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IMPACT OF ULTRAVIOLET-B RADIATION ON PHOTOSYSTEM II ACTIVITY AND ITS RELATIONSHIP TO THE INHIBITION OF CARBON FIXATION RATES FOR ANTARCTIC ICE ALGAE COMMUNITIES¹

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ABSTRACT

One goal of the Icecolors 1993 study was to determine whether or not photosystem II (PSII) was a major target site for photoinhibition by ultraviolet-B radiation (Q_{UVB} , 280–320 nm) in natural communities. Second, the degree to which Q_{UVB} inhibition of PSII could account for Q_{UVB} effects on whole cell rates of carbon fixation in phytoplankton was assessed. On 1 October, 1993, at Palmer Station (Antarctica), dense samples of a frazil ice algal community were collected and maintained outdoors in the presence or absence of Q_{UVB} and /or ultraviolet-A (Q_{UVA} , 320–400 nm) radiation. Samples were then collected at intervals over the day to track the time course of UV inhibition of primary production. The ice algae were assessed for changes in pigment composition and rates of carbon fixation. The quantum yield of PSII (ϕ_{II}^o) was measured by Pulse Amplitude Modulated fluorometry. Over the day, ϕ_{II}^o declined due to increasing time-integrated dose exposure of Q_{UVB} . The Q_{UVB} -driven inhibition of ϕ_{II}^o increased from 4% in the early morning hours to a maximum of 23% at the end of the day. The Q_{UVB} photoinhibition of PSII quantum yield did not recover by 6 h after sunset. In contrast, photoinhibition by Q_{UVA} and photosynthetically available radiation (Q_{PAR} , 400–700 nm) recovered during the late afternoon. Fluorescence-based estimates of carbon fixation rates were linearly correlated ($P = 0.002$, $r^2 = 0.45$) with measured carbon fixation. Fluorescence overestimated the observed Q_{UVB} inhibition in measured carbon fixation rates by 8% in the morning hours; however, the discrepancy increased during the afternoon. Therefore, researchers should be cautious in using fluorescence measurements to

infer ultraviolet inhibition for rates of carbon fixation until there is a greater understanding of the coupling of carbon metabolism to PSII activity for natural populations. Despite these current limitations, fluorescence-based technologies represent powerful tools for studying the impact of the ozone hole on natural populations on spatial / temporal scales not possible using conventional productivity techniques.

Key index words: Antarctic algae; carbon fixation; fluorescence; ozone hole; photoinhibition; photosystem II; ultraviolet radiation

The discovery of the ozone hole (Farman et al. 1985) has raised concerns that elevated levels of ultraviolet-B radiation (Q_{UVB}) during the austral spring might have detrimental effects on the Antarctic ecosystems (cf. Weiler and Penhale 1994). Phytoplankton may be especially sensitive to enhanced Q_{UVB} because the algae are exposed to significant amounts of ultraviolet (UV) radiation (Smith and Baker 1979, Smith et al. 1992) when they bloom during the late austral spring and early summer, when the ozone (O_3) hole is present. Given that phytoplankton are the base of the food chain and represent an important component in the biogeochemical cycles of the Southern Ocean (El-Sayed and Fryxell 1993), a great deal of effort has been invested in measuring the impact of Q_{UVB} on phytoplankton biology (cf. Weiler and Penhale 1994). Despite debate, data collected from numerous groups suggest that Q_{UVB} inhibition of total water column photosynthesis is about 5–6% under normal ozone levels (El-Sayed et al. 1990, Helbing et al. 1992, Smith et al. 1992, Prézelin et al. 1994b) (after the data from the different research groups have been intercalibrated [Prézelin et al. 1994a]); however, re-

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cent reports have shown that inhibition rates are higher under the O₃ hole (Smith et al. 1992). Recent measurements under the O₃ hole have demonstrated that inhibition of *in situ* photosynthetic carbon fixation rates could be as high as 6–18%, depending on the total dose and duration of UV exposure (Smith et al. 1992, Boucher and Prézelin 1993, Prézelin et al. 1994b).

Photoinhibition of photosynthesis by a specific wavelength of light (295–700 nm in nature) at any given time is a function of polychromatic damage and repair processes within an algal cell. The balance between Q_{UVB} damage and repair of damaged sites is a nonlinear function that is sensitive to the physiological state of the phytoplankton (Cullen and Lesser 1991, Lesser et al. 1994). Furthermore, laboratory and a few field studies indicate that algal sensitivity to Q_{UVB} appears to be species-specific (Jokiel and York 1984, Karentz et al. 1991, 1994, Helbing et al. 1992, Smith et al. 1992). Comprehensive analyses of the impact of Q_{UVB} on primary production in the Southern Ocean requires extensive data from field studies where cells are exposed to sunlight in a natural and ozone-depleted atmosphere. However, given the effort and cost required to discern *in situ* inhibition of carbon fixation by enhanced Q_{UVB} in the Southern Ocean, any proxy measurement for carbon fixation that can accurately resolve UV effects is desirable. Most promising are chlorophyll *a* (chl *a*) fluorescence techniques, which reflect the primary photochemical events in carbon fixation (Sivak and Walker 1985). One advantage of these techniques is that they are amenable to mooring technology (Smith et al. 1991, Kolber and Falkowski 1993) and, thus, can potentially provide a continuous time series of data.

The use of chl *a* fluorescence appears to be promising for studying Q_{UVB} effects in particular because there is laboratory evidence that suggests that the major targets for Q_{UVB} inhibition are central to the light reactions of photosynthesis and directly impact the function of photosystem II (PSII) in chloroplasts (Iwanzik et al. 1983, Kulandaivelu and Noorudeen 1983, Greenberg et al. 1989, Renger et al. 1989). In these studies of higher plants and green algae (no chromophytes), the primary action of Q_{UVB} appears to be the degradation of the D1/32-kDa protein complex within PSII. The D1 protein complex appears to be degraded by photosensitizers adjacent to the protein (Greenberg et al. 1989). There is debate as to the identity of the primary photosensitizer, and currently there appear to be two candidates. One candidate is the electron carrier plastoquinone (PQ), which has absorption capabilities in the UV wavelengths of light (Greenberg et al. 1989, Melis et al. 1992, Jansen et al. 1993). The second candidate is thought to reside within the water-oxidizing system on the donor side of PSII, which, when damaged, promotes structural changes in the D1/D2 polypeptide matrix (Richter et al. 1990). Whatever the

mechanism, the damage to PSII will reduce the ability of the algae to generate stable charge separations, which will result in lower carbon fixation rates at the whole cell level. Beyond the photosynthetic light reactions, exposure to Q_{UVB} has been shown to inhibit carbonic anhydrase activity (Dionisio et al. 1989) and the carboxylating enzyme, ribulose-1,5-carboxylase/oxygenase (RUBISCO) (Strid et al. 1990, Neale et al. 1993). Thus, the utility of fluorescence-based estimates to predict Q_{UVB} inhibition of carbon fixation is a direct function of where the major Q_{UVB} inhibition occurs in the photosynthetic process.

Despite the numerous laboratory studies, there has been, until now, no field information on whether or not PSII is a major target for natural communities exposed to the elevated Q_{UVB} associated with the Antarctic ozone hole. We have recently found that Q_{UVB} specifically decreases the quantum yield for PSII activity in a field community of Antarctic ice algae (Kroon, unpubl.). Here we extend these mechanistic studies, specifically questioning the degree to which fluorescence properties can explain Q_{UVB} inhibition of carbon fixation for natural communities of ice algae.

MATERIALS AND METHODS

Sample collection and deckboard incubators. The Icecolors 1993 expedition was conducted during the austral spring of 1993 at both the Palmer station (Antarctica) and aboard the R.V. *Polar Duke*. As part of that larger study, the present manuscript focuses on a series of experiments that was conducted at Palmer Station during the last week of September (Julian days 267–279). The majority of data reported here was collected on 1 October 1993 (Julian day 274). During that week, Authur Harbor was filled with pack ice that had recently entered the region. Cold air temperatures (< –10° C) froze the pack ice into a solid sheet that lasted approximately 12 days, during which divers repeatedly sampled the frazil ice algal community with a small suction pump. The submersible centrifugal pump (Pump Model 24, Diversified Products, Los Angeles, California) was scraped through the soft frazil ice, and the ice slurry was pumped up to darkened carboys at the surface. Samples were returned to the laboratory within 30 min of collection, pooled, and dispersed for experimental analyses within 90 min of collection. Small volume sampling into hand-collected jars indicated that the chl *a* in the frazil ice was 3 orders of magnitude more concentrated than the surrounding water column. Therefore, we believe the majority of the biomass in our sample reflected ice algal communities rather than the dilute plankton communities. Because our samples were unavoidably diluted by the surrounding seawater, we make no attempt to calculate the areal biomass in the ice, and all measurements reported are for the volumetric water samples collected by the pump. Microscopic analysis indicated that ice communities were dominated by diatoms, primarily *Coscinodiscus* sp. and *Nitzschia* sp.

Control experiments assured us that pumping samples had no detectable adverse effect on whole cell rates of photosynthesis (Fig. 1a). In these repeated experiments, ice samples were hand-collected by divers into darkened jars. Half of the sample was kept as a control, and the other half was passed through the suction pump prior to both samples being used to measure photosynthesis–irradiance (P-I) curves.

Experimental samples, which were incubated outdoors under natural light fields, were first aliquoted and sealed into nontoxic polyethylene (PE) bags (Prézelin et al. 1994a, b). Samples were

FIG. 1. Measurements of the effect of sample pumping on a) ice algal rates of carbon fixation rates and b) P-I curves for the ice algal communities used in the present study. The error limits around the P-I curves are also presented. Error limits calculated from procedures described by Zimmerman et al. (1987).

maintained at *in situ* temperature by pumping seawater through the incubation chambers. There were three optically distinct light treatments in the outdoor incubators. The chamber lids were constructed out of three different plastics (UVT, UVT + MYLAR, and UF3) that had different transmission qualities (Fig. 2). The 50% transmittance points for the plastics, each in combination with PE bags, were 299 nm (UVT + PE), 328 nm (UVT + MYLAR + PE), and 414 nm (UF3 + PE). The light exposure within each sample was calculated as the product of the incident spectral irradiance and the transmission qualities of the PE bag and chamber plastic.

Values of Q_{PAR} were measured every 5 min over the day with a 2π -cosine collector (Li-Cor Instruments), which was mounted directly beside the deckboard incubator. UV light levels were measured by the NSF/USAP UV-monitoring network (Booth et al. 1994), which measures light with a spectroradiometer (Biospherical Instruments, Inc., Model SUV-100). Processing and quality control of the UV data were performed by Biospherical Instruments. Samples were retrieved every 2 h during the day for a suite of laboratory measurements. The laboratory measurements were completed in less than 1 h. Samples were collected at 0400 (local daylight time, LT), placed in the outdoor incubators before 0600 LT, and were incubated until 2200 LT. Significant symbols are listed in Table 1.

Analytical measurements. Phytoplankton pigments were measured by high-performance liquid chromatography (HPLC), using the modified procedures of Wright et al. (1991). Replicate

FIG. 2. Comparison of the spectral transmission of broadband cutoff plastics used to construct outdoor incubators and detect Q_{UVA} - and Q_{UVB} -specific effects on the algal communities in the present study.

samples were collected and filtered onto 0.4- μ m 47-mm Nalgene nylon filters. Samples were then frozen at -70° C for at least 2 h and then extracted in 90% ice-cold acetone for 18 h. Samples were centrifuged for 5 min, and a 1-mL aliquot was removed to which 300 μ L H₂O was added. The sample was injected (350 μ L final volume) into a Hitachi HPLC system described by Prézélin et al. (1992). The HPLC system was calibrated over the season with JGOFS standards graciously provided by R. Bidigare (University of Hawaii).

Whole cell absorption spectra [$a_{ph}(\lambda)$, 400–700 nm] were measured using an Aminco DW-2000 spectrophotometer equipped with an integrating sphere. Calibration and performance properties of the sphere have been detailed elsewhere (Nelson and Prézélin 1993). When using the sphere, the spectrophotometer was operated in the dual wavelength mode with a reference wavelength of 750 nm. Samples were prepared as described in Nelson et al. (1993). Samples were gently filtered down onto a 0.4- μ m Nucleopore 47-mm filter and resuspended in 10 mL filtrate. The filter was then agitated on a Sybron Max Mix II Thermolyne shaker, and the absorption spectrum was measured on the resulting particle suspension. Chlorophyll measurements for both the filter and resuspension were made in order to calculate what percentage of the phytoplankton was retained on the filter. Generally the percentage of the phytoplankton retained on the filter was low (<10%). The particulate absorption of the resuspension was corrected for nonphytoplankton absorption following a detrital-correction procedure modified from Kishino et al. (1985). Aliquots of the particle resuspension were refiltered and extracted for at least 24 h in cold methanol. The methanol-extracted particles were resuspended in filtered seawater with the Thermolyne shaker, and the spectral absorption of the extracted resuspended particulate material was determined. This "detritus" spectrum was subtracted from the corresponding particle absorption spectra to yield the phytoplankton absorption [$a_{ph}(\lambda)$]. The absorption spectra were spectrally weighted (see Table 1) to the visible spectral irradiance to yield $\bar{a}_{ph}$ for productivity calculations.

A Pulse Amplitude Modulated fluorometer (PAM-101, Heinz Walz, Effeltrich, Germany) was used to measure the fluorescence characteristics of the algae. Triplicate samples were quickly filtered down onto GF/F Whatman filters and dark-adapted 30 min prior to measurements. During the 30-min dark incubation, samples were maintained in 25 mL seawater. For fluorescence induction measurements, 3-(3,4-dichlorophenyl)-1,1-dimethylurea (20 μ M final concentration) was added at the beginning of the 30-min dark adaptation period (samples were kept in complete darkness). All fluorescence work was conducted in a darkened

TABLE 1. Significant symbols.

a_{ph}	Spectrally weighted phytoplankton absorption (m^{-1}): $\bar{a}_{ph} = \int_{400nm}^{700nm} a(\lambda) \cdot Q(\lambda) d\lambda / \int_{400nm}^{700nm} Q(\lambda) d\lambda$
FII	Fraction of absorbed light that is directed toward PSII.
I_k	Light intensity at which photosynthesis is light-saturated ($\mu mol \text{ photons} \cdot m^{-2} \cdot s^{-1}$).
P_{max}	Light-saturated photosynthetic rate ($mg \text{ C} \cdot m^{-3} \cdot h^{-1}$).
P_{O_2} or C	Volumetric production for oxygen evolution ($\mu mol \text{ O}_2 \cdot m^{-3} \cdot h^{-1}$) and carbon fixation ($mg \text{ C} \cdot m^{-3} \cdot h^{-1}$).
PSII	Photosystem II.
PQ	Photosynthetic quotient (mol O_2 evolved · mol CO_2 fixed $^{-1}$).
$Q(\lambda)$	Spectral irradiance at wavelength λ ($\mu mol \text{ photons} \cdot m^{-2} \cdot s^{-1} \cdot nm^{-1}$).
Q_{PAR}	Photosynthetically available radiation ($\mu mol \text{ photons} \cdot m^{-2} \cdot s^{-1}$) (400–700 nm).
Q_{UVA}	Ultraviolet-A radiation ($\mu mol \text{ photons} \cdot m^{-2} \cdot s^{-1}$) (320–400 nm).
Q_{UVB}	Ultraviolet-B radiation ($\mu mol \text{ photons} \cdot m^{-2} \cdot s^{-1}$) (280–320 nm).
α	Light-limited slope of a P-I curve [$mg \text{ C} \cdot m^{-3} \cdot h^{-1} (\mu mol \text{ photons} \cdot m^{-2} \cdot s^{-1})^{-1}$].
ϕ_{IIe}^o	Maximum quantum yield for stable charge separation in PSII (mol charge separation · mol $^{-1}$ photons).
ϕ_c	Operational quantum yield for carbon fixation (mol carbon fixed · mol $^{-1}$ photons absorbed).
ϕ_{maxc}	Maximum quantum yield for carbon fixation predicted from ϕ_{IIe}^o (mol carbon fixed · mol photons absorbed $^{-1}$).
Γ	Stoichiometric ratio of oxygen evolved per electron generated at PSII (assumed to be constant at a value of 0.25 O_2/e^-).

environmental refrigeration room (7° C) to minimize any temperature effects. Control experiments demonstrated that a gradual temperature increase from outdoor temperatures did not alter the fluorescence characteristics of the cells. Samples were maintained in 100% darkness prior to any measurements. The minimum (F_o) and maximum (F_m) fluorescence levels were determined from the fluorescence induction curve. The maximum quantum yield for stable charge separations at PSII (ϕ_{IIe}^o) was calculated as

$$\phi_{IIe}^o = \frac{F_m - F_o}{F_m} \quad (1)$$

Time-integrated carbon fixation rates for each light treatment were measured outdoors with $H^{14}CO_3$ uptake procedures given by Boucher and Prézélin (1993). Triplicate ^{14}C samples were retrieved every 2 h and filtered onto 0.4- μm 47-mm Nuclepore filters. Samples were suspended in liquid scintillation counting cocktail, and the radioactive uptake was measured on an LKB scintillation counter. The operational quantum yield for carbon fixation (ϕ_c) was calculated from volumetric carbon fixation measurements (PC), spectrally weighted phytoplankton absorption ($\bar{a}_{ph}$), and Q_{PAR} , such that

$$\phi_c = \frac{PC}{\bar{a}_{ph} \cdot Q_{PAR}} \quad (2)$$

Fluorescence-based productivity estimates. A fluorescence-based bio-optical model was used to test how well PSII activity could

explain the observed dynamics in photosynthetic carbon fixation. This approach assumes that carbon uptake rates are a direct function of electron flow (e^-) out of PSII. The model was derived by Kroon (1994), where the rate of oxygen evolution is directly related to the rate of stable charge separations being generated at PSII, such that

$$PO_2 = \Gamma \cdot \frac{d}{dt} e^-, \quad (3)$$

where Γ is the stoichiometric ratio of mol O_2 generated per mol stable charge separations. The value of Γ was taken to be 0.25. This assumes that it takes a minimum of four stable charge separations at PSII to generate one O_2 . Equation 3 can be rewritten in terms of the maximum quantum yield of stable charge separation at PSII (ϕ_{IIe}^o), such that

$$PO_2 = \Gamma \cdot \phi_{IIe}^o \cdot Q_{PAR} \cdot \bar{a}_{ph} \cdot FII. \quad (4)$$

In this formulation, the fraction of light absorbed by PSII (FII) is assumed to be relatively constant. We question this assumption and present a sensitivity analysis later in the paper that quantifies the impact of making this assumption (see Results). To convert the predicted oxygen evolution to carbon fixation, equation 4 needs to be divided by the photosynthetic quotient (PQ, mol O_2 evolved per mol CO_2 fixed). The photosynthetic quotient was assumed to be one. Again, the impact of this assumption was assessed (see Results). The assumptions regarding FII and PQ were mandated by experimental limitations. This formulation assumes that phytoplankton are operating at the maximum quantum yield for carbon fixation (ϕ_{maxc}), and thus predicted photosynthetic rates based on equation 4 are the maximum theoretical photosynthetic rate at any given irradiance.

Determinations of the operational quantum yield of carbon fixation (ϕ_c) are based on the work by Bidigare et al. (1992), where ϕ_c is calculated from ϕ_{maxc} , the light level at which photosynthetic rates are saturated (I_k), and Q_{PAR} , such that

$$\phi_c = \phi_{maxc} \cdot \frac{I_k}{Q_{PAR}} \cdot \tanh\left(\frac{Q_{PAR}}{I_k}\right). \quad (5)$$

Operational photosynthetic rates (PC) can then be calculated from the operational quantum yield, phytoplankton absorption, and Q_{PAR} , such that

$$PC = \phi_c \cdot \bar{a}_{ph} \cdot Q_{PAR}. \quad (6)$$

By combining equations 4–6, a fluorescence-based estimate of the instantaneous rate of carbon fixation can be derived:

$$\text{instantaneous PC} = \Gamma \cdot \phi_{IIe}^o \cdot \bar{a}_{ph} \cdot \frac{FII}{PQ} \cdot I_k \cdot \tanh\left(\frac{Q_{PAR}}{I_k}\right). \quad (7)$$

Values of carbon-based I_k were measured for outdoor samples incubated for 1 h in photosynthetrons, as described by Prézélin et al. (1992) during the prior day. Diurnal variation in I_k was minimal (<20%). The P-I curves in the afternoon had large standard errors; therefore, the daily-averaged I_k value was used in the bio-optical model calculations. Fluorescence and pigment values were measured every 2 h during the experimental run on 1 October. The chlorophyll-specific absorption ($a_{ph} \text{ chl } a^{-1}$) was measured the prior day, and the measured chl a concentrations were used to calculate the volumetric absorption over the experimental day.

RESULTS

Local light environment. There were dramatic changes in the incident spectral irradiance during the Icecolors 1993 field season due to natural seasonal changes and the variable presence of the O_3 hole (Fig. 3). During the early austral spring, the

FIG. 3. Seasonal O_3 and Q_{UVB} climatology at Palmer Station, Antarctica, during the late winter and austral spring of 1993 during the Icecolors 1993 expedition. Overhead concentrations of O_3 are reported in Dobson units. Derived midday estimates of Q_{UVB} are expressed as $\mu W \cdot cm^{-2}$. The sampling date (1 October 1993) relative to the light history of the region is indicated by the vertical arrow.

solar zenith angle decreases dramatically, which results in higher incident irradiance values and longer daylengths. These changes are illustrated by the increased noontime flux of Q_{UVB} at Palmer Station from August through November (Fig. 3). The Antarctic O_3 hole imposes periodic increases in Q_{UVB} levels above those normally associated with the seasonal decrease in solar zenith angle. The oscillating nature of the O_3 hole reflects the undulating clockwise motion of the Southern Polar Vortex on the time scales of days to weeks (Smith et al. 1991). The decrease in the atmospheric O_3 leads to an enhancement of Q_{UVB} while having little impact on Q_{UVA} and Q_{PAR} .

The O_3 concentrations (TOMS database) over Palmer Station on 1 October were low (197 Dobson units) indicating the presence of the O_3 hole overhead (Fig. 3). Dobson units in the 200–250 range generally indicate the outer boundary of the ozone hole. Both Q_{PAR} and UV radiation varied over the day (Fig. 4) with the maximum intensities measured around 1300 LT. There was a short-lived blizzard with "white-out" conditions around 1100 LT. The Q_{PAR} levels were low, never exceeding $800 \mu mol \text{ photons} \cdot m^{-2} \cdot s^{-1}$ (Fig. 4a); however, this was sufficient to light saturate photosynthesis for major portions of the day ($I_k = 130 \mu mol \text{ photons} \cdot m^{-2} \cdot s^{-1}$).

Phytoplankton absorption and pigments. The absorption capabilities of phytoplankton influence both photosynthetic rates and the susceptibility to UV photoinhibition. The prominent features in the absorption spectrum were the DNA absorption peak (280–290 nm), the absorption peak presumably associated with the microsporine-like amino acids (MAAs) in the Q_{UVA} wavelengths (330–350 nm), and finally the absorption by the algal photosynthetic (and photoprotective) pigments in Q_{PAR} (Fig. 5). Ice algal absorption was highest at Q_{UVA} wavelengths,

FIG. 4. Daily patterns in Q_{PAR} , Q_{UVA} , and Q_{UVB} in the outdoor incubators and their relationship to the Q_{PAR} light requirements for frazil ice algae over the course of the day on 1 October 1993 (Julian day 274). a) Incubation Q_{PAR} over the day, expressed as $\mu mol \text{ photons} \cdot m^{-2} \cdot s^{-1}$ compared to the Q_{PAR} required to light-saturate photosynthesis ($Q_{PAR} = I_k$) and the minimum light requirement estimated to induce the onset of bright visible light photoinhibition ($Q_{PAR} = 4 \cdot I_k$). b) Q_{UVB} (280–320 nm) and Q_{UVA} (320–400 nm) expressed as $\mu W \cdot cm^{-2}$ were used to calculate the daily pattern in Q_{UVB}/Q_{UVA} .

which was 23% higher than DNA and protein absorption at 280 nm and 17% higher than the blue absorption peak at 440 nm. The presence of significant MAA absorption (whose presence was confirmed using HPLC by Ondrusek and Bidigare, unpubl.) is evidence for UV-related photoadaptation in the frazil ice algae. The diatom-dominated sample had a chl *a*-specific absorption coefficient at 675 nm

FIG. 5. UV and visible chlorophyll-specific spectral absorption (a_{ph} , $m^2 \cdot mg \text{ chl } a^{-1}$) for frazil ice algae.

FIG. 6. Comparison of time course measurements. a) Chlorophyll *a* abundance ($\mu\text{g chl } a \cdot \text{L}^{-1}$) and b–d) pigment:chl *a* ratios for frazil ice algae incubated outdoors in the presence and absence of UV radiation. The photoprotective carotenoids represent the sum of diadinoxanthin and diatinoxanthin. Each point is the mean of duplicate determinations from separate incubation bags, with the vertical bars indicating the range in the measurements.

of $0.007 \text{ m}^2 \cdot \text{mg chl } a^{-1}$, which was significantly lower than the 0.025 value for unpackaged light absorption by chlorophyll molecules (Morel and Bricaud 1986), which suggests strong pigment packaging effects. This is not surprising given that these algal cells were heavily pigmented and large in size. During the experiment on 1 October, the volumetric absorption for different times of the day was calculated by multiplying the chlorophyll-specific spectrum (Fig. 5) by measured chl *a* concentrations. This approach assumes that the relative shape in the phytoplankton absorption does not change during the experimental period, which is only valid if there were no major changes in the accessory pigment:chl *a* ratios.

The values of the changes in chl *a* and the accessory pigments for the outdoor incubators are the mean ($n = 2$) for replicate samples collected every 2 h from each light treatment, where vertical bars indicate the range around the mean (Fig. 6). There were no statistically significant changes in the concentration of chl *a* among the three light treatments over the day (Fig. 6a). For all light conditions, the weight-specific ratio of fucoxanthin:chl *a* remained high (≈ 0.6) and showed no major changes over the day in any of the three light treatments. Concentrations of chl *c* were high and tightly correlated to the abundance of fucoxanthin (data not shown). Chlorophyll *b*, a chemotaxonomic marker for chlorophytes, was also detectable, and the ratio of chl *b*:chl *a* showed no significant changes over the day and no significant differences among light treatments. In striking contrast, the ratio of the photo-

protective carotenoids (diadinoxanthin/diatinoxanthin, Demers et al. 1991) to chl *a* nearly doubled over the day in all light treatments and did so with nearly identical kinetics. Since the induction of the photoprotective pigments was similar in all light treatments, this was most likely a response to Q_{PAR} . The overall impact of increasing photoprotective carotenoids on cellular absorption was small, as the photoprotective carotenoid concentrations were nearly 10-fold lower than the major photosynthetically active carotenoid (i.e. fucoxanthin). Therefore, we believe that our assumption regarding the constancy of the relative shape of the absorption spectrum for the ice algae is reasonable.

Quantum yields for photosynthesis. The maximum quantum yield for stable charge separation at PSII (ϕ_{IIe}^0) quantifies the maximum efficiency of the primary photochemical events in photosynthesis. Because photosynthesis is a chain of cascading events, values of ϕ_{IIe}^0 set the upper limit for all subsequent photosynthetic efficiencies beyond PSII. The theoretical upper limit maximum quantum yield for carbon fixation can be estimated from ϕ_{IIe}^0 , as it takes at least eight stable charge separations to fix one CO_2 to carbohydrate. Thus, the theoretical upper limit for maximum quantum yield of carbon fixation is equal to $\phi_{\text{IIe}}^0/8$. In all treatments, ϕ_{maxc} displayed a diurnal pattern where values declined in the mid-morning hours and showed a gradual recovery during the late afternoon and early evening (Fig. 7). There was a 3-fold variation of ϕ_{maxc} over the day, regardless of the light treatment. No Q_{UVA} inhibition of ϕ_{maxc} was detectable. Values of ϕ_{maxc} incubated

FIG. 7. The measured variability in the photosynthetic quantum yields on 1 October 1993 incubated under three different UV regimes is presented. Values in the theoretical maximum quantum yield for carbon fixation [derived from the maximum quantum yield for stable charge separations at PSII ($\phi_{\text{IIC}}^{\circ}/8$ absorbed photons), mol carbon fixed $\cdot$ mol $^{-1}$ photons absorbed] is denoted by the gray lines with the vertical bars indicating the standard deviations of the mean. The operational quantum yield (ϕ_c , mol C fixed $\cdot$ mol $^{-1}$ photons absorbed), calculated from measured cumulative carbon fixation, for three different UV treatments are denoted by the lower black lines.

under the full solar spectrum were significantly lower than those measured in the absence of Q_{UVB} . All light treatments showed a similar rate of decline in ϕ_{maxc} during the morning hours, but samples incubated in the presence of Q_{UVB} radiation showed a slower recovery in the afternoon hours. Values of ϕ_{maxc} for the Q_{UVB} -exposed samples were 23% lower than the other samples by the end of the day. The long dark adaptation (30 min) assures that the diurnal ϕ_{maxc} decrease was not driven by nonphotochemical quenching processes related to visible light fluorescence quenching processes. Also, the Q_{UVB} -driven decrease in ϕ_{maxc} was not related to the down-regulation of PSII, which can be identified by a rapid recovery once cells are maintained in darkness (Ort 1994), and samples maintained in complete darkness for several hours did not result in any increase of the ϕ_{maxc} . Therefore, the low quantum yields for the Q_{UVB} -exposed cells reflected damage to the photosynthetic machinery.

The theoretical maximum quantum yield was always 2–3-fold higher than the operational quantum yield of carbon fixation (Fig. 7), in agreement with the fact that the algae were light-saturated for major portions of the day (Fig. 4). Unlike the Q_{UVB} depression in ϕ_{maxc} , we could not resolve any UV suppression of ϕ_c probably as a result of the experimental uncertainty in both the volumetric carbon fixation and the chl *a* concentrations (the chl *a* concentration was used to convert the chlorophyll-specific absorption to a volumetric estimate). Values of ϕ_c were low (<0.03 mol carbon fixed per photons absorbed $^{-1}$), often 10-fold lower than the theoret-

FIG. 8. Comparison of time-integrated measurements. a) PSII activity and b) carbon fixation rates for frazil ice algae incubated in the presence and absence of natural UV radiation on 1 October 1993. The standard deviations of the mean ($n = 3$) measurements at each time of day are indicated by the vertical bars.

ical upper limit of 0.125 mol carbon fixed per mol photons absorbed. The carbon-based quantum yields showed a midday suppression with a slight recovery by the early evening (Fig. 7) and generally approximated the diurnal pattern measured for ϕ_{maxc} .

Any decrease in $\phi_{\text{IIC}}^{\circ}$ directly decreases the flow of electrons out of PSII and, thus, lowers the rates of ATP and NADPH $_2$ formation, which, in turn, slows the enzymatic conversion of CO $_2$ into organic carbon whenever PSII activity is limiting. The potential of PSII to generate electrons over the course of the day can be estimated by multiplying $\phi_{\text{IIC}}^{\circ}$ with Q_{PAR} (Fig. 8a). For the ice algal samples, significantly fewer electrons were generated when cells are exposed to Q_{UVB} while no significant Q_{UVA} inhibition was detectable. Time-integrated estimates of the electrons generated by PSII show a linear increase over the day and leveled out by early evening as incident Q_{PAR} dropped (Fig. 4a). Not surprisingly, the diurnal trend for the measured carbon fixation (Fig. 8b) was similar to that for electrons generated by PSII (Fig. 8a), and samples exposed to Q_{UVB} had the lowest photosynthetic rates (Fig. 8b). In the early night, the concentration of radiolabeled carbon decreased, perhaps due to cellular respiration or excretion of organic carbon (Fig. 8b). The carbon in

FIG. 9. Comparison of carbon fixation rates based on a) PSII activity and b) measured carbon uptake rates for frazil ice algae incubated in the presence and absence of natural UV radiation on 1 October 1993.

the MYLAR incubator showed the lowest decrease in the evening hours, which presumably reflected the transparency of this incubator to Q_{PAR} (the UF3 filter has a 50% cutoff at 414 nm and thus excludes some Q_{PAR} , which will become significant when cells are light-limited). Direct comparison of Figure 8a and 8b requires the estimated electrons generated by PSII to be converted into an estimate of carbon fixation.

Bio-optical model for carbon fixation. Given that ϕ_{IIc} represents a subset of processes that determine ϕ_c , then the assessment of their correspondence provides information on the relative contribution of PSII processes, and indirectly the biochemical processes beyond PSII, to the rates of ^{14}C production. Furthermore, if PSII activity is the primary factor determining overall photosynthetic performance,

then one would expect a linear correspondence, which may or may not have a 1:1 relationship to carbon fixation due to the necessary assumptions required to make a fluorescence-based estimate of ^{14}C production.

Photosynthetic rates predicted from fluorescence and measured by ^{14}C uptake showed no major variations over the day (Fig. 9a, b). The fluorescence-predicted carbon fixation rates consistently overestimated ^{14}C -uptake rates by a factor of 2. Factors that could account for the overestimated carbon fixation rates are discussed later. For both fluorescence-predicted and measured carbon uptake, the samples exposed to Q_{UVB} were significantly lower (ANOVA, 95% confidence levels) than the other spectral treatments (Fig. 9, Table 2). The noise in the ^{14}C data increased over the day, so we were concerned that the analyses of variance (ANOVAs) may have been biased by a nonnormal distribution in the variances, so the ANOVA results were verified using a computer-randomized ANOVA (10,000 randomizations, cf. Manly 1991), which is insensitive to nonnormally distributed data. The computer randomization techniques verified that Q_{UVB} carbon fixation rates were significantly lower than the other treatments. No statistically significant differences could be resolved between the $Q_{PAR} + Q_{UVA}$ and Q_{PAR} treatments, indicating that Q_{UVA} inhibition of carbon fixation was not detectable (Table 2). The fluorescence-predicted carbon fixation rates were linearly correlated with measured ^{14}C -uptake rates ($P = 0.002$, $r^2 = 0.45$). The daily-average inhibition (relative to Q_{PAR}) due to Q_{UVB} was 30 and 14% for the fluorescence-predicted and measured carbon fixation rates, respectively.

Three factors could account for the overestimated carbon fixation rates predicted by fluorescence measurements. In the initial model runs, FII and PQ were assumed to be constant despite the fact that both variables are known to be dynamic. A nomogram is used to illustrate the impact of varying both FII and PQ on the slope of the best-fit line between predicted and measured carbon fixation rates (Fig. 10). Using a range of values for PQ and FII taken from the literature (Laws 1991, Kroon et al. 1993), the slope of correspondence between predicted and measured carbon fixation rates could vary

TABLE 2. Rates of carbon fixation ($mg\ C\ m^{-3}\ h^{-1}$) for phytoplankton exposed to natural sunlight on 1 October 1993. Carbon fixation rates were predicted from fluorescence measurements and measured as ^{14}C uptake. Statistically significant differences (ANOVA, $n = 18$) among the different UV treatments are presented.

Treatment	Carbon fixation rates ($mg\ C\ m^{-3}\ h^{-1}$)	Daily average ($\pm SE$)	Significantly different from following treatments	P-value
Q_{PAR}	Fluorescence-predicted	78.5 ± 4.6	$Q_{PAR} + Q_{UVA} + Q_{UVB}$	≤ 0.001
$Q_{PAR} + Q_{UVA}$	Fluorescence-predicted	73.1 ± 2.6	$Q_{PAR} + Q_{UVA} + Q_{UVB}$	≤ 0.001
$Q_{PAR} + Q_{UVA} + Q_{UVB}$	Fluorescence-predicted	50.2 ± 3.6		
Q_{PAR}	Measured ^{14}C uptake	34.7 ± 1.6	$Q_{PAR} + Q_{UVA} + Q_{UVB}$	0.005
$Q_{PAR} + Q_{UVA}$	Measured ^{14}C uptake	33.4 ± 1.2	$Q_{PAR} + Q_{UVA} + Q_{UVB}$	0.022
$Q_{PAR} + Q_{UVA} + Q_{UVB}$	Measured ^{14}C uptake	28.4 ± 1.5

FIG. 10. A nomogram that illustrates the impact of varying the magnitude of both the photosynthetic quotient (PQ, mol O_2 evolved $\cdot$ mol $^{-1}$ CO_2 fixed) and the fraction of absorbed light harvested by PSII (FII, %) on the slope of the best-fit linear line between measured and fluorescence-predicted carbon fixation rates ($mg\ C \cdot m^{-2} \cdot h^{-1}$).

77% from 0.25 to 0.75. Given the larger natural variability in PQ, it had a larger impact on the slope than did FII. A third factor that might account for the lack of a 1:1 correspondence between fluorescence-based and ^{14}C uptake is the possible variability in the I_k value. We, by necessity, had to assume that a mean carbon-based I_k value (again, the diurnal variation for I_k was $<20\%$) measured the prior day was appropriate. However, prior laboratory work has demonstrated that the I_k for PSII activity and O_2 evolution can be different than a carbon-based I_k (Kroon et al. 1993). Using the solver module of Microsoft Excel, the magnitude of slope for best-fit line between the fluorescence-predicted and measured carbon fixation was driven to 1 by changing the I_k value (assuming $PQ = 1$, $FII = 0.5$). This "required I_k " was 44–58% lower than the carbon-based I_k value used to predict carbon fixation for data collected on 29 September and 1 October 1993, respectively.

The degree to which fluorescence-predicted photosynthetic rates predicted the Q_{UVA} and Q_{UVB} inhibition for measured ^{14}C uptake during the experiment hours was assessed (Fig. 11). The percentage of inhibition due to Q_{UVA} and Q_{UVB} is calculated relative to the Q_{PAR} treatment, and the discrepancy was calculated as the difference between the fluorescence-predicted and measured carbon fixation (Fig. 11). Therefore, a positive value indicates the percentage that carbon inhibition had been overestimated by fluorescence, and negative values represent underestimated inhibition. Fluorescence was

FIG. 11. The discrepancy in UV-inhibition rates between fluorescence-predicted and measured carbon uptake over the daylight hours on 1 October 1993. The relative inhibition due to Q_{UVA} and Q_{UVB} was calculated relative to the Q_{PAR} spectral treatment.

least accurate in predicting the impact of Q_{UVA} during the morning hours, as the inhibition of carbon uptake was underestimated by 42% at 0800; however, for the rest of the day, fluorescence estimates were within 25% of the measured inhibition. Again it should be emphasized that no statistically significant differences could be resolved for the Q_{PAR} and the $Q_{PAR} + Q_{UVA}$ treatments for either the fluorescence-predicted or measured carbon fixation. In contrast to the Q_{UVA} inhibition, fluorescence estimates of the Q_{UVB} inhibition were most accurate in the morning hours (Fig. 11). Fluorescence measurements overestimated the inhibition of ^{14}C uptake by an average of 16%. During the afternoon, fluorescence overestimated the Q_{UVB} inhibition of carbon fixation by as much as 35%. Excluding the afternoon data (1400 and 1600), fluorescence data on average estimated the carbon inhibition to within 8% of the measured Q_{UVB} inhibition. Overestimated Q_{UVB} inhibition could not be related to the visible light quenching of fluorescence that has been frequently documented to occur during the afternoon in field populations (Kiefer 1973) as the data had been normalized to the Q_{PAR} treatment.

DISCUSSION

Predicting the consequences of enhanced Q_{UVB} radiation on photosynthetic rates requires a mechanistic understanding of the damage and repair processes occurring within a cell. Identification of the Q_{UVB} target sites within the phytoplankton and their sensitivity to incoming radiation under a variety of natural conditions should allow mathematical parameterizations of the UV-induced damage and repair rate processes. In particular, knowledge of UV target sites may allow for an estimation of the upper and lower limits for biological weighting functions quantifying the UV sensitivity of photosynthesis. With this long-term goal in mind, one objective of Icecolors 1993 was to elucidate the major target sites

for Q_{UVB} inhibition for photosynthesis in field populations.

UV radiation and the photosynthetic light reactions. It has been documented in laboratory studies that the light reactions are adversely impacted by Q_{UVB} . Exposure to Q_{UVB} promotes damage to intrinsic membrane proteins and electron carriers between PSII and PSI (Greenberg et al. 1989, Melis et al. 1992, Jansen et al. 1993). Most laboratory work on the UV effects on photosynthesis has been conducted on isolated chloroplasts exposed to artificial light, which makes extrapolation to field populations problematic (Prézelin et al. 1994a). Isolated chloroplasts also do not have cellular repair capabilities, and thus inhibition effects will be larger than might be expected for natural communities.

This study and a companion study (Kroon, unpubl.) clearly demonstrated the impact Q_{UVB} on PSII activity. On the same ice algal community, Kroon (unpubl.) used *in vivo* fluorescence induction and decay transients to characterize the location Q_{UVB} induced damage on the light reactions of photosynthesis. Fluorescence induction and decay transients can be used to characterize both the light-harvesting and electron transport capabilities of PSII (Owens 1986, Cao and Govindjee 1990). The magnitude of ϕ_{Ile}^o is related to the efficiency of energy transfer from the accessory pigments to the P680 reaction center and the efficiency with which an electron is passed from P680 to the primary electron acceptor Q_A . While there was clear Q_{UVB} inhibition in ϕ_{Ile}^o , there were no detectable UV effects in the absolute absorption cross-section of PSII (Kroon, unpubl.). Apparently there was no damage in the light-harvesting complexes serving PSII or in the P680 reaction center. The inhibition of ϕ_{Ile}^o must have occurred in the electron transport processes beyond the P680 reaction center up to the Q_A molecule. Quinones have absorption maxima in the Q_{UVB} spectral bands (Jones and Kok 1966), and ϕ_{Ile}^o values are strongly dependent on the amount of reducible Q_A in thylakoid preparations (Melis et al. 1992). The same study showed that the fraction of PSII reaction centers capable of fast electron transfer from Q_A to Q_B were always lowest for cells exposed to Q_{UVB} radiation. Such changes have been hypothesized to reflect alterations in the D1- Q_B binding characteristics. Fast electron transfer is related to bound Q_B while slow electron transfer is related to the Q_B that must migrate into the D1 protein prior to electron transfer (Cao and Govindjee 1990). Overall, our findings support the hypothesis that Q_{UVB} radiation specifically hits several targets on the electron transport side of the PSII reaction center, thereby lowering the output of the photosynthetic light reactions (Greenberg et al. 1989, Melis et al. 1992, Jansen et al. 1993). It should be noted that electron transport rates between Q_A and Q_B were diminished by Q_{UVB} , and this effect was not included in our fluorescence-based model. If incorporated, the flu-

orescence-based carbon fixation rates for the Q_{UVB} treatments would be even lower than predicted by the quantum yield of PSII activity alone. This mechanism would not account for the overestimated fluorescence production estimates for the treatments that were not exposed to Q_{UVB} .

UV radiation and the photosynthetic dark reactions. While our study suggests there is dramatic Q_{UVB} inhibition at PSII, other studies have suggested that much of the UV inhibition is attributable to biochemical processes beyond PSII. The impact of Q_{UVB} radiation on the dark reactions has been related primarily to the degradation of RUBISCO in higher plants (Strid et al. 1990). More relevant to the present study, a major study has documented the impact of Q_{UVB} on the dark reactions of photosynthesis on Antarctic diatoms (Neale et al. 1993). Exposure to light under the ozone hole induced a 20% drop in the RUBISCO:chl *a* ratio in the algae, coincident with a 25% drop in P_{max} . Ideally, what remains to be determined is whether the drop in RUBISCO proteins reflected a lowering of RUBISCO activity, which directly impacts light-saturated rates of photosynthesis, or the protein pool of RUBISCO was being tapped to resupply the damaged PSII proteins. The algal cells were light-saturated for major portions of the day when photosynthetic rates were limited by RUBISCO activity (Orellana and Perry 1992). If RUBISCO was a major Q_{UVB} target, the relative inhibition of carbon fixation should be larger than measured for PSII activity alone, which is in contrast to our findings that PSII activity showed a larger Q_{UVB} inhibition than carbon fixation (Fig. 8). Therefore, we hypothesize that Q_{UVB} inhibition of the carboxylation processes was secondary to UV impact on the photosynthetic light reactions on the time scale of this experiment. It is possible that the relative inhibition and associated repair rates for PSII and RUBISCO may operate on different time scales, as the Q_{UVB} inhibition of RUBISCO occurred after several days of UV exposure (Neale et al. 1993). Because the UV and non-UV treatments overestimated carbon fixation, the Q_{UVB} inhibition of RUBISCO could not account for the overestimates in the fluorescence-based estimates of carbon fixation. A more likely explanation is related to the assumed magnitudes of PQ, FII, and I_k .

While fluorescence-based photosynthetic estimates show great promise (Falkowski and Kolber 1993, Kolber and Falkowski 1993), finding reliable proxy measurements for photosynthetic dark reactions remains a challenge. Variability in FII appears to be relatively small (Kroon et al. 1993, Kroon 1994). Therefore, the error in assuming a constant value is minimal (Fig. 10). Values of I_k appear to be predictable. Local robust empirical relationships can be derived for water masses characterized by diverse phytoplankton communities (Schofield et al. 1993), but these empirical determinations still need to be validated in diverse oceanic regions. Also, fluores-

cence techniques can be used to predict I_k for oxygen evolution within 10% (Kroon et al. 1993). The use of I_k appeared to be effective in predicting the operational quantum yield from the maximum quantum yield for stable charge separations at PSII. Therefore, the development of I_k -based fluorescence models of primary production is desirable, as field studies have shown that I_k -dependent models are more accurate than the $P_{\max}$ -dependent bio-optical models (Smith et al. 1989). The remaining obstacle in utilizing fluorescence-based predictions of I_k is understanding differences between oxygen and carbon-based values.

Reconciling the magnitude of the fluorescence-based estimates with the measured carbon fixation will require a better understanding of the environmental variability in the photosynthetic quotient. Values of PQ are sensitive to the physiological state of the algae, largely due to shifts in the types of biochemical end products of the photosynthetic energy conversion (Laws 1991). The biochemical end products are influenced by both the light and nutrient history of the algae (Myers 1980, Falkowski et al. 1985). Until more information is collected on the dynamic nature of PQ for natural populations, it will be difficult to parameterize, and this will ultimately limit the utility of fluorescence-based techniques for quantitatively predicting carbon fixation.

Time scales of photoinhibition and repair over a diurnal light cycle. Consistent with other Antarctic studies (Prézelin et al. 1994b), Q_{UVB} inhibition of photosynthesis varied with time of day. It was shown in those earlier studies that the quantum requirement for carbon loss was much lower at the ends of the day than around solar noon. While UV damage to the photosynthetic light reactions was clearly evident, the degree to which PSII and carbon uptake were coupled appeared to vary over the course of a day. The UV damage to PSII activity occurred within the first few hours of solar illumination and remained relatively constant throughout the entire day (Kroon, unpubl., Fig. 9a); in contrast, the incorporation of carbon was inhibited in early morning hours, and the relative inhibition decreased during the early afternoon. The presence of carbon incorporation pathways such as CO_2 -concentrating mechanisms (Raven and Johnston 1991) and/or β -carboxylation processes (Mortrain-Bertrand 1988) may account for some of the differences between fluorescence-predicted and measured carbon fixation. It has been demonstrated that Antarctic phytoplankton are capable of relatively high rates of light-independent carbon fixation via the β -carboxylation processes (Mortrain-Bertrand 1988). If oxygen evolution rates mirrored PSII activity and carbon-uptake rates were relatively constant due to the presence of any carbon concentrating mechanisms, then PQ would decrease over the day for the cells exposed to Q_{UVB} . This would result in smaller carbon inhibition rates predicted by PSII activity (by ex-

perimental necessity, our model assumed a constant PQ value over the day). Presumably a greater understanding of the environmental regulation of PQ would clarify many of these differences and eventually allow fluorescence estimates to provide useful proxy measures for carbon fixation; however, until this is accomplished researchers should remain cautious in replacing carbon fixation measurements with fluorescence-based models.

The apparent lack of a cumulative dose-dependent relationship in both the fluorescence-predicted and measured carbon fixation rates strongly suggests that cellular repair processes were significant in these ice algal populations (Lesser et al. 1994). These findings are consistent with laboratory studies that suggest that Q_{UVB} inhibition of primary production is a reflection of the combined kinetics of damage and repair processes occurring within a cell (Cullen and Lesser 1991, Lesser et al. 1994). Hence, a mechanistic understanding of the impact of elevated Q_{UVB} for *in situ* phytoplankton communities requires knowledge of the time scales of mixing and the variable rate constants for UV damage and repair (Prézelin et al. 1994b). Furthermore, comparison of data collected on different time scales will be difficult to reconcile, and intercalibration will require information on the diurnal kinetics of the parameter of interest. Measuring the daytime kinetics for *in situ* communities is difficult using traditional productivity-buoy deployments and generally requires deckboard incubations. Nonintrusive fluorescence measurements can be modified for buoy deployments and has the potential for providing *in situ* diurnal data. Given the strong Q_{UVB} inhibition of PSII, fluorescence will be useful for studying the impact of the Antarctic ozone hole on larger spatial and temporal scales than has been possible using traditional techniques.

In conclusion, Q_{UVB} damages PSII electron transport in natural field populations, and the damage most likely occurs at Q_A . Similarly, Q_{UVB} inhibited carbon fixation during the day, and a simple fluorescence-based model of PSII activity was linearly correlated with measured carbon fixation. The coherence between the Q_{UVB} inhibition of the fluorescence-predicted and measured carbon uptake was within 8% during the morning hours; however, fluorescence measurements overestimated the relative inhibition of Q_{UVB} in the afternoon. Therefore, while fluorescence-based photosynthetic estimates show great promise in elucidating Q_{UVB} damage, more information on the environmental regulation of PQ is required before fluorescence data can be reliably applied to model the ecosystem impact of decreasing ozone levels on phytoplankton carbon fixation in the Southern Ocean.

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PHOTOSYNTHETIC CHARACTERISTICS OF THE COCCOLITHOPHORID *EMILIANA HUXLEYI* (PRYMNESIOPHYCEAE) EXPOSED TO ELEVATED CONCENTRATIONS OF DISSOLVED INORGANIC CARBON¹

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ABSTRACT

Light-saturated photosynthesis ($P_{\max}$) of *Emiliana huxleyi* (Lohmann) Hay et Mohler is known to be carbon-limited at natural concentrations of dissolved inorganic carbon (DIC). In the present study, light-limited and light-saturated photosynthetic rates of *E. huxleyi* were studied at three concentrations of DIC (2.4, 7.4, and 12.4 mM) for high-calcite ($C_{\text{in}}/C_{\text{tot}} = 0.48$) and low-calcite ($C_{\text{in}}/C_{\text{tot}} = 0.08$) cells of the same strain. The photosynthetic efficiency (α) and the maximum quantum yield ($\Phi_{\max}$) increased by more than a factor of 2 from the lowest to the highest DIC level. $P_{\max}$, α , and $\Phi_{\max}$ were always higher

for the high-calcite than for the low-calcite cells at identical DIC levels. This may indicate that the calcification process acts as an extra supplier of CO₂ for photosynthesis making the CO₂ shortage at natural DIC levels a little smaller for high-calcite than for low-calcite *E. huxleyi*. A dependency of $\Phi_{\max}$ on DIC has not previously been shown for marine phytoplankton. $\Phi_{\max}$ is a key parameter in recent biooptical models of phytoplankton productivity, and the results from the present study are therefore important for modeling the productivity of *E. huxleyi*.

Key index words: calcification; carbon-limitation; CO₂; Coccolithophoridae; *Emiliana huxleyi*; photosynthetic rates; phytoplankton; Prymnesiophyceae; quantum yield; respiration

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