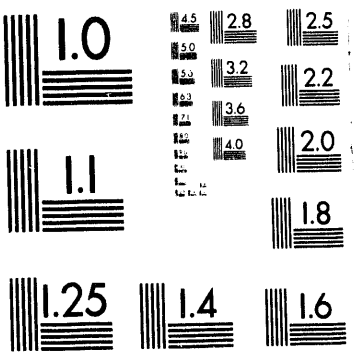
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LIGHT UTILIZATION AND PHOTOINHIBITION OF PHOTOSYNTHESIS IN MARINE PHYTOPLANKTON

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CONTENTS

23.1 Introduction to Phytoplankton. Based on the record of the oldest identifiable fossils, the first oxygenic photosynthetic organisms appeared about 2 x 10^9 years ago in the form of marine single celled, planktonic[1] procaryotes (Riding, 1992; Sarmiento and Bender, 1993). In the intervening eons, phytoplankton have evolved and diversified; presently they represent at least 11 classes of procaryotic and euacaryotic photoautotrophs. While the carbon of these organisms cumulatively amounts to only 1 to 2% of the global plant biomass, they fix between 35 and 50 gigatonnes (x 10^9 metric tons) of carbon annually, about 40% of the global total (Falkowski and Woodhead, 1992). On average, each gram of phytoplankton chlorophyll converts about 6% of the photosynthetically active radiation (440 to 700 nm) incident on the sea surface to photochemical energy (Morel, 1978). Despite a great deal of variability in ocean environments, this photosynthetic conversion efficiency is relatively constant for integrated water column production (Morel, 1978; Falkowski, 1981; Platt, 1986; Morel, 1991). Here we review the factors determining light utilization efficiency of phytoplankton in the oceans, and the physiological acclimations which have evolved to optimize light utilization efficiency.

23.2 The Marine Light Environment. Compared with the atmosphere, the ocean has an extremely high attenuation coefficient of incident solar irradiance. The average exponential attenuation coefficient ($k = \ln I_{z+1}/I_z$, where I_z is the irradiance at depth z and I_{z+1} is the irradiance depth z + 1 meter) for photosynthetically active radiation varies from about 0.30 to 0.025 m^{-1}. The average depth of the ocean is 4000 m; rarely does 1% of the incident photosynthetically active irradiance penetrate below 100 m. Thus, net photosynthesis is restricted to a relatively thin upper layer of the ocean, amounting to about

[1]planktos: from Greek - to drift.

2% of the total volume. The carbon fixed in this thin layer fuels almost all the respiratory processes in the ocean.

Incident irradiance is not attenuated uniformly across the spectrum. As a consequence of absorption and molecular scattering of water itself, far-red wavelengths are absorbed in the upper few centimeters and red and green wavelengths of light are attenuated more rapidly than blue (Kirk, 1983). Consequently, in the clearest open ocean waters, the spectrum of downwelling irradiance narrows to a band centered between 450 and 500 nm at the base of the euphotic zone. In coastal waters, the relatively high concentrations of both phytoplankton and dissolved yellow organic materials (gelbstoff) further modify the absorption of visible irradiance. In such waters not only is the overall attenuation of light much higher, but blue light is absorbed more rapidly and the spectrum shifts to longer wavelengths, centered at about 540 nm. These two optical regimes are loosely called "blue" (i.e., open ocean) and "green" (i.e., coastal) waters, respectively.

23.3 Diversity in Light Harvesting Properties of Phytoplankton. In any liter of seawater from the upper ocean, one is likely to find numerous (> 100) species of phytoplankton. Because the diversity and complexity of phytoplankton communities is extremely high, bulk measurements of physiological functions, such as photosynthesis or variable fluorescence, represent the ensemble of a community, not the response of an individual species.

There is a great deal of diversity in the photosynthetic pigments in the algal classes (Larkum and Barrett, 1983); this diversity is often exploited as a taxonomic tool (Bidigare et al., 1992). The variations in pigmentation are represented by diversity in chlorophylls such as chlorophyll c_1, c_2, and c_3 and other accessory pigments, including fucoxanthin, peridinin,

violaxanthin and phycobilins (Jeffrey, 1980). All accessory chlorophylls and most accessory pigments transfer energy from light to the reaction centers with relatively high efficiency (Owens, 1991). In general, these pigments allow increased light absorption in the both the blue and green regions of the spectrum; regions where light absorption by water and dissolved organic materials is minimal.

23.4 The Vertical Distribution of Phytoplankton. Light enters the ocean from the surface, but phytoplankton are distributed throughout the water column and are not fixed in space. Because of turbulence in the upper portion of the ocean, resulting from wind stress and tidal energy, cells are constantly transported vertically (Falkowski and Wirick, 1981; Falkowski, 1983; Denman and Marra, 1986). In the central open ocean, the base of the upper mixed layer of water is determined by the thermal gradient which produces a density discontinuity called a thermocline. The thermocline is a relatively quiescent layer of water several meters thick separating deep, cold, nutrient-rich water from the overlying warm, frequently nutrient-limited, waters. The highest phytoplankton biomass is found in, or immediately above, the thermocline, where nutrient fluxes are high but light is low. This so-called deep chlorophyll maximum (Fig. 1) is an almost universal feature of the open ocean (Cullen, 1982). The concentration of chlorophyll in the deep chlorophyll maximum can easily be 10 times higher than in the overlying waters.

Phytoplankton in the ocean are generally limited by nutrients both in terms of biomass and growth rates (Falkowski et al., 1992). In the upper mixed layer of the upper ocean, the concentration of inorganic nutrients is often vanishingly small; NO_3^- concentrations of 10 nM or less are typical, and NH_4^+ is usually < 30 nM. Such low nitrogen concentrations are far below the half-saturation constant for the uptake of the nutrient (ca. 100 to 1000 nM)

(Eppley et al., 1969). Nutrient limitation is a consequence of weak of physical mixing between the upper ocean and nutrient rich deep waters. Throughout most of the open ocean, the distribution of phytoplankton is most strongly related to the vertical flux of nutrients rather than the gradient in irradiance (Ketchum et al., 1958; Dugdale, 1967; Walsh et al., 1978; Yentsch, 1980; Laws et al., 1987; Lewis et al., 1988; Platt and Sathyendranath, 1988; Lewis, 1992; Geider et al., 1993); this has important implications for light utilization.

23.5 Measurements of Light Utilization Efficiency. Phytoplankton photosynthesis, P, is most often measured by the rate of radiocarbon incorporation into acid-stable material as a function of irradiance, E. The radiocarbon assimilation rate can be measured with precision and sensitivity within relatively short incubation periods, of 20 min to 2 h. This method is commonly used to generate a series of photosynthesis-irradiance curves (so-called P *vs* E curves) for whole water samples taken from discrete depths and from different times throughout the day (Platt et al., 1982; Lewis and Smith, 1983; Bidigare et al., 1992). There is a large database of archived P *vs* E curves from all major areas of the world oceans. These data, in conjunction with remotely sensed (e.g. satellite) and ship-based measures of ocean chlorophyll concentration, serve as the basis for constructing global ocean productivity estimates (Platt et al., 1988; Morel, 1991; Balch et al., 1992).

All P *vs* E curves display similar features. At low light levels, photosynthetic rates approach a linear function of irradiance, and as light is increased, the realized quantum yield of photosynthesis decreases (Fig. 2) . The initial slope of the photosynthesis irradiance curve, α, can be defined as the product of the spectrally integrated optical absorption cross section for the ensemble of pigments which absorb light, a^*, and the maximum quantum yield of photosynthesis;

$$\alpha = a^* \phi_{max} \quad (1)$$

The optical absorption cross section, a* (described in detail below), can be related to the number (n) of photosynthetic units (PSU, as defined by Emerson and Arnold; i.e., containing both PSII and PSI reaction centers) and the optical absorption cross section of a PSU ($\sigma_{PSU_{O_2}}$) (Mauzerall and Greenbaum, 1989):

$$a^* = n \sigma_{PSU_{O_2}} \quad (2)$$

The maximum quantum yield of photosynthesis can be expressed as the ratio of two absorption cross sections, namely that for the entire photosynthetic unit to that of a PSII reaction center:

$$\phi_{max} = \sigma_{PSII} / \sigma_{PSU_{O_2}} \quad (3)$$

σ_{PSII} is sometimes called the "effective" or "apparent" absorption cross section for PSII (Ley and Mauzerall, 1982). This cross section can be derived from a cumulative one-hit Poisson fit of the flash intensity saturation curve for O_2 or variable fluorescence (Ley et al., 1982; Falkowski et al., 1986; Genty et al., 1990):

$$Y_{(I)}/Y_{(max)} = 1 - e^{-\sigma PSII\ I}, \quad (4)$$

where $Y_{(I)}$ is the yield of oxygen or variable fluorescence induced by a flash with intensity I, $Y_{(max)}$ is the saturated value, and σ_{PSII} is the effective photon target size for a PSII reaction center. Eq. 3. provides insight into the variations in quantum efficiency in photosynthetic organisms; these may be brought about by alterations in the effective absorption cross section of PSII, changes in the optical absorption cross section of the ensemble of photosynthetic pigments, or by changes in the number of functional (i.e., O_2 evolving) reaction centers.

At light saturation the rate of photosynthetic electron transport is independent of light absorption, but is limited by the maximum rate of whole chain electron transport. While

determining the actual rate limiting step(s) has occupied plant physiologists and biophysicists for decades, P_{max} can be conveniently described as the ratio of the number (n) of photosynthetic units (i.e., the reciprocal of the Emerson-Arnold number) and $1/\tau$, the maximum rate at which an electron can be transferred from water to a terminal electron acceptor (e.g., CO_2):

$$P_{max} = n/\tau \tag{5}$$

From Eqs. 2 and 3, Eq. 1 can be rewritten :

$$\alpha = \sigma_{PSII}\, n \tag{6}$$

The inflection point at which light becomes saturating for photosynthesis, E_k, is defined as:

$$E_K = P_{max} / \alpha \tag{7}$$

From Eqs. 5 and 6, Eq.7 can be rewritten:

$$E_k = 1/(\tau\, \sigma_{PSII}) \tag{8}$$

Eq. 8 provides an objective measure of the highest irradiance level which supports photosynthetic rates at (near) maximum efficiency. At irradiance levels higher than E_K, light is in "excess" and quantum yield declines as the reciprocal of the incident irradiance. Except on the cloudiest days at high latitudes, incident light is always in excess (i.e. $> E_k$) at the surface of the ocean, while deeper in the water column, light is always limiting ($< E_k$).

2.5.1 Optimizing Light Harvesting - Photoacclimation. E_k is not a static number (Falkowski, 1980; Prezelin, 1981; Platt et al., 1982; Richardson et al., 1983; Falkowski and LaRoche, 1991). Changes in E_k can be brought about by altering either the functional absorption cross section of PSII or the maximum rate of whole chain electron throughput, or both, on a variety of time scales (Perry et al., 1981; Falkowski, 1984). The photosynthetic apparatus in phytoplankton is extremely plastic. On time scales of hours to a day cells can

add or remove pigments in the process of photoacclimation (Sukenik et al., 1989). Photoacclimation can alter both the number of photosynthetic units and their optical cross section (Falkowski and Owens, 1980; Dubinsky et al., 1986). Photoacclimation also can lead to changes in the ratio of Rubisco/electron transport capacity; this ratio is linearly correlated with $1/\tau$ (Sukenik et al., 1987). On short time scales of a few minutes, cells can effect changes in the apparent absorption cross section of PSII *via* state transitions and a variety of thermal deactivation mechanisms in the pigment bed. As will be discussed, the changes in σ_{PSII} are often rapidly reversible, and allow dynamic adjustment of the quantum efficiency of the cell as irradiance changes.

There are, of course, limits to photoacclimation. These limits are imposed genetically in both in the rate at which the photosynthetic apparatus can respond to changes in irradiance, and the magnitude of the changes. However, there may also be external limitations imposed, for example, by temperature or nutrient availability. Hence, the realized quantum yield of photosynthesis can be highly variable, and determined by many factors other than irradiance (Falkowski et al., 1991).

We now examine some of the factors influencing light utilization efficiency by phytoplankton in the ocean. We first address subsaturating irradiances.

*23.6 **Light Utilization at Low Irradiance Levels.*** Determining the quantum yield of photosynthesis in natural phytoplankton communities is far more difficult than in higher plant systems. Only a small fraction of the incident irradiance is absorbed by the phytoplankton; other particles such as bacteria have high back-scatter cross sections and contribute to the total apparent absorption (Morel, 1978). Because absolute absorptivities are extremely low, derivation of absorption from total attenuation using common optical approaches, such as an

integrating sphere, are not practical; hence it is difficult to directly measure the fraction of incident irradiance absorbed by the phytoplankton *per se*. To solve this problem, photosynthetic carbon assimilation is often normalized to chlorophyll *a*, rather than area or volume. If chlorophyll specific photosynthetic rates are plotted as a function of incident irradiance, the initial slope of the P *vs* E curve can be related to the maximum quantum yield of carbon fixation by the optical absorption cross section of chlorophyll *a* as described by Eq. 1.

23.6.1 *Determination of the Optical Absorption Cross Section.* It is difficult to determine the fraction of incident light absorbed by phytoplankton. A common approach to this problem is to derive the spectrally averaged optical absorption cross section normalized to chlorophyll (Bannister, 1974; Dubinsky and Berman, 1976; Dubinsky et al., 1986). In this approach the optical absorption cross section is measured at each wavelength λ and normalized to chlorophyll thus:

$$a^*_\lambda = \frac{-\ln (I_\lambda / I_{o\lambda}) \ \ln 10}{\text{Chl}a} \tag{9}$$

The values of a^*_λ can then be integrated over the range of photosynthetically active radiation

$$a^* = \int_{400}^{700} a^*_\lambda \, d_\lambda \tag{10}$$

The optical absorption cross-section integrates all pigment absorption bands, whether they be from carotenoids, phycobilipigments, etc., and "assigns" them to chlorophyll *a*. There is no implicit assumption about energy transfer in this calculation. The optical cross section describes the average target for the absorption of photons by the photosynthetic apparatus, and is dependent upon spectral quality of the incident irradiance, but not the absolute intensity (Berner et al., 1989).

Until the mid 1980s it was generally assumed that a* was constant in phytoplankton and hence α reflected the maximum quantum yield of photosynthesis (Kiefer and Mitchell, 1983; Bannister and Weidemann, 1984). In the mid 1980s, however, it became increasingly clear from careful laboratory measurements that a* was highly variable and depended upon cell size, pigmentation, and the concentration of chlorophyll within the cell (Bricaud et al., 1983; Falkowski et al., 1985; Dubinsky et al., 1986). For example, phytoplankton acclimate to changes in irradiance by altering both the cellular concentration and composition of pigments (Falkowski et al., 1991). Cells growing deep in the water column tend to have high chlorophyll concentrations, high concentrations of accessory pigments which transfer excitation energy to the reaction centers, but relatively few photoprotective accessory pigments, such as zeaxanthin or β-carotene. Increases in intracellular chlorophyll *a* almost always lead to decreases in a* due to packaging (i.e., self-shading) effects (Bricaud and Morel, 1986; Berner et al., 1989). Thus, for example a doubling of cell chlorophyll might only increase light absorption by 25% (Morel, 1991). The realization that a* could vary, provided an impetus to measure optical absorption cross sections of phytoplankton in nature (Cleveland and Perry, 1987; Bidigare et al., 1989; Smith et al., 1989; Morel, 1991).

The measurement of a* in natural phytoplankton communities is not trivial. Because phytoplankton are so dilute in seawater, direct measurement of absorption requires a long pathlength, which introduces a difficulty in accounting for scattering. To overcome this problem, large volumes of seawater (5 to 10 l) are usually filtered onto glass fibre filters and the absorption is measured on the filters. This method is complicated by multiple scattering of the cells within the filter pad, which leads to an overestimate of the absorption cross

section, especially if the cells are small. Empirical optical correction factors have been developed to correct for the filter effect (Morel, 1978; Bricaud et al., 1983; Kishino et al., 1985; Bricaud et al., 1986; Bidigare et al., 1992). Although precise measurements of the a* have been made using this technique, the method is extremely tedious (Fig. 3). The few simultaneous measurements of a* and α in natural phytoplankton communities reveal large variations in ϕ_m (Cleveland et al., 1989; Platt et al., 1992). ϕ_m theoretically approaches 0.125 moles CO_2 fixed/ mole absorbed quanta if NH_4^+ is the nitrogen source (Kok, 1948; Myers, 1980; Ley et al., 1982), and such values can be obtained under idea conditions in algal cultures (Myers, 1980), typical values for the open ocean are often an order of magnitude larger (Cleveland et al., 1987). The deviation from the maximum achievable quantum yield is primarily related to the rate of supply of inorganic nutrients, especially nitrogen and iron (Falkowski et al., 1992).

23.7 Light Utilization at High Irradiance Levels. The optimum irradiance photosynthesis (i.e., the E_k value) is dependent on both the apparent absorption cross section of PSII and the maximum rate of electron transport. Both of these parameters can be modified by physiological acclimation to irradiance level (i.e., the light history of the cell), genetic constraints (interspecific differences), as well as nutrient supply and temperature. In some extreme examples, phytoplankton found in the chlorophyll maximum become light saturated between 25 and 50 μmol quanta m^{-2} s^{-1}, while cells 100 m higher in the water column have E_k values in excess 400 μmol quanta m^{-2} s^{-1} (Fig. 4).

The maximum rate of whole chain photosynthetic electron transport ($1/\tau$) is far from constant and is not theoretically constrained by the Z-scheme. Myers and Graham observed that $1/\tau$ could be varied by a factor of about 5 in *Chlorella* simply by changing growth

irradiance (Myers and Graham, 1972). However, as chlorophyll/cell increased, $1/\tau$ decreased, such that the maximum photosynthetic rate per cell was relatively unchanged. Based on the assumption that the average size of the photosynthetic unit is ca. 2000 Chl/O_2, and using the empirical relationship between chlorophyll/cell and $1/\tau$, a maximum photosynthetic rate of 25 mg^{-1} Chl h^{-1} at light saturation can be derived (Falkowski, 1981). To support this photosynthetic rate, requires a $1/\tau$ of 1000 s^{-1}; this electron throughput rate approaches that of the reoxidation rate of Q_a^- (ca. 2000 s^{-1}) under steady state photosynthesis (Crofts and Wright, 1983; Falkowski et al., 1986).

Photosynthetic rates of ca. 20 mg C mg^{-1} Chl h^{-1} have been reported for warm nutrient-rich areas (e.g,. eutrophic estuaries in the summer) however, such high rates are rare (Malone and Neale, 1981). More commonly, in the open ocean, maximum photosynthetic rates of 3 to 10 mg C mg^{-1} Chl h^{-1} are measured (Cullen et al., 1992). Assuming that the photosynthetic unit size is relatively constrained, these light saturated rates suggest that $1/\tau$ is between 30 and 400 s^{-1}. Such slow rates of whole chain electron transport tend to decease E_k, and hence reduce light utilization efficiency at high irradiances.

23.8 Analysis of Variable Fluorescence. It is possible to derive light utilization efficiency from changes in the maximum variable chlorophyll fluorescence yield. This approach offers high sensitivity, and specificity, and is not complicated by direct measurements of absorption. Changes in F_v/F_m or F_v/F_o can be quantitatively related to the photochemical conversion efficiency of PSII (Falkowski and Kiefer, 1985; Krause and Weis, 1991; Owens, 1991). It should be pointed out this efficiency is not identical to the quantum yield for carbon fixation or oxygen evolution. The quantum efficiency of PSII is related to

to that of carbon fixation through the apparent absorption cross section of PSII and the number of PSII reaction centers per photosynthetic unit.

Changes in variable fluorescence yield can be made very rapidly and conveniently *in situ* using either pump-and-probe or fast-repetition rate fluorescence techniques (Falkowski and Kolber, 1990; Kolber et al., 1990; Falkowski et al., 1991; Kolber and Falkowski, 1992; Geider et al., 1993). These methods have allowed changes in the quantum efficiency of PSII to be studied over the scale of 100's or even 1000's of kilometers (Kolber et al., 1990; Falkowski et al., 1991; Geider et al., 1993; Greene et al., 1994).

Using either of the single-turnover flash fluorescence techniques mentioned, the quantum efficiency of PSII is remarkably constant for nutrient replete phytoplankton, independent of species. Maximum values for F_v/F_m are ca. 0.65 (maximum values of F_v/F_o are ca. 1.65). This efficiency is lower than that reported for higher plants (Björkman and Demmig, 1987; Krause and Weis, 1991; Baker and Ort, 1992), but is remarkably independent of growth irradiance, as long as nutrients are saturating and the cells are fully photoacclimated to the irradiance (Kolber et al., 1988). In nutrient-limited chemostat cultures, where a steady-state growth rate of cells can be maintained at a constant irradiance, variable fluorescence decreases as a hyperbolic function of nutrient limitation (Kolber et al., 1988).

Horizontal and vertical profiles of F_v/F_m in the ocean reveal the maximum quantum efficiency of PSII is highly variable in the ocean (Kolber et al., 1990; Falkowski, 1991; Falkowski and Woodhead, 1991; Geider et al., 1993). The spatial variations cannot be explained by irradiance. For example, in the equatorial and subtropical Pacific, F_v/F_m values are typically 0.35 to 0.45 throughout the entire euphotic zone (Greene et al., 1994), and

similar values are found in the subtropical Atlantic (Falkowski et al., 1992; Falkowski, 1993; Falkowski and Kolber, 1993). Such values imply that only 50 to 60% of PSII reaction centers are photochemically competent. Measurements of F_v/F_m made on dark-adapted samples in the central open ocean often reveal maxima in the quantum yield of photochemistry where nutrient fluxes are highest (Fig. 5). For example, in an a highly productive upwelling area off the coast of Northwest Africa, F_v/F_m values approach 0.65, and comparably high values can be observed during the productive spring bloom in coastal regions in the Northwest Atlantic. The variation in F_v/F_m results suggest that nutrients, especially fixed inorganic nitrogen and iron, affect the quantum yield of PSII *in vivo*. Supplementation of samples of natural phytoplankton with micromolar concentrations of nitrate or nanomolar concentrations of Fe^{2+} often lead to increased levels of F_v/F_m within 24 to 36 h. These observations appear to sharply contrast with terrestrial ecosystems, where F_v/F_m values appear to be relatively constrained (Long et al., 1994).

Measurements of the effective absorption cross section of PSII based on single turnover flash saturation profiles of variable fluorescencesuggest that the apparent antenna size averages 200 to 400 $Å^2$. Interestingly, this apparent cross section of PSII appears to be more constrained (varying by about a factor of three) than $1/\tau$ (which varies by a factor of about 10). At fluence rates of 1000 umol quanta $m^{-2}s^{-1}$, each PSII reaction center receives 1500 photons per second. Thus, only 5 to 25% of the photons absorbed can be effectively for photochemical energy conversion. The remaining 75 to 95% of the photons are wasted because of biochemical or biophysical constraints (Sukenik et al., 1987; Long et al., 1994) .

Both the radiocarbon-based estimates of the maximum quantum yield of photosynthesis (Cleveland et al., 1989; Platt et al., 1992) and the fluorescence based

estimates of the maximum quantum yield of photochemistry in PSII (Kolber et al., 1990; Falkowski et al., 1992; Geider et al., 1993) strongly suggest that in the ocean phytoplankton utilization of subsaturating irradiance is far less than the maximum achievable.

23.9 Molecular Bases for Nutrient Stress Changes in F_v/F_m. The molecular mechanisms for the nutrient-stress induced reduction of PSII quantum efficiency in phytoplankton are unclear (Kolber et al., 1988; Falkowski et al., 1989; Greene et al., 1992). Western blots of nitrogen limited cells reveal that both D1 and CP47 are markedly reduced relative to LHCII (Kolber et al., 1988). While nitrogen limited cells are chlorotic, the fraction of total cell nitrogen in the LHCP's remains relatively constant (Falkowski et al., 1989), but the number of functional (O_2 evolving) PSII reaction centers decreases (Herzig and Falkowski, 1989). One possibility for the decrease in variable fluorescence under nitrogen limitation is that the pigment bed is poorly coupled energetically to the reaction center (Greene et al., 1991; Greene et al., 1992).

In iron-limited cells, low temperature fluorescence emission reveals an increased in the absolute quantum yield at 710 nm. The fluorescence level in this band can be increased in iron replete cells by the addition of DCMU, suggesting it is associated with PSII. Fluorescence lifetime analyses reveals that a 50 fold increase in the 1.2 ns component at the expense of the 155 and 550 ps components (Falkowski et al., 1993). Addition of nanomolar levels of iron leads to marked decreases in the 710 nm band over a period of ca. 24 h, which is accompanied by an increase in the relative amplitudes of the 155 and 550 ps lifetimes. Western blots of CP43, CP47 and D1 do not show any major alterations protein composition of PSII relative to LHC. These data suggest that primary charge separation of the radical pair is strongly inhibited by lack of iron.

Both iron and nitrogen limitation lead to *increases* in the effective absorption cross section of PSII (Kolber et al., 1988; Greene et al., 1991). This apparent paradox can be related to the loss of functional PSII reaction centers for the ensemble of antenna. Thus, antenna which could supply excitation for two, three or more reaction centers, have only one functional trap. Kinetic analysis of energy migration within the bed suggests that, under iron limited conditions, excitation energy does not visit multiple reaction centers before becoming trapped, rather the flash intensity saturation curve for fluorescence closely follows a cumulative one-hit Poisson function (Greene et al., 1992), implying no energy transfer between functional reaction centers (Ley and Mauzerall, 1986). We infer from these observations that iron-limited cells are statistically populated with a large fraction of reaction center proteins which are photochemically non-functional and effectively disconnected from their antenna.

23.10 Photoinhibition. Early on, phytoplankton ecophysiologists noted that in cells are exposed to irradiances beyond some optimum, the maximum rate of photosynthesis declines (Ryther, 1956; Neale, 1987). In phytoplankton ecology, the notion of photoinhibition therefore is commonly taken to be a reduction in P_{max} at "supraoptimal" irradiance levels. Since the early work of Kok, the reduction has been more or less assumed to arise from damage to PSII reaction centers (Kok, 1956), although the experimental proof of this phenomenon in natural phytoplankton communities is scant (Neale, 1987; Long et al., 1994). An alternative definition of photoinhibition, based, for example, on a reduction in F_v/F_m, is experimentally verifiable; however, its effect on photosynthetic performance in nature is not easily assessed.

Direct measurements of photosynthetic rates at ambient irradiance provide an indication of photoinhibition. For example, incubation of natural phytoplankton samples in bottles suspended *in situ* often reveals a suppression of radiocarbon assimilation normalized to Chl *a* in the upper portion of the water column (Steemann Nielsen and Hansen, 1961; Lorenzen, 1963; Smith et al., 1980). This photoinhibitory effect has been shown to be dependent on time and light-intensity; the degree of inhibition does not obey rules of reciprocity (Takahashi et al., 1971). Differential incubation with glass, plastic and quartz bottles *in situ* has revealed a contribution of UV-B to the photoinhibitory damage although UV-B is attenuated relatively rapidly compared with PAR in natural waters (Steemann Nielsen et al., 1961; Lorenzen, 1963; Smith et al., 1980).

A consequence of photoinhibition is a hysteresis in the P *vs* I curve (Long et al., 1994). Photosynthetic rates measured with a succession of increasing irradiance levels are often higher than the rates measured with a series of decreasing irradiances. This diagnostic of photoinhibition can be misleading. As phytoplankton are exposed to increasing irradiance levels, they tend to synthesize more carbohydrate as an endproduct of their carbon assimilatory pathway. Unlike higher plants, however, phytoplankton do not store carbohydrate in non-photosynthetic tissue; in essence these cells are protein factories. To utilize carbohydrate for protein synthesis, the cells increase mitochondrial respiration in the light (Grande et al., 1989; Weger et al., 1989). Thus, mitochondrial respiration increases with increasing irradiance. As the respiratory pathways are metabolically far removed from carbon fixation, changes in respiration lag changes in carbon fixation. Thus, when cells are exposed to decreases in irradiance the ratio of respiration/photosynthesis is higher than when cells are exposed to the same irradiance levels in an increasing order. This phenomenon can

produce a large hysteresis in P *vs* E curves, yet has little to do with photoinhibition (Falkowski and Owens, 1978). Consequently, a hysteresis in a P *vs* E curve is not a reliable diagnostic of photoinhibition of phytoplankton photosynthesis in nature.

A major uncertainty to emerge in the interpretation of the high light reduction in P_{max} from *in situ* bottle incubations is the degree of vertical mixing which occurs in natural phytoplankton communities (Marra, 1978; Marra, 1980; Denman et al., 1986). The vertical motions of water are extremely difficult to measure; however, measurements of the dissipation of turbulent kinetic energy suggest that vertical motions of phytoplankton strongly influence light history (Falkowski, 1983; Lewis et al., 1984). Simulated mixing of phytoplankton in bottles sometimes yields higher integrated photosynthetic rates (Marra, 1978). This phenomenon only occurs because there is hysteresis in the P *vs* E curve. It has been suggested that the simulated mixing can lead to higher integrated photosynthetic rates because, in part, there is a reduction in the duration of exposure of cells to supraoptimal irradiance levels. Such simulations are unsatisfactory, however, because it is impossible to predict with certainty the degree of vertical mixing or the trajectory.

Measurements of changes in variable fluorescence from natural phytoplankton communities offer an alternative means of assessing photodamage to PSII (Vincent et al., 1984; Neale, 1987). Fluorescence approaches are attractive because they are rapid and do not require an incubation *in situ*; i.e., they more accurately reflect the physiological state of the phytoplankton community. Time series of changes in F_v/F_m, measured using both a fast repetition rate fluorescence system (Kolber and Falkowski, in press) from the upper 5 m in the subtropical Pacific Ocean are shown in Fig. 6. The data, taken after a 30 m dark adaptation, reveal a mid-day depression in F_v/F_m, which persists until the end of the day.

Recovery occurs within 2 - 4 h at night. The effect of irradiance on both F_o and F_m suggest that the reduction in F_v/F_m is related quenching of both fluorescence components. These data reveal dynamic changes in photochemical efficiency due to non-photochemical quenching in natural phytoplankton communities. What is the origin and effect of non-photochemical quenching on light utilization?

23.11 Dynamic Changes in Photosynthetic Parameters

23.11.1 State Transitions. One of the first observations related to nonphotochemical quenching of fluorescence in algae was the discovery of the state transitions in *Chlorella* (Bonaventura and Myers, 1969). The subsequent elucidation that a redox-sensitive phosphorylation of LHCII was correlated with the change in fluorescence yields (reviewed by Allen, 1992; Bennett, 1991) led to extensive investigations as to the molecular mechanism, metabolic regulation, photobiological purpose and physiological consequence of the state transitions.

State transitions can be experimentally produced by differentially exciting one of the other photosystem. In the classical case of Chlorella a "PSII" light (a short wave red light, which is primarily absorbed by Chl *b*) leads to a reduction in the quantum yield of fluorescence and a concomitant increase in the quantum yield of oxygen evolution. A PSI light (e.g., a red or far red light which is primarily absorbed by Chl *a*) does the opposite. These effects have been (arguably) suggested to result from changes in the effective absorption cross section of PSII (Barber et al., 1989). It is not at all clear that changes in the effective PSII cross section are reciprocated by changes in the effective PSI cross sections, thereby optimizing the distribution of absorbed quanta between the two photosystems.

Do state transitions occur in nature? In the ocean (or any aquatic system, for that matter), light is not monochromatic, and the region where irradiance is enriched in PSI light is found in the upper portion of the water column (Kirk, 1983). If an organism used PSI wavelengths as a cue to increase PSII cross sections, it would increase light absorption exactly where it would do the most harm, at high photon flux densities. Conversely, at low irradiance levels, light becomes more enriched in PSII wavelengths, and a reduction in PSII cross section would be counter productive for light harvesting. Moreover, in chromophyte (Chl c-containing) algae, such as diatoms, the light harvesting complex(es) appear to deliver excitation energy to both PSI and PSII with comparable efficiency (Owens, 1988). These organisms are extremely common in many parts of the ocean.

We propose that the state transitions do occur as a first line of regulation to small changes in irradiance *level*. The state transitions are not so much dependent upon the wavelength of excitation as the reduction level of the plastoquinone pool (Allen, 1992). At high irradiance levels the PQ pool has a tendency to become reduced, and a decrease in PSII cross section would lead to a proportional increase in quantum yield. Similarly, at low fluence rates, such as found deeper in the water column, light harvesting becomes rate limiting and an increase in PSII cross section, triggered by a largely oxidized PQ pool, would be beneficial.

It should be pointed out that in most organisms the state transitions only afford about a 10% change in cross section in PSII (Ley, 1980; Falkowski and Fujita, 1987). While such changes lead to proportional changes in photosynthetic electron flow at low irradiance levels, the effect is much too small to significantly impact community productivity.

23.12 Non-photochemical Quenching. An alternative mechanism for dynamically altering photosynthetic parameters is to thermally dissipate absorbed excitation energy, either within the pigment bed or in the reaction center. *In vivo* chlorophyll fluorescence was introduced as a means of estimating photoplankton chlorophyll without extracting pigments in the 1960s (Lorenzen, 1966). Literally tens of thousands of profiles of fluorescence have been made in the oceans using a variety of commercial instruments. Early on it was noted that the quantum yield of *in vivo* fluorescence was highly variable, and was light dependent. This variability was a source of frustration to oceanographers who desired to establish simple regression relationships between *in vivo* and extracted chlorophyll fluorescence (Slovacek and Hannan, 1977). Attempts to decrease the variability by the addition of DCMU or exposure to far-red light were generally not successful (Falkowski and Kiefer, 1985). To most biological oceanographers, non-photochemical quenching is a nuisance because it interferes with the exact determination of chlorophyll by fluorescence!

Non-photochemical quenching can be easily related to irradiance level by correlating the passing of clouds with the fluorescence level. An example of the kinetics of the decay of non-photochemical quenching for a natural phytoplankton sample is shown in Fig. 7. The data reveal two components; a fast component which relaxes with a half time on the order of 5 to 10 min., and which has little effect on F_v/F_m. There is a second, slow component, with a half-time on the order of 2 h, which is correlated with an increase in F_v/F_m.

23.12.1 Origin of Non-photochemical Quenching. The question of the origin of non-photochemical quenching is related to the photobiological function of the quenching process(es). If quenching occurs only in the pigment bed, it should be associated with a change in the effective absorption cross section of PSII. This effect is *independent of any*

effect on the quantum yield of photochemistry within the reaction center. Shade adapted cells with large PSII cross sections have the same values of Fv/Fm as cells adapted to high light with small PSII cross sections (Kolber et al., 1988). Thus, a reduction in Fv/Fm must have origins in the reaction center. To resolve this problem we consider the following model based on target theory (Fig. 8). A loss of quantum efficiency in photochemistry of PSII, resulting from an increase in non-photochemical quenching within the reaction center, would lead to a reduction in the saturation level of a flash intensity saturation curve for variable fluorescence (or oxygen evolution), without invoking any change in the effective absorption cross section of PSII. Thermal dissipation in the bed competes the reaction center for excitation energy and would be reflected in a decrease in the flash intensity saturation curve for fluorescence (or oxygen evolution) (Genty et al., 1990; Olaizola, 1993). The bipartite model predicts that bed quenching results in quenching of the F_o state, while reaction center quenching does not. However, it is difficult to resolve which of these two phenomena is responsible for the observed non-photochemical quenching if both quenching processes occur simultaneously.

Non-photochemical quenching plays an important role in regulating light harvesting of phytoplankton. The apparent absorption cross section of PSII changes markedly (Fig. 6 bottom). The change in cross section, amounting to almost 50%, is correlated with relative changes in both F_o and F_m, but because the absolute value of F_m is greater, there is a loss of F_v/F_m during the day. Both the quantum efficiency of photochemistry and the apparent absorption cross section of PSII increase at night. Both of these phenomena are suppressed to a great extent deep in the water column. We infer from the behavior of fluorescence quenching in natural phytoplankton communities, that non-photochemical quenching in the

pigment bed increases upon exposure to high light. This process, which can occur with a half-time of 5 to 15 min in phytoplankton (Mortain-Bertrand and Falkowski, 1989; Falkowski, 1992; Olaizola, 1993) leads to an increase in E_k, thereby dynamically altering the functional photosynthesis-irradiance relationship. The alteration in cross section can be very effective, preserving almost total photochemical efficiency (Fig. 7). However, if cells are exposed to high irradiance levels for extended periods, the reduction in effective cross section is not sufficient to prevent photoinhibitory damage to PSII reaction centers. The damage is repaired overnight. Such is the daily cycle of non-photochemical quenching in phytoplankton in the sea.

What causes antenna quenching? A portion of non-photochemical quenching has been correlated with the xanthophyll cycle in higher plants. In marine phytoplankton there are two known xanthophyll cycles. In the chlorophyll *b* containing eukaryotes the cycle is the sequential, reversible, de-epoxidation of violatathin to antheroxanthin to zeaxanthin (Demming-Adams, 1990). In the chromophyte algae, the cycle contains only the mono-epoxide diadinoxanthin which is converted to the de-epoxide diatoxanthin in high light and the reverse reaction occurs in low light or darkness (Olaizola and Yamamoto, 1993). The location of these two xanthophylls in major or minor light harvesting complexes is unknown. Dithiothreitol block the de-epoxidation precess in both types of xanthophyll cycles (Olaizola, 1993).

While the xanthophyll cycle may operate in eukaryotic cells, throughout most of the open ocean cyanobacteria and Prochlorophytes are the dominant organisms (Chisholm et al., 1988). In the subtropical Pacific the Prochlorophytes appear to be responsible for up to 50% of the total phytoplankton biomass. The accessory carotenoid of both cyanobacteria and the

prochlorophytes is zeaxanthin, which does not transfer its excitation energy to PSII (Falkowski, unpublished). The zeaxanthin also does not appear to result from a xanthophyll cycle. The mechanism of non-photochemical quenching in the light harvesting antenna of these abundant prokcaryotes remains an enigma.

23.13 Light Utilization Efficiency on a Community Level. A column of water in the open ocean can never be light saturated. Because of Beer's law and the high attenuation coefficient of seawater, for all practical purposes all the light entering the ocean is absorbed (between 1 and 5% leaves the ocean as backscattered irradiance, depending on the optical properties of the specific water body). Thus, as a first approximation, phytoplankton photosynthesis in the ocean *must* be limited by availability of light on the community level. This hypothesis can be tested.

A plot of net water column carbon fixation, integrated over the entire euphotic zone, and normalized to chlorophyll biomass, also integrated over the euphotic zone, as a function of incident solar irradiance at the seasurface is shown in Fig. 9. The slope of the line Ψ, has the units identical to α, the initial slope of the P *vs* I curve. Ψ appears to be relatively highly constrained for nutrient rich areas of the world ocean, averaging 0.4 g C g^{-1} Chl *a* m^{-2} $mole^{-1}$ quanta (Falkowski, 1981; Platt, 1986; Morel, 1991). Thus, for one mole of quanta (400 - 700 nm) incident on one square meter of the sea surface, we expect that each gram of chlorophyll under that surface area to fix ca. 400 mg of carbon. That value, obtained from empirical measurements for widely differing irradiance regimes, does not saturate. Thus, while individual cells or portions of the water column may exposed to irradiance levels that are in excess of their photosynthetic capacity, from the viewpoint of the integrated water column, there is no "excess" light. Phytoplankton utilization of photosynthetically active

radiation is extremely high, and remarkably linear. The high light utilization is manifested in the globally high productivity in the oceans relative to the meager biomass of photosynthetic organisms.

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Figure Legends

Fig. 1. A typical vertical profile in the central subtropical ocean showing the chlorophyll maximum associated at the base of the thermocline. The thermocline is the layer of water between 60 and 100 m where temperature decreases from 23.5 to 21.5° C. Below the thermocline nitrate concentrations increase markedly from undetectable levels (< 5 nM) to 2 μM. The maximum chlorophyll concentration in the thermocline, 0.4 μg/l is about 10 times greater than in the surface waters.

Fig. 2. A schematic representation of a P vs E curve. The initial slope of the curve, α, is the maximum light utilization efficiency. This efficiency is related to the maximum quantum yield of photosynthesis through the optical absorption cross section (refer to Eq. 1). The intersection between α and the light saturated rate of photosynthesis, P_{max}, is the optimal photosynthetic irradiance, E_k. Irradiance levels higher than E_k are in "excess" for photosynthesis. At "supraoptimal" irradiance levels, photosynthesis declines. This decline is commonly taken by phytoplankton ecologists as photoinhibition.

Fig. 3. A vertical profile showing the changes in the optical absorption cross section normalized to chlorophyll *a*, a*, in the open ocean (see Eq. 10). The data are plotted as a function of optical depth (the e-folding depth of light). The depth corresponding to 1% of the surface irradiance is equivalent to an optical depth of 4.6. Note that in the upper portion of the water column, a* is larger as cells adapt to higher irradiance levels. This increase is primarily due to the decrease in self-shading within the thylakoids, as the cells reduce the total pool of intracellular chlorophll (Berner et al, 1989).

Fig. 4. Changes in E_k values (see Fig. 2) as a function of optical depth for a station in the subtropical Atlantic Ocean. The values of E_k were derived from P *vs* E curves from each of

the depths with a 1 h incubation with radiocarbon. The changes in E_t optimize light utilization throughout the water column.

Fig. 5. Changes in dark-adapted values of F_v/F_m as plotted as function of optical depth (see Fig. 3). In a nutrient rich upwelling region off the coast of northwest Africa F_v/F_m averaged about 0.6; the maximum value in phytoplankton in culture is about 0.65. In a nutrient poor region of the subtropical Atlantic, the maximum value of F_v/F_m is about 0.45. Below an optical depth of about 7 (0.1% of surface light), irradiance is so low that cells become senescent and F_v/F_m declines rapidly.

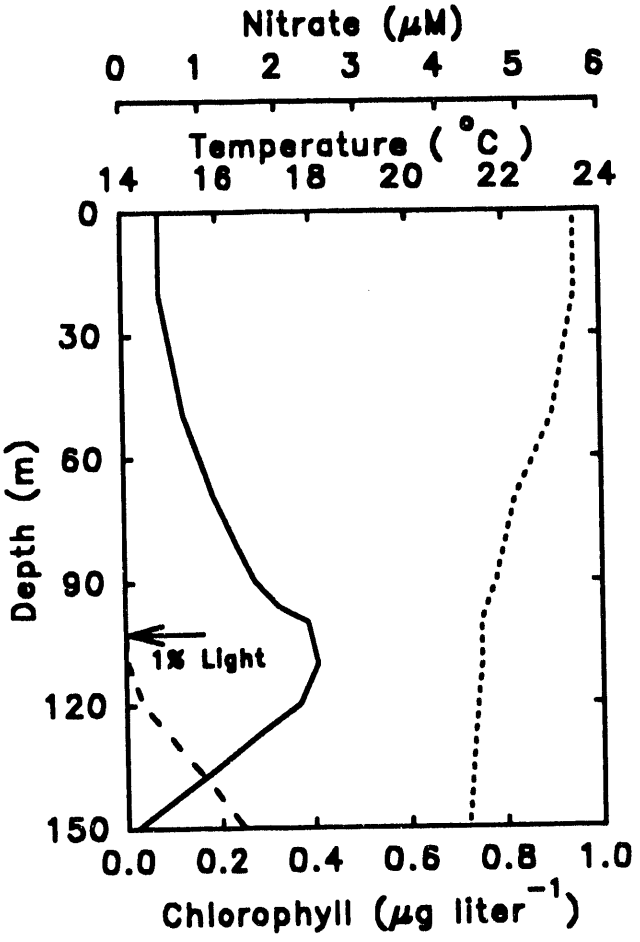
Fig. 6. Top: Diurnal changes in F_o (open circles), F_m (closed circles) and F_v/F_m (open squares) taken from the upper 10 m at three areas in the suptropical Pacific Ocean between 0° and 18° N in May 1992. Note the large quenching of both F_o and F_m and the mid-day depression of F_v/F_m. Bottom: the changes in the effective absorption cross section of PSII measured from the flash intensity saturation profiles of variable fluorescence (see Fig. 7). The decrease in F_o and F_m in mid-day is accompanied by a 50% loss of effective cross section.

Fig. 7. The kinetics for the relaxation of photochemical (q_P) and non-photochemical (q_N) quenching in a natural phytoplankton community in a well mixed water column. q_N relaxes in two phases; the fast relaxation occurs with a half-time of about 15 min and is not accompanied by an increase in q_P. The second, slow phase has a half time of about 130 min and is correlated with a slight increase in q_P. We attribute the fast phase to relaxation of bed quenching, and the second to relaxation of reaction center quenching (see Fig. 7).

Fig. 8. A schematic representation of a target theory approach to differentiating between non-photochemical quenching in the reaction center and the pigment bed. The effective

absorption cross section of PSII can be derived from a flash intensity saturation curve of variable fluorescence (Falkowski et al., 1986). The curve closely follow a cumulative one-hit Poisson function. If quenching only occurs in the reaction center, it would phenomenologically appear to lead to reduction in the saturation level for variable fluorescence, without any change in the intensity of a flash required to produce half-saturation. On the other hand, if the quenching occurs only in the bed, the saturation value remains constant, but the intensity required to saturate the fluorescence increases; i.e., the curve shifts to the right. The extent of the shift can be quantitatively related to a change in the effective absorption cross section of PSII (Falkowski et al., 1986; Genty et al., 1990).

Fig. 9. The relationship between phytoplankton photosynthesis (normalized to chlorophyll *a)* integrated over the water column and integrated surface incident photosynthetically active radiation. The data are taken from the northwest Atlantic Ocean throughout the year. The slope of the curve is has the same units as α (Fig. 2). On a community level, phytoplankton photosynthesis is never light saturated; i.e. , the integrated response is always functioning as if irradiance was $< E_t$.



Falkowski fig 1

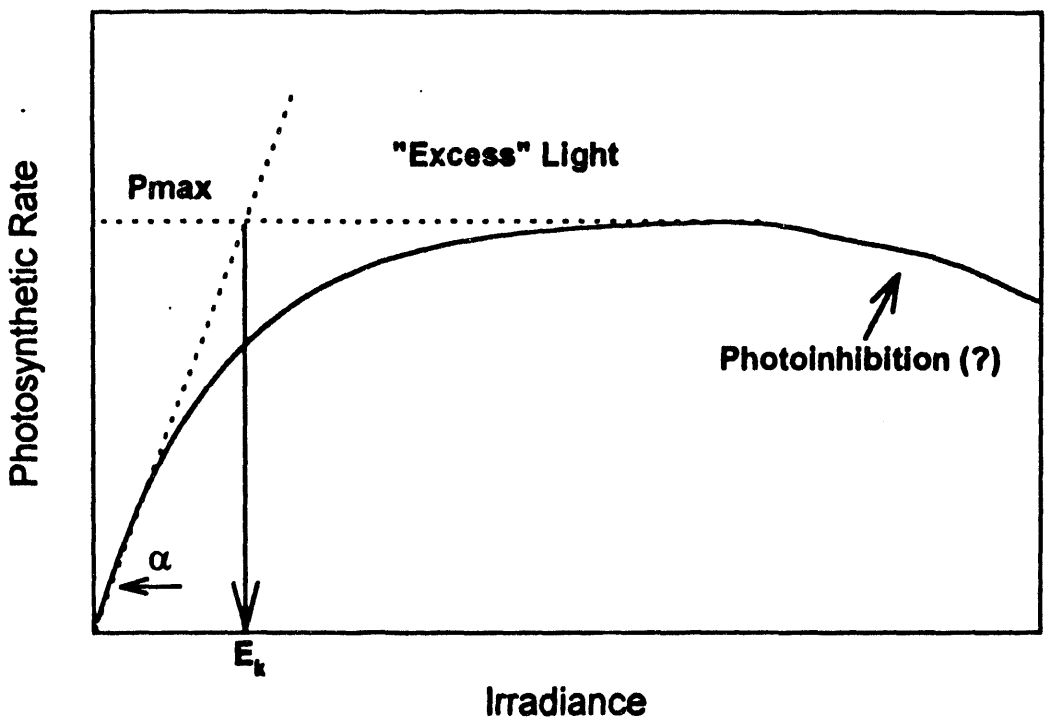


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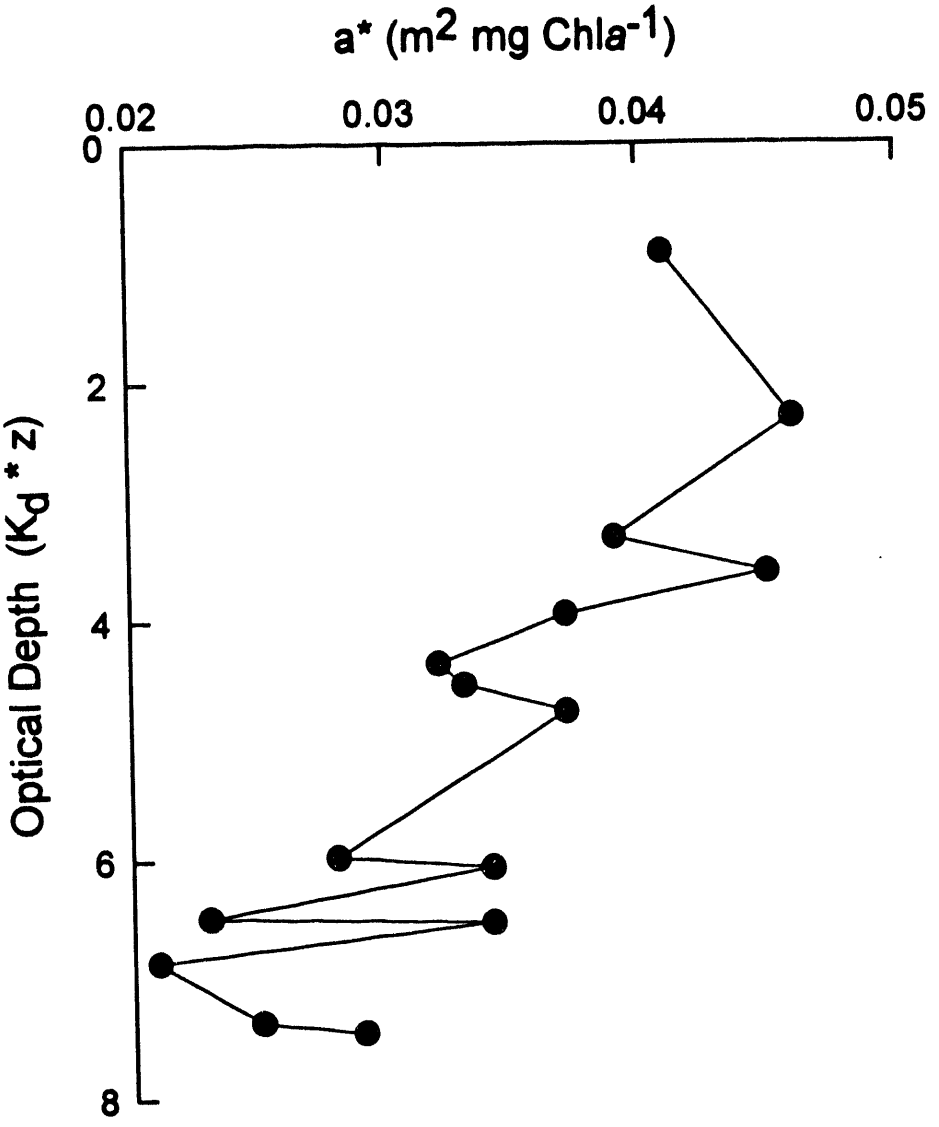
Fig 2


a* (m2 mg Chla-1)
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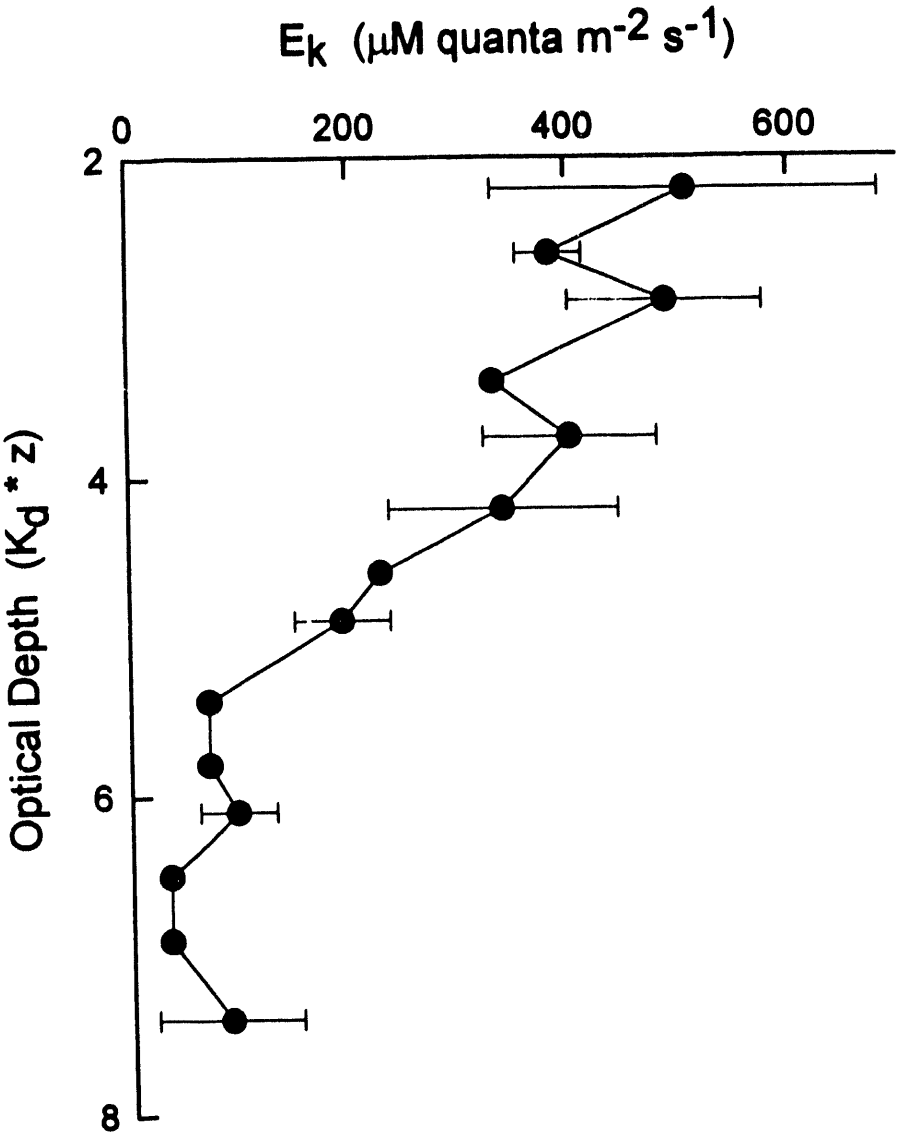
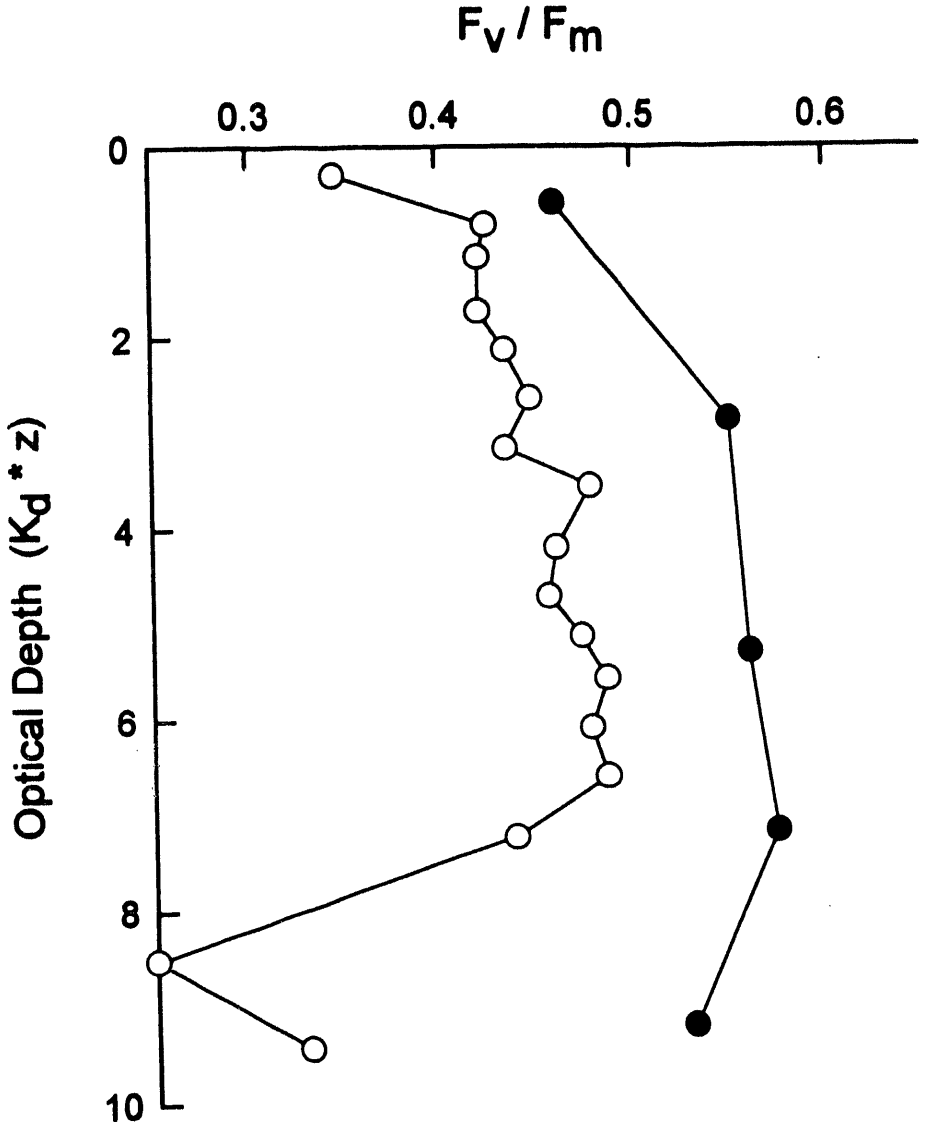
0.03
0.04
0.05
0
2
4
6
8
Optical Depth (Kd * z)



Fallowfield
Fig 4



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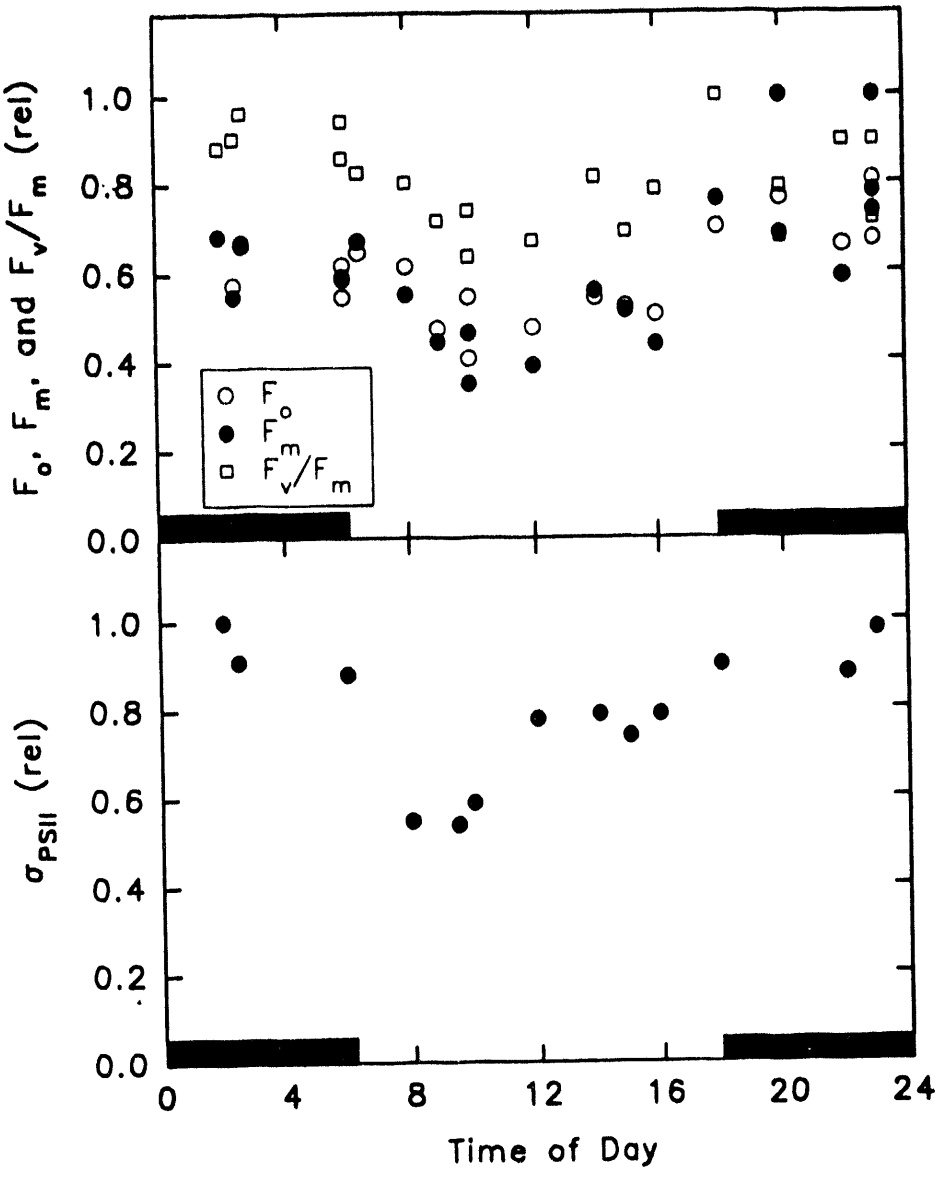

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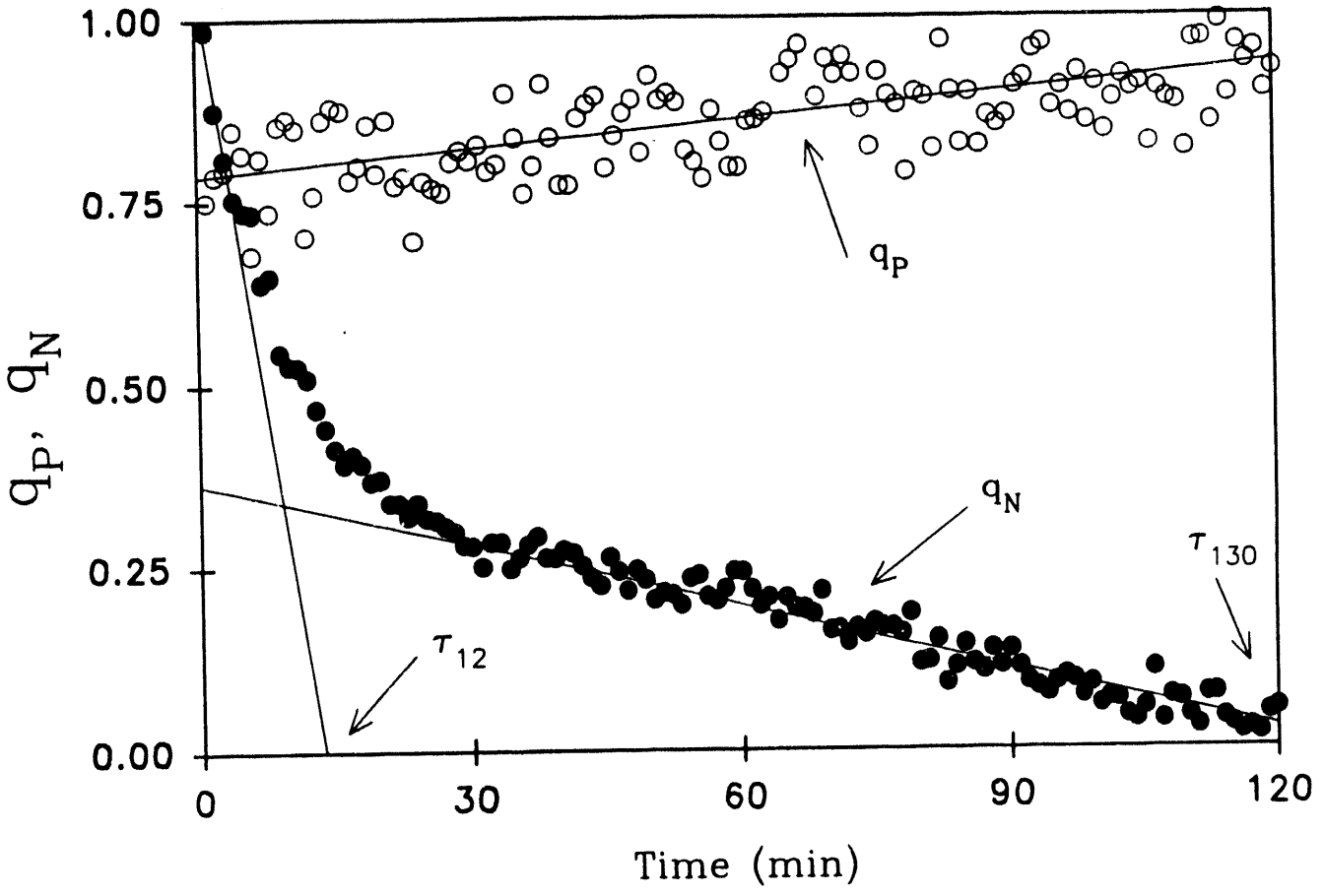
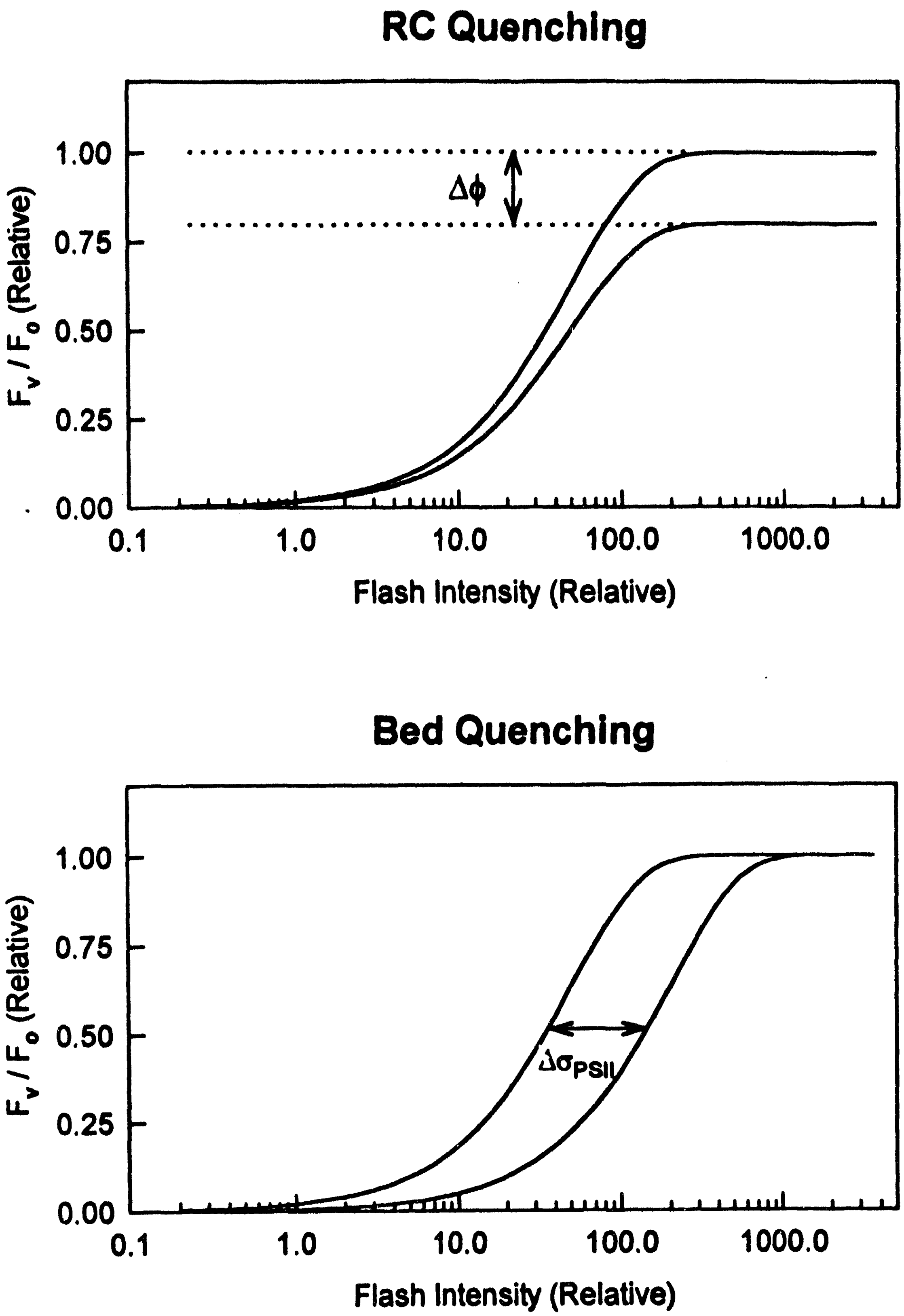
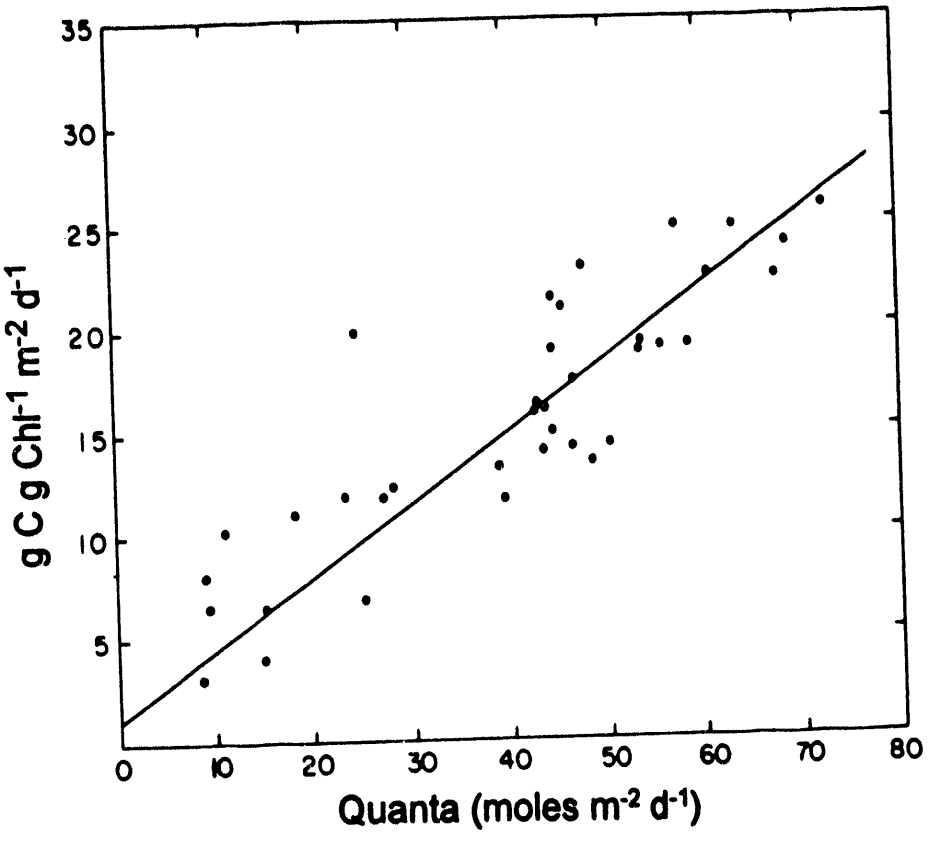


Falkenhagen Fig 7



Falkowski
Fig 8



Falkowski Fig 1

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