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## **Quantum Yields in Aquatic Photosynthesis**

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1. Introduction

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#### 1.1. Photosynthetic efficiency

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Primary productivity is the product of the light energy absorbed by plants and the efficiency by which this energy is stored as a photosynthate. The quantum yield ( $\phi$ ) of photosynthesis is defined (Eq. 1) as the molar ratio between oxygen released in photosynthesis (or carbon assimilated) to photons absorbed in the process (Fig. 1) (Dubinsky, 1980; Dubinsky & Berman, 1976, 1979, 1981; Dubinsky et al., 1984). The quantum yield is, therefore, equal to the ratio of photosynthetically stored radiation (PSR) to the energy absorbed photosynthetically usable radiation (PUR)[for definitions, see Morel (1978)].

$$\phi = \frac{\text{moles oxygen evolved (CO_2 \text{ absorbed})}}{\text{moles light quanta absorbed}} = \frac{\text{PSR}}{\text{PUR}}$$
(1)

To calculate  $\phi$ , we need to know the fraction of incident light that is absorbed by phytoplankton cells (Morel, 1978). This fraction is proportional to the product of the photosynthetic pigment concentration and a<sup>\*</sup> - the specific *in vivo* absorbance constant of pigments (Dubinsky, 1980, 1992; Kirk, 1994). For *in situ* studies, both the spectral absorbance of the cells and the intensity and spectrum of ambient light are taken into account as the k<sub>c</sub> parameter (Dubinsky, 1992; Dubinsky et al., 1986; Schanz et al., 1997) whose dimensions are m<sup>2</sup> mg<sup>-1</sup> chl. Thus, the absorbed light is proportional to k<sub>c</sub>, the *chlorophyll a* concentration, and light intensity (E).

Early attempts to define and measure the quantum yield were published by several pioneers in photosynthesis research. Some of the symbols for quantum yield used in the past and references are listed in Table 1. The present review focuses on the measurement of the quantum yields of photosynthesis in the aquatic domain.

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**Figure 1.** Scheme of quantum yield, which is the ratio between the energy in photochemistry products to photons absorbed from sunlight in the photosynthesis process, whereby the major initial loss is thermal dissipation (see chapter by Pinchasov, this volume), and minor ones are fluorescence emitted primarily by PSII and marginally by PSI.

Source	Symbol	Value
Aruga and Ichimura, 1968	ε	0.0184
Taling, 1970	K <sub>s</sub>	0.01-0.12
Megard, 1972	K <sub>s</sub>	0.01-0.12
Bannister, 1974	K <sub>c</sub>	0.016
Ganf, 1974	ε <sub>s</sub>	0.012-0.016
Berman, 1976	ε <sub>s</sub>	0.006
Jewson, 1976	ε <sub>s</sub>	0.011
Bindloss, 1976	K <sub>s</sub>	0.0086
Dubinsky and Berman, 1979	$k_c$ , from $\eta^n_{450}$	0.0121
Dubinsky and Berman, 1979	$k_c$ , from $\eta^n_{560}$	0.005
Dubinsky and Berman, 1979	$k_c$ , from $\eta^n_{650}$	0.0112
Dubinsky and Berman, 1979	$k_c$ , from $\eta^n_{PhAR}$	0.0067

Table 1. Specific extinction coefficients of chlorophyll (in units\* mg <sup>-1</sup>Chl\*m<sup>-2</sup>) (Dubinsky & Berman, 1979)

#### 1.2. Maximal quantum yield

In principle,  $\phi_{max}$  cannot exceed 0.125 since four electrons are required for the evolution of one molecule of O<sub>2</sub> from water. According to the "Z" diagram of photosynthesis (Emerson & Lewis, 1943), each electron is driven by two photons, each absorbed in PSII and PSI, resulting in a minimal photon requirement (1/ $\phi$ ) of eight (Fig. 2).



**Figure 2.** The "Z" scheme of photosynthesis, demonstrating the minimum requirement of  $2 \times 4$  photons for the evolution of one molecule of O<sub>2</sub> and the concomitant assimilation of CO<sub>2</sub>.

In cases where the nitrogen source was nitrate, not ammonium, at least two more photons were consumed to provide for its reduction to cell components, reaching  $\phi_{max}$  values <0.1. High values, approaching the theoretical maxima, were observed only under low light. Under high light, the rates of photon absorption by antennae exceed the rates of energy utilization in photochemical processes. These rates were limited by the bottleneck of electrons shuttling through the quinone pool from PSII to PSI. The excess energy had to be dissipated as heat following absorption by photoprotective pigments, such as peridinin and astaxanthine, and by means of the xanthophyll cycle. Table 2 lists some  $\phi_{max}$  values found in different regions.

In all studies, an increase in  $\phi_{max}$  values with depth from the surface to the deepest samples, was observed. Morel (1978) estimated  $\phi_{max}$  values at the surface based on <sup>14</sup>C incubation data in the oligotrophic Sargasso Sea and the highly productive Mauritanian upwelling zone. In the eutrophic, green Mauritanian data,  $\phi_{max}$  was considerably higher than in the Sargasso area, as would be expected in a nutrient-replete environment, and reached 0.012. In the oligotrophic Sargasso Sea,  $\phi_{max}$  was found to be only around 0.003, reflecting the oligotrophic conditions in that region. Kishino et al. (1985), working in the Pacific, south of Japan, reported values of 0.004-0.01 at the surface and 0.01-0.026 at the 10-20 m level, where the peak of photosynthesis was found. Values increased further up to 0.026-0.075 at the deep chlorophyll maximum (DCM), at 70 m. During the annual *Peridinium* bloom in the monomictic, mesotrophic Lake Kinneret (Israel), Dubinsky and Berman (1981) observed an increase from 0.025 at the surface to 0.043 at 3 m, below the euphotic zone. During vernal stratification with nutrients in the epilimnion (the nutrients were exhausted in that period), phytoplankton was dominated by minute chlorophytes and  $\phi_{max}$  values were lower as expected: 0.0126 at the surface and a maximum of 0.06 at 5-7 m.

Locality	Depth	φ	Reference
Sargasso Sea, Mauritania	Surface	0.003	Morel (1978)
	Surface	0.012	
Pacific Ocean, south of Japan	Surface	0.004-0.01	Kishinoet al. (1985)
	10-20 m	0.01-0.026	
	70 m	0.026-0.075	
Gulf of Eilat, Israel.	Surface	0.00025	Iluz (2008)
winter.	80 m	0.110	
Gulf of Eilat, Israel. summer	Surface	0.00087	
	80 m	0.0266	
Lake Kinneret, Israel.Winter	Surface	0.025	Dubinsky and Berman (1981)
Lake Kinneret, Israel.summer	3 m	0.043	
	Surface	0.0126	
	5-7 m	0.06	
Zooxanthellae <i>in hospice</i>		0.001 <sup>1</sup> -0.125 <sup>2</sup>	Dubinsky et al. (1984)
<sup>1</sup> From high-light corals			
<sup>2</sup> From low-light corals			

**Table 2.** Quantum yield ( $\phi$ ) values found in different regions

In the Gulf of Eilat, we found an increase in  $\phi_{max}$  values with depth for all profiles (Fig. 3). However, it is noteworthy that the correlation coefficient between light and  $\phi$  was only R<sup>2</sup> = 0.7 for all profiles, whereas in summer it was 0.85 and in winter it reached 0.91. For the pooled data, these differences indicate that additional factors besides light intensity do affect the quantum yields of photosynthesis. The seasonal trend lines clearly point towards the effect of nutrients. In summer, lack of nutrients does restrict photosynthetic efficiency, whereas in winter, due to vertical mixing, no such effect is evident (Iluz et al., 2008).

The trends observed in quantum-yield values are in agreement with their oceanic distributions. For instance, Prezelin et al. (1991) found  $\phi$  ranging from0.01 to 0.06 in a transect 200 km south of California. These differences were linked to different water masses and depths. Some of these spatial changes were related to the taxonomic differences between phytoplankton assemblages. For instance, diatom-dominated sites had  $\phi$  twice as high as those consisting of picoplankton at the DCM (Schofield et al., 1991). However, these represent complex differences, not necessarily taxonomic *per se*. Diatoms thrive in nutrient-rich situations, whereas picophytoplankton outcompete all larger eukaryotes in oligotrophic waters due to their higher surface/volume ratios. Furthermore, the DCM is found at the very bottom, or even just below, the euphotic depth at very low light, where higher  $\phi$  values are always to be expected.

In their study on the Sargasso Sea, Cleveland et al. (1989) reported an inverse correlation between  $\phi$  values ranging from 0.033 to 0.102, and the distance from the nitrocline. These results are in accord with those of Kolber et al. (1990) from the Gulf of Maine. In both cases,



**Figure 3.** Linear regression of the quantum yield vs. light intensity for all profiles down to 100 m depth, between 24.10.94 and 18.06.96 (n= 56).

the difference in quantum yields was explained by the flux of nitrogen from deep waters into the euphotic zone. A diel pattern superimposed upon the spatial differences in  $\varphi$ , peaking in the morning and declining in the afternoon (Kishino et al., 1985; Prezelin et al., 1987, 1991), was also reported. Such an "afternoon nap" (Schanz & Dubinsky, 1988; Walsby et al., 2001) was also seen by Tilzer (1984) in Lake Konstanz, where threefold diel changes in  $\varphi$  exceeded their seasonal amplitude. Here, too, values decreased from morning to afternoon. In general, other than in their universal bathymetric trend, quantum yields of photosynthesis [e.g., Cleveland et al. (1989)] and the related fluorescence yields (Falkowski, 1991; Kolber et al., 1990)reveal the overriding control of nutrients over oceanic primary productivity.

## 2. Methods based on measuring light absorption and photosynthesis rates

To calculate the quantum yield most ways, we need to measure the rate of photosynthesis (but see below the sections on photoacoustics and variable fluorescence) and light absorption (Eq. 2).

#### 2.1. Absorbed light

The denominator of that fraction, the absorbed light, was calculated as follows (Dubinsky & Berman, 1981). From the vertical attenuation coefficient, the total light absorbed in the slice was calculated as the difference between light entering the top of the layer and that at the bottom. It was then partitioned into that absorbed by the phytoplankton and all other light-absorbing substances in the water according to:

$$K_{d} = k_{w'} + k_{c} chl and k_{w'} = k_{w} + k_{g} + k_{tr}$$
 (2)

where  $K_d$  is the attenuation coefficient PAR [ln units m<sup>-1</sup>],  $k_c[m^2mg^{-1}chl a]$  is the spectrally averaged, in situ, specific extinction coefficient of *chlorophyll a*, and chl is *chlorophyll a* concentration [mg *chl a* m<sup>-3</sup>].  $k_w$  is attenuation coefficient due to water alone,  $k_g$  is gilvin, and  $k_{tr}$  is tripton - all of these in ln units m<sup>-1</sup>.

Thus the absorbed light, given in mole quanta is:

$$\frac{(PARz_1 - PARz_2)k_c^* chl}{K_d}$$
(3)

From these, using <sup>14</sup>C tracer incubations (Steemann-Nielsen, 1952) in order to estimate the enumerator of the quantum yield fraction, the authors were able to calculate the ratio of mole carbon stored as photosynthate in a defined water volume to that of light quanta absorbed by the phytoplankton in the same water volume and at the same time interval.

By dividing primary production rates for the same time interval and volume as the absorbed light, we obtained the values of  $\phi$  for all depths as molar ratios O<sub>2</sub>/quanta.

A part of the light impinging on a phototroph cell is absorbed according to the relation between the absorbance spectrum of that cell's pigment assortment and the spectral distribution of the surrounding underwater light field. The fate of harvested light and the losses incurred until the remainder is stored in a generalized algal cell, and until it becomes available as a substrate for life-supporting respiration and building blocks for cell growth and multiplication, are summarized in Figure 1.

Under low-light intensity, photosynthesis is proportional to photon flux. In the light-limited range of the photosynthesis versus energy curve (P vs. E\*), the quantum yield remains maximal,  $\phi_{max}$ . This is equal to the ratio between  $\alpha$  and  $k_{o}$ , when  $\alpha$  is defined as the initial slope of the P vs. E curve and expressed as moles O<sub>2</sub> evolved per mg chlorophyll. Chlorophyll unit *in vivo*:

$$\alpha = \frac{\text{mole } O_2 \text{mg}^{-1} \text{chl s}^{-1}}{\text{mole photons } \text{m}^{-2} \text{s}^{-1}} = \phi_{\text{max}} k_c$$
(4)

From here we can release  $\phi_{max}$  without knowing the amount of absorbed light at any given depth (Dubinsky et al., 1986; Falkowski et al., 1990).

The maximum quantum yield  $(\phi_{max})$  is measured when photosynthesis is light-limited, a situation diagnosed by a linear relationship between photosynthesis and photosynthetic photons, also incorrectly termed photon flux (flux already implies density!) density (PPFD).

Theoretically,  $\phi_{max}$  is 0.125, since 8 moles of photons are required for a mole of oxygen to evolve from water according to the "Z" scheme of photosynthesis (Emerson & Arnold, 1932) in two photoactivations per electron, and concomitantly reduce 1 mole of CO<sub>2</sub> in the absence of photorespiration. Because there is some cyclic photophosphorylation,  $\phi_{max}$  may be closer to 0.112 in most plants (Long et al., 1993). Furthermore, whenever the source of nitrogen is nitrate rather than ammonia,  $\phi_{max}$  is further reduced due to the energy required for its reduction

#### 2.2. Carbon

Primary production is usually measured in terms of the amount of biomass, carbon fixation, or oxygen produced. Gross primary production (Pg) is the rate of photosynthesis, the total amount of fixed energy (sunlight that has been transformed into the chemical energy of organic materials, i.e., photosynthesis):

$$Pg = R + Pn \tag{5}$$

where R is the energy that has been used by the autotrophs themselves in their respiration, and Pn is the energy that was not consumed, and results in growth or food for grazers.

The most common method for measuring aquatic photosynthesis is based on <sup>14</sup>C assimilation, which is briefly summarized below. Samples for <sup>14</sup>C productivity measurements -P(<sup>14</sup>C)- are usually incubated in 60-ml polycarbonate bottles. Carbon uptake is measured with a modified <sup>14</sup>C uptake technique (Steemann-Nielsen, 1952). A spike of approximately 8 mCi of [<sup>14</sup>C] bicarbonate is added to each bottle. After incubation, the samples are filtered under light vacuum (about 100 mm Hg) onto 25-mm 0.45-m filters (Millipore), rinsed with 15 ml of filtered lake water, and briefly fumed in HCl vapor to eliminate any remaining traces of inorganic <sup>14</sup>C. Control samples poisoned by Lugol's iodine at time zero were run with each experimental series to compensate for nonbiological adsorption to filters. The total added <sup>14</sup>C is also checked for each sampling series by counting 0.1-ml portions directly from each of the incubated bottles. Total radioactivity and the radioactivity in the particulate fraction retained on the filters are determined by liquid scintillation with quench correction. From the ratio of <sup>14</sup>C added to <sup>12</sup>C in the water, <sup>14</sup>C assimilation factor of 1.06.

#### 2.3. Oxygen

Whenever quantum yields are based on oxygen evolution rates, there is an inherent difficulty since measured changes in oxygen concentration are net rates (Eq. 6), where  $P_G$  stands for gross

photosynthesis, the parameter needed for the calculation of quantum yields,  $P_N$  is the measured, net photosynthesis rate, and R is respiration, usually measured in the dark. This assumes that dark respiration is the same as in the light, which is likely to be an underestimate, resulting in too low estimates of  $P_G$  and, consequently, of the quantum yield.

Oxygen exchange by photosynthesis and respiration is the largest biogeochemical cycle in aquatic systems, and the major biogeochemical cycle in the biosphere. In order to understand this cycle, it is necessary to know the gross rates of the major processes involved in oxygen production and uptake. The production of  $O_2$  is known to occur in a four-step process in photosystem II, but  $O_2$  consumption in aquatic organisms takes place by several reactions. These include ordinary respiration through the cytochrome oxidase pathway, respiration by the alternative oxidase pathway, Mehler reaction, and photorespiration. The first two processes take place in the light as well as under dark conditions, whereas the latter two occur only under illumination. Although the presence of the above-mentioned mechanisms has been established in different studies, their quantitative importance in the overall  $O_2$  uptake in aquatic systems is not well known, and it is necessary to assess their role in natural environments. In this respect, ordinary  $O_2$  incubation methods, which are very useful for the assessment of photosynthetic production from light- and dark-incubation experiments [e.g., Williams &Purdie (1991)], do not provide the necessary information.

Clark electrodes were used to measure the effect of intermittent light on photosynthetic oxygen evolution and on dark respiration rates. The main parameters of photosynthesis will be derived from the generated photosynthesis versus energy (P vs. E) curves (Fig. 4), including  $\alpha$ , the initial slope of light-limited photosynthesis, and  $\varphi$ , the quantum yield of that process.  $E_k$  (=I<sub>k</sub>), the irradiance level of incipient light saturation, the light saturated rate of photosynthesis,  $P_{max}$ , the light compensation point  $E_c$  (=I<sub>c</sub>), and dark respiration R (Fisher et al., 1996), will also be obtained. The enhanced post-illumination respiration (EPIR) rates will be determined according to Falkowski et al. (1985) and Beardall et al. (1994). The Arnold and Emerson number will be determined from the evolution of oxygen per short, saturating flash, as chlorophyll molecules/O<sub>2</sub> molecules evolved (Emerson & Arnold, 1932).

#### $E_k = I_{k'} I_c = E_c$ .

### 2.3.1. Stable isotopes

The main drawback of the above methods is their inability to measure the rate of respiratory  $O_2$  uptake in the light, and it is assumed that the rates of dark and light uptakes are equal. The rates of gross production as well as light  $O_2$  uptake can be estimated in field incubation experiments using  $H_2^{18}O$  as a spike (e.g., (Bender et al., 1987, 1999; Luz & Barkan, 2000). However, this method alone cannot help to characterize the type of the respiratory mechanisms involved in aquatic  $O_2$  uptake.

The discrimination against <sup>18</sup>O associated with the cytochrome oxidase pathway is 18‰ (Guy et al., 1992), but with the cyanide-resistant alternative oxidase pathway (AOX) it is much greater: 31‰ in green tissues and26‰ in nongreen tissues (Robinson et al., 1992). The discrimination in the Mehler reaction is 15‰ and in photorespiration – 21‰ (Berry, 1992; Guy



Figure 4. Light response curve of photosynthesis versus light intensity (Grobbelaar, 2006).

et al., 1993).  $d^{18}O$  of  $O_2$  in a purified oxygen–argon mixture determined by dual inlet mass spectrometry.

## 3. Methods that do not require light absorption and photosynthesis rates

#### 3.1. Variable fluorescence

Using a custom-built fluorescence induction and relaxation (FIRe) instrument, as described in Gorbunov and Falkowski (2004). The FIRe technique is based on recording fluorescent transients (called "variable fluorescence") induced by a sequence of excitation flashes of light with precisely controlled intensity, duration, and intervals between flashes. Analysis of the fluorescence signals provides a comprehensive suite of photosynthetic characteristics of the organism, including the minimum ( $F_o$ ) and maximum ( $F_m$ ) fluorescence yields corresponding to open and closed reaction centers of PSII, respectively, variable fluorescence component ( $F_v$ ), the quantum yield of photochemistry in PSII (simply put - photosynthetic efficiency), the functional absorption cross section of PSII, and the rates of photosynthetic electron transport down to PSII (Gorbunov & Falkowski, 2004; Kolber et al., 1998) (Fig. 5). The size of the plastoquinone (PQ) pool (i.e., the number of PQ molecules per reaction center) can be determined from the comparative analysis of the fluorescence induction on the millisecond time scale in the absence and presence of (3-(3,4-dichlorophenyl)-1,1-dimethylurea) (DCMU). The redox state of the PQ pool is also assessed from the shape of the fluorescence induction curve. Variable fluorescence measurements under ambient light provide information about the

efficiency of non-photochemical quenching (NPQ) and the rates of photosynthetic electron transport as a function of light intensity. A computer-controlled ambient light source is integrated into the FIRe instrument for fully automatic measurements of the above variables. The photoinhibition of PSII by supra-optimal light will be estimated from the reduction in dark-adapted values of Fv/Fm compared to their night values (Long et al., 1994).



**Figure 5.** The parameters obtainable from FIRe measurements: the minimum ( $F_o$ ) and maximum ( $F_m$ ) fluorescence yields corresponding to open and closed reaction centers of PSII, respectively, variable fluorescence component ( $F_v$ ), the quantum yield of photochemistry in PSII (simply put - photosynthetic efficiency), and the functional absorption cross section of PSII.

#### 3.2. Fast Repetition Rate (FRR) fluorescence

The simultaneous response of  $\sigma_{PSII}(\text{Å}^2 \text{ quanta}^{-1})$  and  $\tau(\mu s)$  reveals important information about the photosynthetic response to the growth environment. Specifically, the light saturation parameter ( $E_{K}$ , µmol photons m<sup>-2</sup> s<sup>-1</sup>) was estimated as [1/( $\tau \sigma$ )] 1.66 × 10<sup>8</sup> (Falkowski & Raven, 2007), where the factor 1.66 × 10<sup>8</sup> accounts for the conversion of Å<sup>2</sup> to m<sup>2</sup>, quanta to µmol quanta (photons), and µs to s (e.g., Moore et al. (2006). The actual value of  $E_{K}$  is dependent upon both the wavelength used to generate  $\sigma_{PSII}$  as well as which time constant associated with the FRR relaxation phase is used to describe  $\tau$  (Kolber et al., 1998).

#### 3.3. Photoacoustics

Energetics of photosynthesis determined by pulsed photoacoustics. This methodology directly determines the light energy not stored in photosynthesis. It is, thus, ideal for determining the

changes in stored energy on the microsecond, i.e., the photochemical time scale, caused by the differing light regimes. The methodology has been described and protocols given for measurements of both reaction centers and whole cells (Boichenko et al., 2001; Hou et al., 2001a, 2001b). The method has been successfully applied to the measurement of biomass (Dubinsky et al., 1998), to discriminate between taxa of phytoplankton (Mauzerall et al., 1998), and to study the physiological state of phytoplankton (Pinchasov et al., 2005). The efficiency of energy storage will be determined in the sample before and after a light regime that affects the growth rate and/or oxygen production rate of the organism. The variable light regime is continued until a steady state is reached and the photoacoustic measurements can be made in a shorter time compared to that of the light regime. For the slower intermittent light-dark regimes, one may be able to measure the state of the system in each phase. The results will indicate if the variable light effect is caused by a change in the efficiency of light utilization at the photochemical level. If a change is seen then, energy utilization has changed and the xanthophyll cycle will be implicated. If no change is seen, then the change has occurred on the long time scale, such as in the case of  $CO_2$  fixation.



Figure 6. Photoacoustic phytoplankton cell.

## 4. Factors affecting quantum yields

#### 4.1. Photoacclimation and photoinhibition

Phytoplankton photosynthesis at any depth depends principally on the intensity and spectral quality of the ambient light. However, the amount of light harvested by phytoplankton also depends on the quantity of chlorophyll present and on the variable, average, spectral in vivo attenuation coefficient,  $k_c$  (Dubinsky & Berman, 1981; Schanz et al., 1997). Moreover, as available light changes, so does the fraction of the harvested light that can be transduced by the cell into photochemical products - this fraction is  $\phi$ . Contrary to what has been discussed above, happening under limiting light, at high irradiances the photon flux harvested by the

photosynthetic pigments exceeds the rate at which these photons can be utilized by the photochemical reaction centers. In such light-saturated situations, an increased fraction of the harvested light will be dissipated by nonradiative decay as heat, and emitted as fluorescence. Under such conditions, the photosynthetic apparatus may be temporarily or irreversibly damaged, leading to photoinhibition and ensuing reduction in quantum yields. In a bathymetric profile, in any water body (Fig. 7) exposed to full sunshine, the photosynthesis of phytoplankton is inhibited at the surface due to supra-optimal irradiance levels, photosynthesis is inhibited, and quantum yields are low, as light reaches limiting levels at ( $E_k$ ), and below that depth throughout the photic zone, photosynthesis is light limited and quantum yields are constant (Fig. 7). All these depth-related changes in irradiance, chlorophyll,  $k_{cr}$  and  $\phi$  are essential inputs for modeling and predicting the depth-distribution of photosynthesis in aquatic environments.



Figure 7. Profile of irradiance, photosynthesis and quantum yield.

In the laboratory, Dubinsky et al. (1986) exposed different cultures to different light levels and found changes in quantum yield ( $\phi$ ) vs. light intensity (Fig. 8).

Additional features emerge when summer (June 1995, June 1996) data are compared to winter (February 1995, December 1996) data (Fig. 9). Winter  $\phi$  values decreased steeply at high



**Figure 8.** Quantum yield ( $\phi$ ) values found in cultures, after Dubinsky et al. (1986).

irradiance levels, reaching undetectably low ones at I>400 µmole quanta m<sup>-2</sup>s<sup>-1</sup>, whereas in summer samples, values were measurable even at irradiances twice as high. We attribute the high sensitivity of summer phytoplankton to light intensity to the fast vertical mixing characteristic of that period, which did not allow sufficient time for photoacclimation (Falkowski & Wirick, 1981). The phytoplankton organisms acclimate to a light intensity that is the average over the entire mixing depth of ~400 m, resulting in cells with far too much pigmentation not to be damaged or at least strongly photoinhibited upon exposure to near-surface irradiances. That also explains why they fare better under dim light, under which the nearly optically black cells maximize light harvesting and its efficient utilization. Conversely, during summertime, stratification cells acclimate to the light intensity at each depth, thereby mitigating the effects of light gradients. However, the shortage of nutrients limits the ability of phytoplankton to fully exploit the advantages of photoacclimation.

At all times, the quantum yields of photosynthesis are strongly reduced under high light since non-photochemical quenching (NPQ) excess-energy–dissipating processes avert photodynamic damage. Furthermore, not only is there, under high light, a mismatch between light harvesting and end-electron flow rates, but also between the fast light-driven carbon assimilation and the Redfield rate supply of nitrogen and phosphorus [see (Dubinsky & Berman-Frank, 2001)], all depressing the quantum yields of photosynthesis. Under low light approaching ~1% of the subsurface, light-harvesting rates, being in step with  $\tau$  values, allow quantum yields to reach their theoretical upper boundaries of 8-10 photons per mole O<sub>2</sub> evolved.



Figure 9. Linear regression of the quantum yield vs. light intensity, comparison between summer (June 1995, June 1996) and winter profiles (February 1995, December 1996) down to 100 m depth.

#### 4.2. Nutrient status

Al Qutob et al. (2002) showed the co-limitation of phytoplankton photosynthesis in the gulf by both nitrogen and phosphorus. During thermal summer stratification, nutrient depletion was severe, and no nitrite could be detected in the upper 70 m. Their field data suggest that the accumulation of nitrite is associated with nutrient-stimulated phytoplankton growth. This hypothesis was supported by nutrient-enrichment bioassays performed concomitantly: only when phytoplankton growth was stimulated by nutrient additions, did nitrite accumulate in the water., Using photoacoustics, Pinchasov et al. (2005) showed the depression of photosynthetic efficiency of several phytoplankton species under iron deficiency (Fig. 10) and under nitrogen and phosphorus starvation (Fig. 11) (Pinchasov et al., 2005).

There is a dependence of quantum yields on light intensity (Dubinsky, 1992; Dubinsky & Berman, 1981; Morel, 1978). However, quantum yields depend not only on ambient light. It was also reported that in laboratory experiments, nutrient limitation lowers quantum yields (Cleveland et al., 1989; Falkowski, 1991; Kolber et al., 1990). Where the specific importance of an individual nutrient is concerned, Kolber et al. (1988) showed the effects of lack of nitrogen, Greene et al. (1991) showed the effects of lack of iron, and Falkowski (1991) reported the effects of phosphorus limitation. The impact of these shortages depends on their cellular requirements for balanced growth, N>P>Fe, which differ among phytoplankton taxa, but also in their amounts stored in cells [*sensu*cell quota, Droop (1983)]. In the case of the Gulf of Eilat, during



**Figure 10.** The effect of changing iron concentration on photosynthetic energy storage for *Isochrysis galbana*. The iron concentrations in the cultures were 0 mg L<sup>-1</sup>, (\*); 0.03 mg L<sup>-1</sup>, (o); 0.09 mg L<sup>-1</sup>, (\*); 0.18 mg L<sup>-1</sup> ( $\Delta$ ); and for the control, 0.6 mg L<sup>-1</sup> (\*). The maximal storage in the nutrient-replete control was taken as 100%.

summertime stratification, there is a concomitant shortage of both nitrogen and phosphorus as their winter concentrations of  $NO_3^- = 0.2 \ \mu mol \ l^{-1}$  and  $PO_4^{-3} = 0.1 \ \mu mol \ l^{-1}$  in winter, drop to  $PO_4^{-3} = 0.02 \ \mu mol \ l^{-1}$  and  $NO_3^- = 0.04 \ \mu mol \ l^{-1}$  in summer, respectively (Al-Qutob, 2001; Al-Qutob et al., 2002; Genin et al., 1995; Iluz et al., 2008; Labiosa et al., 2003; Lazar & Erez, 1992; Levanon-



**Figure 11.** The effect of nutrient limitation on the relative photosynthetic energy storage in the three algae, *Nannochloropsis* sp., *Phaeodactylu mtricornutum*, and *Isochrysis galbana*. For each species, photosynthetic energy storage of the nutrient-replete control was taken as 100%. Controls (clear columns) were grown in nutrient-replete media, whereas in the P (oblique hatch) and N (horizontal hatch) cultures, phosphorus and nitrogen were omitted from the medium.

Spanier et al., 1979; Lindell & Post, 1995; Reiss et al., 1984). It seems that due to the limited availability of nitrogen and phosphorus in the gulf, it is these two nutrients that control the annual phytoplankton cycle in the gulf (Al-Qutob et al., 2002). Thus, the changes in iron availability (Chase et al., 2006) themselves may play, at most, a minor role in that cycle, even though iron does affect the supply of the two major nutrients.

In the Gulf of Eilat, the quantum yields of photosynthesis are constrained in summer by low nutrient supply and in winter by vertical mixing rates being too fast to allow for effective photoacclimation (Iluz et al., 2008).

#### 4.3. Pollutants

Like exposure to excessive light intensity and nutrient limitation, pollutants may also affect the normal function of various components of the photosynthetic apparatus, leading to decreased quantum yields. Pinchasov et al. (2006) reported a biphasic decrease in the quantum yield of the cyanobacterium *Synechococcusleopoliensis*. A rapid decrease in the very first minutes of exposure was followed by a slower decline over the next few hours, probably due to harm to different components of the photosynthetic apparatus (Fig. 12).



## 5. Importance

#### 5.1. Ecology

Hyperspectral satellite-image–based global oceanic primary productivity estimates use a universal factor of  $\phi$  for converting absorbed light to primary productivity (Kolber et al., 1990). These values should be determined for each oceanic province and, other than in the

tropics, are adjusted for seasonal differences. Parallel approaches are also applied in terrestrial ecology.

In ecological studies, in many cases the preferred efficiency parameter is not the quantum yield, where the energy absorbed by the ecosystem's primary producers is difficult to estimate. In such cases, the denominator used is the total light energy impinging on the area studied. This ecological efficiency parameter is always considerably smaller than the quantum yield, since usually all of the solar energy is absorbed by phototrophs, except in dense plant cover or hypertrophic water bodies. The ecological efficiency parameter allows the comparison of natural and man-made ecosystems, and of aquatic and terrestrial ecosystems, whereas the quantum yield reports the physiological status of the plants. High ecological light utilization efficiencies form the basis for high-biomass ecosystems, such as tropical rainforests, upwelling oceanic regions, and coral reefs, whereas desert and steppe biomes are biomass-limited by low ecological light-utilization efficiencies.

#### 5.2. Biotechnology

The economic viability of photobioreactors and algal mass culture ponds depends, to a large extent, on the quantum yield of the algae, since that translates into harvested product per insolation both for the same time interval and area. That easily determines into annual income per surface devoted to that crop.

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