR measurements at 30 and 40 m, it is difficult to judge which method is more accurate. The  $a_g$  values determined from the  $R_{\text{rs}}$  model inversion, however, are closer to the measured values reported by Walsh *et al.* [1992], with an average difference of only about 18%. The calculated  $\phi$  values by both methods are consistent with values reported elsewhere [Tyler, 1975; Dubinsky *et al.*, 1984; Kishino *et al.*, 1986] and are less than the  $0.12 \text{ mol C (mol photons)}^{-1}$  theoretical maximum.

Part of the error in  $\phi$  calculation comes from estimates of PAR( $z$ ) and measurements of  $a_{\text{ph}}(\lambda)$ . As the error of PAR

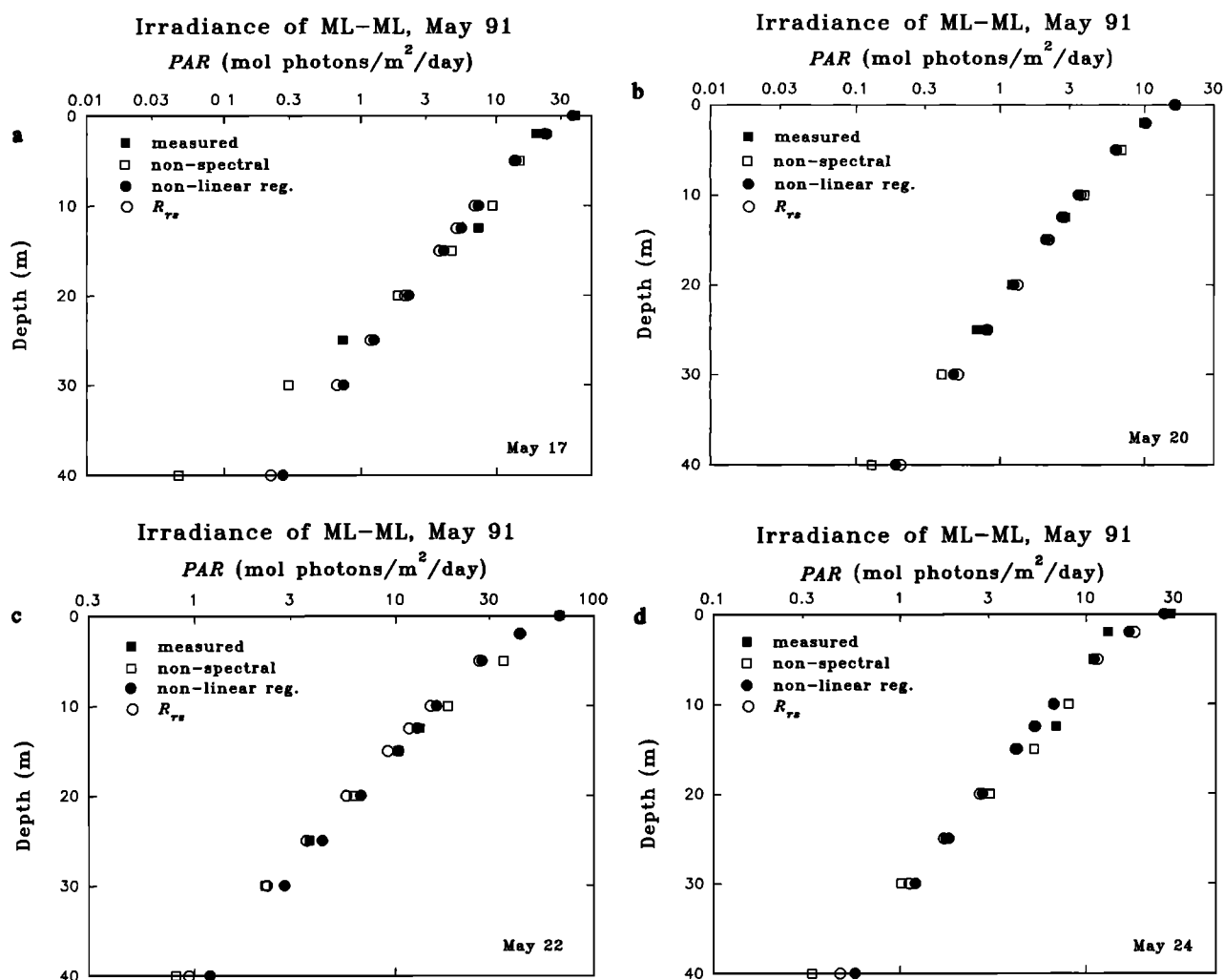


Figure 4. Depth profiles of measured PAR versus calculated PAR on (a) May 17, (b) May 20, (c) May 22, and (d) May 24.

was 19% using the  $R_{rs}$  method, if the error in measuring  $a_{ph}$  was 10%, then the error in  $\phi$  would be about 22%.

The error in  $\phi$  caused by errors in  $a_g$  varies with the relative contribution of  $a_g$  to the total absorption, and also varies with depth. For the waters studied, a 100% error in  $a_g(440)$  would cause a factor of 2 error in  $\phi$  at the bottom of the euphotic zone, whereas it would only contribute an error of about 10% in  $\phi$  for the surface layer. However, a recent study [Lee, 1994] shows that the average error of  $R_{rs}$ -derived total absorption is only about 30%. Therefore the error in  $\phi$  is expected to be much less than a factor of 2, especially when  $a_{ph}(\lambda)$  is measured.

Figures 6a and 6b show calculated  $\phi$  versus PAR values using the nonlinear regression method and the  $R_{rs}$  method, respectively. These figures are similar in shape to those reported by Tyler [1975] and Kishino *et al.* [1986]. If we ignore the  $\phi$  values at 40 m as being less reliable,  $\phi$  values for both methods can be expressed as suggested by Steele [1962]:

$$\phi = \phi_m e^{-\alpha PAR}, \quad (13)$$

where  $\phi_m$  and  $\alpha$ , derived from the  $\phi$  results of the two methods, are shown in Table 2 as a function of time. All the

$\phi_m$  values are consistent with the maximum quantum yield values reported by Welschmeyer and Lorenzen [1981] (0.040–0.074 mol C (mol photons)<sup>-1</sup>), Kiefer and Mitchell [1983] (0.05 mol C (mol photons)<sup>-1</sup>), Langdon [1988] (0.034–0.10 mol C (mol photons)<sup>-1</sup>), and Cleveland *et al.* [1989] (0.033–0.102 mol C (mol photons)<sup>-1</sup>). It is clear that the differences in  $\phi_m$  and  $\alpha$  as calculated by the two methods are smaller than the differences due to changes in the water column over the four days. The  $\phi_m$  values for the last three sampling days were fairly consistent and about 40% larger than on the first day, but the slope value  $\alpha$  increased more than twofold between the first two days before dropping to an intermediate level. The daily change of  $\phi_m$  and  $\alpha$  can be caused by changes in physiological parameters, such as nutrients, adaptation, species, and light level.

Table 1 summarizes the above results along with the column-integrated (within the euphotic zone) chlorophyll *a* and primary production. The column-integrated chlorophyll *a* decreased from the beginning to the end of the cruise. Also, for the four days, PAR(0) and chlorophyll *a* changed markedly ( $\approx 4\times$  and  $3\times$ , respectively), but the integrated primary production did not vary as much ( $<2\times$ ). This was especially interesting for the last three days, which included

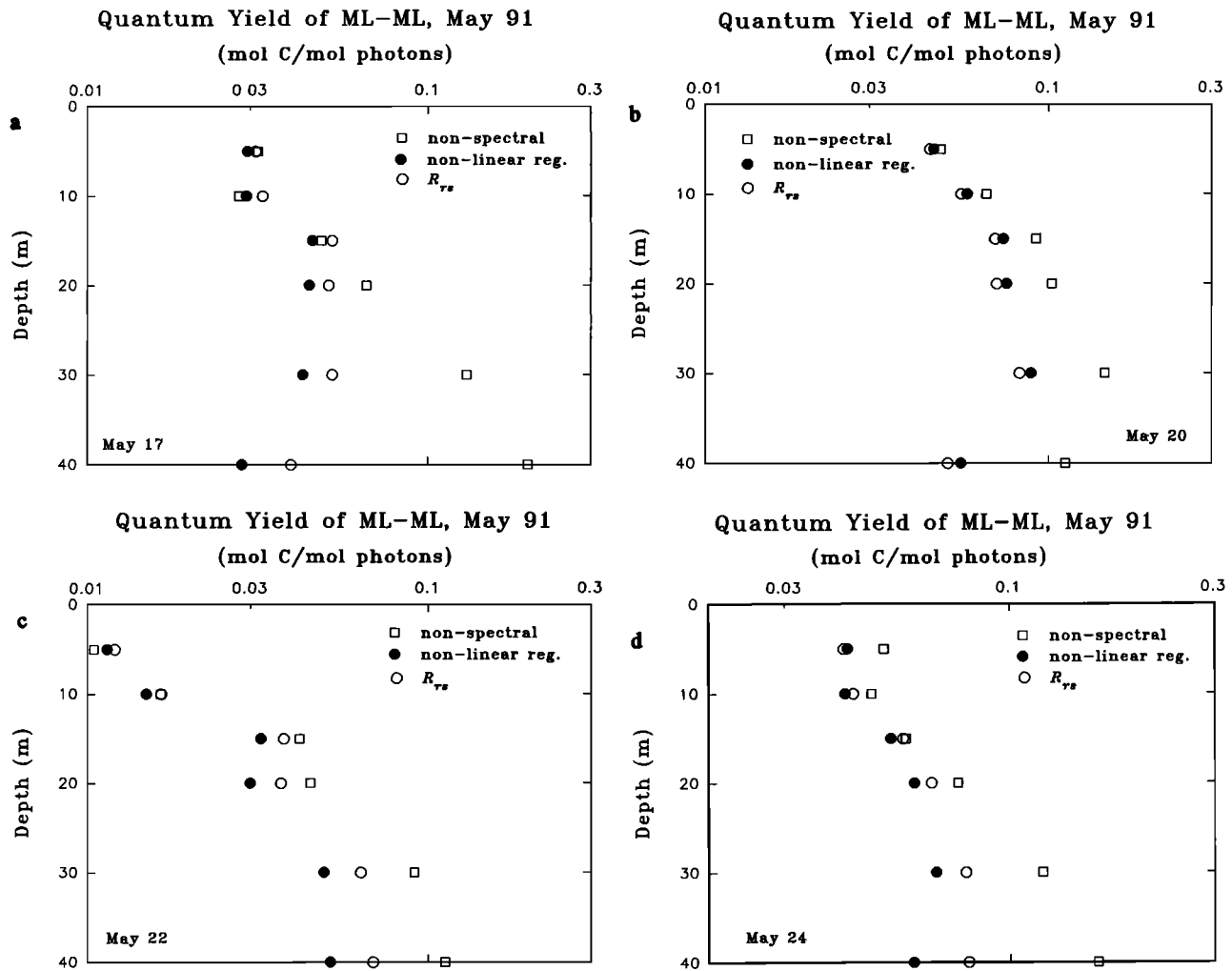


Figure 5. Depth profiles of quantum yield on (a) May 17, (b) May 20, (c) May 22, and (d) May 24.

a sunny day (May 22), when the productivity near the surface on that day appeared to have been significantly reduced by photoinhibition.

May 22 was the only sunny day for the entire cruise; the populations presented would have been low-light adapted. The threefold to fourfold reduction in surface  $\phi$  values for the rare sunny day compared with values for the previous two stations suggests that great care must be taken in interpreting satellite estimates of primary production in light-changing environments. The occasional view of the ocean that a satellite observes on a rare sunny day may be accompanied by perturbations in the photosynthetic perfor-

mance of the phytoplankton because of a light-history factor that is not well understood at this time.

### Summary

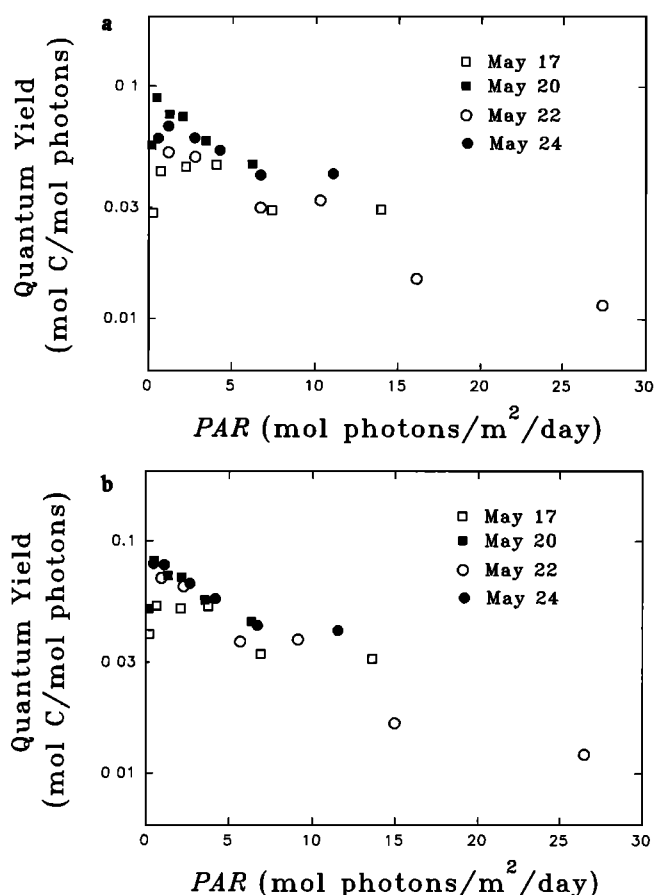
1. Three methods of estimating the absorbed photons at depth were evaluated, one of which was nonspectral.
2. The spectral methods (the nonlinear regression and remote sensing reflectance approaches) both provide good alternatives to model the spectral light field at depth for reasonably well mixed water columns such as the MLML site. The PAR values for the nonspectral method were too

Table 2. Calculated Maximum Quantum Yield

Day	Nonlinear Regression Method		$R_{rs}$ Method		Average of Methods, %	
	$\phi_m$	$\alpha$	$\phi_m$	$\alpha$	$\phi_m$	$\alpha$
May 17	0.047	0.038	0.056	0.049	$0.052 \pm 8.8$	$0.044 \pm 12.6$
May 20	0.091	0.118	0.085	0.106	$0.088 \pm 3.4$	$0.112 \pm 5.4$
May 22	0.058	0.071	0.074	0.088	$0.066 \pm 12.1$	$0.080 \pm 13.2$
May 24	0.069	0.056	0.081	0.073	$0.075 \pm 8.0$	$0.065 \pm 13.2$
Average over days, %	$0.066 \pm 20.8$	$0.071 \pm 33.6$	$0.074 \pm 12.2$	$0.079 \pm 22.8$	$0.070 \pm 18$	$0.075 \pm 29$

Units for  $\phi_m$  are mol C (mol photons)<sup>-1</sup> and for  $\alpha$  are (mol photons/m<sup>2</sup>/d)<sup>-1</sup>.





**Figure 6.** Quantum yield versus PAR calculated (a) by nonlinear regression method and (b) by  $R_{rs}$  method.

low and resulted in theoretically unrealistic quantum yield values.

3. Calculated quantum yield values by the two spectral methods are consistent with each other and with values reported by other studies. The equation

$$\phi(z) = 0.070e^{-0.075PAR(z)} \quad (14)$$

provides an estimate of the average quantum yield with PAR for the MLML site. Combining surface PAR values [e.g., Gregg and Carder, 1990; Bishop and Rossow, 1991] with (9) or (10) allows PAR(z) calculations to be made on the basis of remotely sensed data.

4. The daily PAR(0) varied fourfold, and the column-integrated chlorophyll *a* varied threefold during the cruise. The column-integrated primary production varied only two-fold, however. This argues for the need to better understand factors affecting the quantum yield and the light field with depth in order to improve model simulations of primary production.

5. The methods suggested here are alternatives for full-spectra measurements when only data of PAR(z) or  $R_{rs}$  are available. If possible, measurements of time series of the spectral light field at the incubation depths would be the best choice. Also, time series of  $R_{rs}(\lambda)$ ,  $E_q(0, \lambda)$ , and  $a_{ph}(z, \lambda)$  would help to improve the suggested methods and to understand in situ  $\phi$ .

6. The reduction exhibited in surface  $\phi$  values for a rare sunny day suggests that primary production estimates based

upon satellite measurements of ocean color for regions with a history of cloud cover may be in serious error if light history of the region is not considered in assessing effects of photoinhibition.

### Notation

- $a(\lambda)$  total absorption coefficient, equal to  $a_w(\lambda) + a_g(\lambda) + a_p(\lambda)$ ,  $m^{-1}$ .
- $a_d(\lambda)$  absorption coefficient of detritus,  $m^{-1}$ .
- $a_g(\lambda)$  absorption coefficient of Gelbstoff,  $m^{-1}$ .
- $a_{ph}(\lambda)$  absorption coefficient of phytoplankton pigments,  $m^{-1}$ .
- $a_w(\lambda)$  absorption coefficient of pure water,  $m^{-1}$ .
- AP absorbed photons by phytoplankton, mol photons/ $m^3/d$ .
- $b_b(\lambda)$  backscattering coefficient,  $m^{-1}$ .
- $E_q^*(\lambda)$  specific quantum irradiance, equal to  $E_q(\lambda)/PAR(0)$ ,  $nm^{-1}$ .
- $E_q(\lambda)$  quantum irradiance,  $\mu mol$  photons/ $m^2/nm/s$ .
- $K_{PAR}$  attenuation coefficient for PAR,  $m^{-1}$ .
- $\{K(\lambda)\}$  vertically averaged attenuation coefficient for downwelling irradiance,  $m^{-1}$ .
- $n$  refractive index of seawater.
- PAR photosynthetically available radiation (integrated from 400 to 700 nm), mol photons/ $m^2/d$ .
- PP primary production, mol C/ $m^3/d$ .
- $PAR(0)_{der}$  derived surface PAR, mol photons/ $m^2/d$ .
- $R_{rs}(\lambda)$  remote sensing reflectance, ratio of upwelling radiance to downwelling irradiance above the sea surface,  $sr^{-1}$ .
- $T$  integration or incubation period of time, hours or day.
- $\alpha$  slope to describe  $\phi$  changes with PAR, (mol photons/ $m^2/d$ ) $^{-1}$ .
- $\phi$  quantum yield, mol C (mol photons) $^{-1}$ .
- $\phi_m$  maximum quantum yield, mol C (mol photons) $^{-1}$ .
- $\lambda$  wavelength, nm.
- $\tau$  air-sea surface transmittance.
- $\mu_0$  subsurface average cosine for downwelling irradiance.

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