Solar ultraviolet-B radiation and aquatic primary production: damage, protection, and recovery

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The continuing degradation of the Earth's ozone layer by atmospheric pollutants has generated concern about the impact of increased solar ultraviolet-B radiation (UV-B) on aquatic ecosystems. UV-B is a small (less than 1% of total energy) but highly active component of the solar spectrum that can penetrate to biologically significant depths in lakes and oceans. It has the potential to cause wide-ranging effects, including mutagenesis, chronic depression of key physiological processes, and acute physiological stress that may result in death. There are major uncertainties at present about the appropriate time scales and bioassay protocols for assessing such effects. Algal and cyanobacterial cells have four lines of defence against the toxic effects of UV-B. Some species avoid UV exposure by their choice of habitat or by migration strategies. Many species produce sunscreening pigments that filter out UV wavelengths; mycosporine-like amino acids are an especially important and ubiquitous class of such compounds. Most cells have a variety of defences against the toxic end products of UV radiation, such as radical scavenging by carotenoid pigments and superoxide dismutase. Finally, most cells have at least some ability to identify and repair the UV damage of DNA and other biomolecules. There is a large interspecific variability in the extent of each of these defence strategies. Continuing ozone depletion is not likely to cause an abrupt collapse of photosynthetic production, but may result in subtle, community-level responses that could ultimately impact on higher trophic levels.

Key words: Arctic, Antarctic, photosynthesis, UV radiation, UV-B, ozone, atmospheric pollutants.

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La dégradation continue de la couche d'ozone de la terre par des polluants atmosphériques a engendré une préoccupation au sujet de l'impact d'une augmentation de la radiation solaire ultraviolette B (UV-B) sur les écosystèmes aquatiques. Les UV-B sont un constituant minime (moins de 1% de l'énergie totale), mais hautement actif du spectre solaire qui peut pénétrer à des profondeurs significatives dans les lacs et les océans. Ils ont la capacité d'entrainer des effets très divers incluant la mutagénèse, le dérèglement chronique de processus physiologiques fondamentaux, ainsi qu'un stress physiologique aigu qui peut conduire à la mort. Il y a présentement de grandes incertitudes quant aux échelles de temps appropriées et aux protocoles expérimentaux pour évaluer de tels effets. Les cellules des algues et des cyanophycées montrent quatre lignes de défense contre les effets toxiques des radiations UV-B. Certaines espèces évitent l'exposition aux radiations UV en choisissant leur habitat ou en adoptant des stratégies de migration. Plusieurs espèces produisent des pigments qui agissent comme filtre en éliminant les radiations UV; des acides aminés ressemblant à la mycosporine constituent une classe particulièrement importante et ubiquiste de tels composés. La plupart des cellules ont une gamme de défenses contre les sous-produits toxiques de l'activité des UV, tel que l'élimination des radicaux par les pigments caroténoïdes et la dismutase superoxyde. Enfin, la plupart des cellules possèdent au moins une certaine capacité à identifier et à réparer les dommages subis par l'ADN et autres bio-molécules. Il existe une importante variabilité interspécifique dans l'étendue de chacune de ces stratégies de défense. La diminution continuelle de l'ozone ne conduira vraisemblablement pas à une baisse drastique de la production photosynthétique, mais pourrait se traduire par des réactions subtiles au niveau des communautés, suivies de conséquences ultérieures aux niveaux trophiques supérieurs.

Mots clés : Arctique, Antarctique, photosynthèse, radiation UV, UV-B, ozone, polluants atmosphériques.

[Traduit par la rédaction]

Introduction

There is mounting evidence that the solar flux of ultraviolet-B radiation (UV-B) has begun to rise at certain locations over the surface of the Earth (Crutzen 1992). This increase has been attributed to the continuing destruction of the ozone layer by atmospheric pollutants, in particular chlorofluorocarbons (CFCs). Although these pollutants are mainly released from human activities in the Northern Hemisphere, the effects have been most clearly identified in the Antarctic region, where a unique combination of extreme cold and stratospheric circulation (the polar vortex) results in conditions that are favourable for the CFC–ozone reactions (Anderson *et al.* 1991). A spring "ozone hole" containing ozone concentrations depleted to 60% or less now forms across Antarctica each year over a region that is slightly larger than Canada (e.g., Smith *et al.* 1992). Reliable measurements of UV radiation did not begin in Antarctica until 1988, but the observations to date show a close, inverse relationship between stratospheric ozone concentration and ground-level UV-B. With the annual breakup of the Antarctic ozone hole each year, ozone-depleted air spreads out over the Southern Hemisphere; this has resulted in record-low concentrations of stratospheric ozone over temperate regions such as southern Australia and New Zealand in early summer (Toon and Turco 1991).

Ozone depletion has been more recently reported in the north polar region (Hofmann and Deshler 1991). Model calculations using atmospheric ozone data collected over the period 1979–
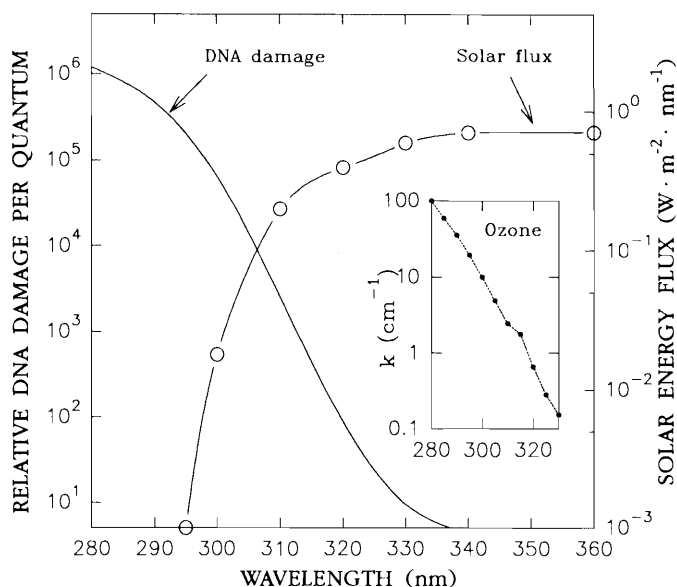
FIG. 1. UV-B is a small but highly reactive component of solar radiation that reaches the surface of the planet. The absorption of UV by stratospheric ozone rises exponentially with decreasing wavelength (insert, derived from Caldwell et al. 1980). As a result the ground-level radiation flux drops by about three orders of magnitude between 330 and 295 nm (open circles, from solar noon data for the mid-temperate zone given in Frederick and Snell 1988). However, over the same wavelength range the sensitivity of DNA to photochemical damage rises by five orders of magnitude (solid line with no symbols, derived from Caldwell 1979).

1989 indicate that although the largest absolute rise in solar UV-B flux has occurred over Antarctica in September–November, substantial increases have also occurred in the Northern Hemisphere during this decade, as far south as 30°N during January–March (Madronich 1992). The increases in atmospheric carbon dioxide anticipated over the next 50 years are expected to amplify this effect, perhaps leading to an Arctic ozone hole as severe as that over Antarctica (Austin et al. 1992). These carbon dioxide increases are expected to cool the lower stratosphere, in turn leading to the increased formation of polar stratospheric ice clouds that catalyse the CFC–ozone reactions.

It takes several years for CFCs to be dispersed throughout the lower atmosphere, but several decades for the transfer across the tropopause into the stratosphere. Ozone destruction is therefore believed likely to intensify and to spread to a broader range of latitudes throughout the next century despite international efforts to reduce the usage and emission of CFCs and related compounds (Toon and Turco 1991).

The environmental impact of this predicted rise in solar UV-B has recently become a source of much concern and speculation in the public as well as scientific media, encouraged by headlines such as "Vanishing ozone—the danger moves closer to home" (Time Magazine, New York, 17 Feb. 1992) and "Prospects for an Arctic ozone hole" (Nature (London), 19 Nov. 1992). UV-B is a small but highly reactive component of the total solar radiation flux (Fig. 1). It is known to have wide-ranging biological effects that can include mutagenesis, chronic depression of key physiological processes such as photosynthesis, and acute physiological stress that may ultimately result in death. All plant, animal, and microbial groups appear to be susceptible to UV-B, but to a highly variable extent that depends on the individual species and its environment.

This variability in response has resulted in a great deal of controversy and confusion about the implications of increasing UV-B for specific ecosystems. For example, the predicted impact of the spring ozone hole on primary productivity and food-chain processes in the Antarctic Ocean has ranged from negligible to catastrophic (Roberts 1989). The stratified surface waters associated with the marginal ice zone of this region were initially identified to be an environment of extreme UV-B sensitivity (Smith 1989). However, a UV-focused oceanographic research program conducted during a cruise in spring 1990 in the marginal ice zone concluded that the ozone hole resulted in a minimum of 6–12% reduction in primary production, which translated into an overall 4% decrease for the Antarctic Ocean during the ice-free season (Smith et al. 1992). Similarly, measurements of the primary production by Antarctic sea ice communities showed that the UV-B intensities likely to be experienced during the spring ozone hole could reduce photosynthesis by about 5% (Ryan 1992). These values seem low relative to the magnitude of spatial and interannual variability in primary production rates and do not lend credence to the predictions of imminent food chain collapse in this part of the world ocean.

The aim of this article is to try to reconcile some of the disparate and sometimes contradictory views about UV-B penetration and damage to the base of the food chain in marine and freshwater ecosystems. We first review the physical characteristics of underwater UV radiation, its photochemical effects (both positive and negative), and the known sites, mechanisms, and biological response curves for UV injury. We then examine the broad range of avoidance, protection, and recovery strategies that allow many photosynthetic as well as other organisms to survive in environments exposed to solar UV-B and which may ultimately dictate the ecosystem-level response to any future increases in the ambient UV field.

The underwater UV-radiation field

UV radiation is traditionally divided into three wavebands: from 320 to 400 nm are referred to as UV-A; from 280 to 320 nm, referred to as UV-B; and from 190 to 280 nm, referred to as UV-C. The UV waveband spans the portion of the electromagnetic spectrum between X-ray radiation and the visible-light waveband; the latter extends from about 400 to 700 nm, which corresponds to the photosynthetically available radiation (PAR) waveband. UV is thus of shorter wavelength, of higher frequency, and is more energetic than PAR.

About one-half of the solar flux at the Earth's surface is in the PAR waveband. UV-A is strongly attenuated by the atmosphere but is not absorbed by ozone; at ground level on a sunny day in the mid-temperate zone it is equivalent to about 4% of the PAR energy input. UV-B is strongly absorbed by the upper atmosphere ozone layer, and on a sunny day its energy content is equivalent to about 20% of the UV-A and 0.8% of the PAR. UV-C is absorbed by molecular oxygen, which in the process is photochemically converted to ozone, thereby forming the upper atmosphere ozone layer. The attenuation of UV-C by ozone is orders of magnitude higher than the attenuation by oxygen, and negligible UV of wavelengths less than about 290 nm reaches the Earth's surface. The extremely high efficiency of this absorption is underscored by considering the global magnitude of ozone: in the rarefied upper atmosphere the layer with the highest mixing ratio of ozone extends over the altitude range from 12 to 50 km above the Earth (Anderson et al. 1991); at standard temperature and pressure this quantity

of ozone would compress to a layer only 3 mm thick (Caldwell 1979).

The incident flux and spectral distribution of solar UV are dependent on atmospheric clarity and cloud cover (e.g., Bachelet *et al.* 1991), as well as latitude and altitude. For example, there is about a 14–18% increase in UV-B with every 1000-m increase in altitude. The absorption curve for UV radiation by ozone rises exponentially with decreasing wavelength (Fig. 1), and thus the depletion of stratospheric ozone has a major influence not only on the absolute intensity of UV-B radiation, but also on its spectral composition and on the ratio of UV-B to UV-A or to PAR. During the Icecolors 1990 cruise in the Antarctic Ocean, the near-surface ratio of UV-B to PAR + UV-B + UV-A varied by more than a factor of 2 and was attributed to a similar magnitude of variation in the upper atmosphere ozone concentrations (Smith *et al.* 1992). Such changes are of biological importance because it appears ·that certain damage–repair effects are responsive to wavelength ratios in the incident-light field (e.g., Hiroshawa 1984).

UV-B radiation is maximal in the tropics and, in the absence of ozone hole effects, drops substantially at higher latitudes (see Frederick *et al.* 1989). This is the result of two factors: the total stratospheric ozone column increases by 50% from the equator to the poles during the periods of maximum radiation, and the greater solar angles from the zenith at high latitudes result in a longer radiation path length through the atmosphere. In combination these two factors cause not only a large decrease in the ambient UV-B at the poles, but also a truncation of the shorter, biologically most active wavelengths. For example, a total (global plus diffuse) radiation value of $4.5~mW \cdot m^{-2} \cdot nm^{-1}$ was recorded for 302-nm light at a coastal lowland Alaska site at 70°N; the same measurement for a comparable solar angle at a tropical (11°S), alpine (3050 m) site was $17.9~mW \cdot m^{-2} \cdot nm^{-1}$ (Caldwell *et al.* 1980).Ozone depletion over the poles is considered of special ecological concern because components of the biota may have evolved under UV-B conditions that are substantially less, in both intensity and spectral range, than those experienced at lower latitudes.

Pure water is relatively transparent to UV in comparison with longer wavelength visible light and infrared radiation (Fig. 2). However, the penetration of UV wavelengths into natural waters is highly dependent on the concentration of dissolved organic compounds (especially humic materials, the so-called gelbstoff or "yellow substances") and of particulate material (seston). In clear, ultraoligotrophic lake and ocean environments (Fig. 2), the depth of 1% of surface radiation is 70 m for 550-nm light (midpoint of the PAR spectrum), 132 m for 360-nm light (UV-A), and 30 m for 300-nm light (UV-B). In many lakes and ponds (e.g., in the Arctic tundra, Fig. 2), dissolved humic materials dominate the underwater absorption of light and are likely to cause a strong attenuation of UV-B. Lakes on the Canadian Shield appear to be becoming clearer as a result of reduced concentrations of these dissolved organic substances. This effect has been attributed to the changing water balance of the lakes and their catchments as a result of global warming (Schindler *et al.* 1990), and it is likely to result in a much deeper penetration of UV wavelengths. In general, however, there is a paucity of spectral data in the UV range for freshwater as well as marine habitats. The current generation of commercial radiometers can now measure UV-B to depths of several tens of metres in clear oceanic waters.

Prolonged periods of ice cover are a feature of many freshwater habitats in the temperate and polar zones, and sea ice extends over vast areas of the polar oceans for at least 6 months
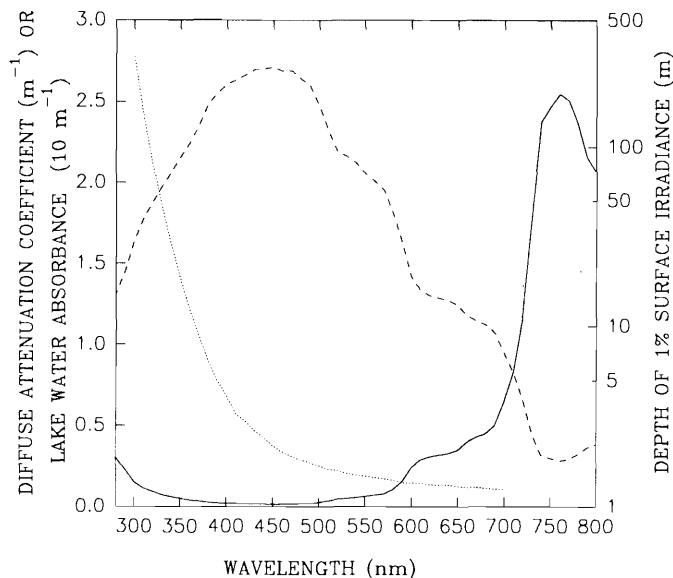

FIG. 2. UV radiation penetrates deeply in clear waters. The solid line is the diffuse attenuation coefficient derived from measurements in ultraoligotrophic (highly transparent) lakes and oceans (Smith and Baker 1981). The broken line shows the same information expressed in terms of the depth where 1% of the surface irradiance is attained for each wavelength. In many lake and inshore marine environments the penetration of UV-B will be substantially reduced by dissolved humic substances. The dotted line is an absorption curve for a surface, unfiltered water sample from Toolik Lake, a humic-stained lake in the tundra zone, northern Alaska (sampled 19 June 1992).

of the year (e.g., Vincent 1988). Spectral measurements of light penetration indicate that the algal cells growing within or immediately below the ice may not be protected from UV-B exposure. Antarctic sea ice, for example, may be especially transparent to UV-B during spring when the ozone depletion is most severe (Trodahl and Buckley 1989), a period that also coincides with the early growth phase of the bottom-ice algal community. However, snow has a very high albedo, and thus any snow cover over the sea ice will substantially lessen the transfer of radiation at all wavelengths, including UV-B (Karentz 1991).

Ecological impacts of UV-B

Solar UV-B has a broad range of direct and also indirect effects on the aquatic biota. Most analyses of such effects in the ocean suggest that continued ozone depletion will result in a decline in primary production rates (Smith 1989; Cullen and Lesser 1991; Hader and Worrest 1991) and a change in phytoplankton community composition through the differential sensitivity of individual species (Calkins and Thordardottir 1980; Worrest 1983; Smith *et al.* 1992; Helbling *et al.* 1992). Many aquatic herbivores, including insects, corals, and zooplankton (e.g., Karanas *et al.* 1981; Bidigare 1989), are known to be sensitive to UV-B, and changes in grazing pressure may also contribute to the long-term community-level responses in marine and freshwater environments.

Photochemical damage

The direct biological effects of UV-B result from the absorption of specific wavelengths by biomolecules and the resultant dissipation of that energy by photochemical reactions (Fig. 1). The clearest example of such effects is the response by nucleic acids; both DNA and RNA react to UV-B exposure by the

formation of base lesions. The most common DNA lesion induced by UV radiation is the formation of dimeric photo-products between adjacent pyrimidines, such as (5-6) cyclo-butyl pyrimidine dimers and pyrimidine (6-4) pyrimidone photoproducts (Karentz et al. 1991a). The (5-6) cyclobutyl dimers are the most abundant and probably most cytotoxic lesions, but the (6-4) photoproducts may have more serious, potentially lethal, mutagenic effects (Franklin and Haseltine 1986). The (6-4) photoproducts are formed at a rate of about 10–15% of that for the pyrimidine dimer lesions in mammalian cells (Haseltine 1983) and at more variable rates for other spe-cies (Karentz et al. 1991a); but unlike the (5-6) dimers, the (6-4) lesions cannot be excised and repaired by enzymatic pho-toreactivation (Brash et al. 1985). The stable, unrepaired (6-4) photoproducts thus remain within the DNA, where they interfere with RNA transcription and DNA replication, ulti-mately leading to mutation (Asata 1972) or death.

UV radiation is also known to have specific effects on the primary light reactions as well as the dark reactions of photo-synthesis. UV-B causes an inactivation of photosystem II reac-tion centres (Noorudeen and Kulandaivelu 1982; Iwanzik et al. 1983), whereas photosystem I appears to be much less sensi-tive (Van et al. 1977; Iwanzik et al. 1983, Strid et al. 1990). The primary mechanism of photosystem II inactivation is still uncertain, but may involve structural changes in the polypep-tide matrix at the catalytic site of water oxidation (Renger et al. 1989). UV-B can also inhibit photosynthetic enzyme activities (e.g., Rubisco, ATP-synthase) and the biosynthesis of certain photosynthetic pigments, including chlorophyll a (e.g., Strid et al. 1990). In phytoplankton the UV-B inhibition of photo-synthesis has been shown to be a function of UV intensity and duration, but it is also influenced by endogenous factors such as the nitrogen status of the cells (Döhler 1989; Cullen and Lesser 1991).

UV-B absorption has a range of more general effects on cellular proteins. Microalgae exposed to UV-B have shown a linear decrease in protein content with increasing UV dose (Döhler 1984), an increase in the cellular free amino acid pool, and changes in the uptake rate for inorganic nitrogen (Döhler 1985; Döhler et al. 1985, 1987). It is not known, however, to what extent these effects result from a direct impact on enzyme activity or whether enzyme synthesis is affected via RNA dam-age (Döhler 1989). UV-induced protein damage can influence the ion permeability of cellular membranes and processes such as nitrogen fixation by cyanobacteria via inactivation of the nitrogenase enzyme (Häder and Worrest 1991). UV-B is also known to damage pigment proteins; for example, the proteins that carry the photoreceptor (eyespot) chromophores of the phytoflagellate Euglena (Häder and Worrest 1991), and the phycobiliproteins of cyanobacteria and certain phytoflagellates (e.g., Fischer and Häder 1992).

The effects of UV-B on photosystem II activity and protein synthesis may weaken the ability of cells to cope with addi-tional environmental stress. For example, the repair of PAR-induced photoinhibition requires substantial rates of protein synthesis to rebuild the damaged photosynthetic reaction centres (see Vincent 1990). The xanthophyll cycle, a series of reactions that are thought to protect algal and higher plant cells against bright light, is also inhibited by UV-B radiation, prob-ably via the impairment of the de-epoxidase enzyme and of plastoquinone reduction by photosystem II (Pfündel et al. 1992). Thus the exposure of cells to UV-B may reduce their capacity for protection as well as recovery from photoinhibi-tion by bright light in the PAR waveband.

Strong UV radiation can photo-oxidize and thereby bleach all types of photosynthetic pigment (Häder and Häder 1991). At lower dosages, UV-B sometimes causes a depression of cel-lular chlorophyll a, chlorophyll c, and carotenoids via reduced rates of biosynthesis. On the other hand, carotenoids have been implicated in UV and bright light photoprotection of surface blooms of freshwater cyanobacteria (Paerl et al. 1983). An elevated carotenoid content has been reported in a UV-resistant strain of cyanobacteria (Buckley and Houghton 1976). Benthic communities of cyanobacteria in exposed habitats are often rich in specific cellular carotenoids such as canthaxanthin and myxoxanthophyll (e.g., Palmisano et al. 1989a, 1989b; Que-sada and Vincent 1993).

Primary production responses

Studies on the effects of UV radiation on algal growth and photosynthesis date back to the 1950s. These early investiga-tions examined the influence of germicidal lamps with a peak output at 254 nm, well below the lower wavelength limit of solar UV at the Earth's surface. These studies established a difference in sensitivity between algal species (Holt et al. 1951) and ascertained that radiocarbon uptake (as a measure of photosynthesis) was most sensitive to UV-C radiation for algal cells in their late exponential stage of growth (McLeod and McLachlan 1959). The latter effect needs to be carefully re-examined under ambient levels of UV-B and UV-A.

Emphasis on the precise measurement of primary production in the late 1970s and early 1980s led to studies on the impact of the use of UV-filtering glass bottles for measuring radio-carbon uptake in the sea and lakes (Lorenzen 1979; Hobson and Hartley 1983; Maske 1984). These results indicated that with the use of standard glassware, primary production would be overestimated by a factor as high as 1.5 on sunny days (Lorenzen 1979). This factor, however, differed greatly between studies. Spring populations of phytoplankton were found to be highly sensitive to UV-B, whereas summer pop-ulations showed no differences between UV-filtering and non-UV-filtering bottles (Hobson and Hartley 1983). Six phyto-plankton species belonging to various algal groups differed greatly in their magnitude of growth inhibition by near-surface intensities of UV (Jokiel and York 1984). This study showed that the effects were mostly due to UV, not PAR, and that long-term exposure to either UV-A or UV-B could be damaging. Similar species-specific differences in the photosynthetic response to UV-B were noted for six marine diatom species (Calkins and Thordardottir 1980).

Large differences have been observed in the response of phytoplankton from different physical environments to changes in incident UV-B. Such differences may be a function of the species composition of the community as well as their previous exposure to light, and their photoadaptive characteristics. For example, phytoplankton photosynthesis in samples from the Antarctic Ocean was enhanced by 82% when the UV-B radia-tion was selectively screened out; samples from a more strat-ified environment (mixing to 35 m), and also incubated under surface conditions of bright sunlight, showed a 30% enhance-ment. Similar experiments with phytoplankton samples from tropical waters showed a very small enhancement for surface communities (12%), with a greater enhancement (27%) for communities from well below the pycnocline. In all of these experiments the additional screening of the UV-A or of the high ambient PAR resulted in a much greater enhancement of photosynthesis (Helbling et al. 1992), indicating that UV-B was a contributing, but not dominant cause of photoinhibition.

The formation of temporary thermoclines towards the top of the water column is a common feature of many lake and marine environments, and such conditions prolong the residence time of phytoplankton near the surface. These short-lived stratification events usually coincide with periods of highest incident solar radiation, resulting in a combination of factors that is likely to maximize the UV-B dosage experienced by phytoplankton in the upper euphotic zone. In a high-altitude tropical lake, phytoplankton cells trapped near the surface during diurnal stratification were strongly photoinhibited in terms of their chlorophyll a fluorescence response (a measure of cellular photochemical capacity) induced by 3-(3,4-dichlorophenyl)-1,1-dimethylurea (DMCU) and their radiocarbon incorporation rates. The exposure of these communities to UV accelerated the decline of photosynthesis and fluorescence, and depressed these cellular properties to a lower plateau than with bright PAR alone (Vincent et al. 1984). The same type of phenomenon has been studied in Lake Windermere, England, where it appears that the combination of high irradiances and temporary surface stratification not only results in photoinhibited near-surface production rates, but may also lead to accelerated sinking of diatom populations during the final stages of the spring maximum (Neale et al. 1991). The relative role of UV-B, UV-A, and bright PAR, however, is not yet known.

To what extent do these photosynthetic effects translate into an inhibition of growth? There is little concrete information, but the evidence to date suggests there may not be a close relationship between short-term photosynthetic responses and longer term growth. For example, although the samples of phytoplankton from the Antarctic Ocean (as described above) showed a highly significant photosynthetic response to UV-B screening in 6 to 10-h incubations, a 16-day incubation showed no significant differences between treatments in either growth rate or final yield (Helbling et al. 1992). Such growth experiments are extremely difficult to control and are prone to container effects and other artefacts of prolonged incubation. Nonetheless, there is a clear need for an improved understanding of the longer term growth and population responses by algae and cyanobacteria to raised UV-B levels. Further evidence of the inconsistency between UV experiments at different time scales comes from a study of freshwater periphyton growth in continuous-flow experimental flumes (Bothwell et al. 1993). During the first 2–3 weeks the log-phase growth rate of the diatom community was inhibited by 30–40% relative to treatments that were screened from solar UV radiation. However, by 5 weeks this trend was reversed and the diatom biomass was 2 to 4-fold higher in the UV-exposed communities. The authors suggest that this changing pattern of response may have been the result of UV effects on trophic interactions.

Indirect cellular effects

High-energy UV radiation has a variety of indirect effects on aquatic ecosystems. For example, certain pollutants are photochemically degraded by UV-B, thereby reducing the physiological stress to organisms in aquatic environments that receive toxic waste inputs. However, some organics are photochemically converted into more toxic forms. UV-B radiation will lessen the survival rates of pathogenic microbes such as viruses and fungi discharged via domestic wastes and may thus reduce their influence on the natural biota. Conversely, UV-B can induce viral replication within host cells. UV-toxicity responses by herbivores or by animals at higher trophic levels have the potential to cause changes in algal biomass and (or) primary production rates via the complex sequence of effects that propagate downwards through the food web (top down controls).

The photochemical interaction between UV, humic materials, and iron may stimulate aquatic productivity. High molecular weight humic materials can be photoreduced by solar UV (e.g., Stewart and Wetzel 1981), and the resultant lower molecular weight carbon substrates may then fuel bacterial production and microbial food web processes. Photochemical reduction reactions between UV and organic or inorganic ferric complexes can release iron into the medium in the potentially more available ferrous form (O'Sullivan et al. 1991); such effects are of special interest because the biological availability of iron may be a controlling factor for phytoplankton production in parts of the ocean. UV-induced photoreduction of ferric–humic complexes may also increase the biological availability of phosphorus through the liberation of orthophosphate that is usually adsorbed to such complexes (Francko and Heath 1982). The spectrum of beneficial roles played by UV-B in the natural environment is still poorly understood, but the high energy content of this waveband implies that it may have a wide-ranging influence on many biogeochemical processes.

The interaction between UV-B, oxygen, and certain organic compounds can also result in the production of reactive oxidants that are highly toxic to many forms of aquatic life. UV absorbance by humic substances results in the production of hydrogen peroxide (Cooper et al. 1989). Hydroxyl radicals can also be generated photochemically in natural aquatic environments (Mopper and Zhou 1990). Such reactions also occur within the cell and can result in the further production of superoxide, hydroxyl radicals, hydrogen peroxide, and singlet-state oxygen. These toxic photochemical products have a broad range of destructive effects on cellular macromolecules (e.g., Asata 1972, Fridovich 1986). They may accumulate to especially high concentrations in certain types of environment, e.g., in lakes with shallow mixed layers, in thick-film periphytic communities, or under conditions of oxygen supersaturation. Concentrations of hydrogen peroxide up to several hundred micromoles per cubic metre have been recorded in stratified lake environments (Cooper et al. 1989).

Biological response functions

Three environmental factors influence the magnitude of the toxicity responses to UV-B: the intensity, the duration of exposure, and the spectral composition of the incident radiation. The last is especially important, in part because the most severe biological effects rise precipitously with decreasing wavelength below about 350 nm and a simple measure of total UV irradiance may be highly misleading (Fig. 1). For this reason the UV exposure is often expressed in terms of a biologically effective dosage (D), whereby the intensity at each UV wavelength ($E(\lambda)$) is multiplied by a weighting factor ($f(\lambda)$), and the resultant values are then summed:

$$D = \int_{280 \text{ nm}}^{400\text{nm}} E(\lambda) f(\lambda) \, d\lambda$$

This weighting factor is set to 1 at the λ of maximum biological effect (usually the shortest wavelength of interest) and then decreases with increasing wavelength according to some theoretical or measured response function; for example, the photochemical damage of DNA, as in Fig. 1.

In practice, biological response functions are difficult both to obtain and to interpret. They require a sophisticated level of instrumentation in which the UV dose is delivered at precise intensities and wavelengths. Furthermore, the phytoplankton
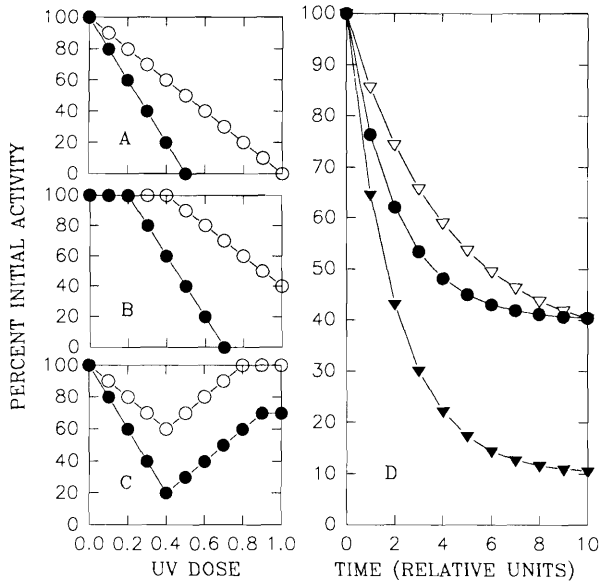
FIG. 3. Dose or dosage rate? UV-B response curves are typically expressed as a function of the cumulative UV radiation dose $(J \cdot m^{-2})$ or time; the latter is also equivalent to dose if the dosage rate, i.e., the UV intensity $(W \cdot m^{-2})$, is held constant. Potential responses include increasing inhibition with increasing dose (model A), inhibition beyond a threshold (model B), inhibition then recovery (model C), or inhibition to an asymptotic minimum (model D). Different dosage rates, however, may greatly modify the slope and shape of the dose–response curve (open symbols represent low UV intensity; closed symbols represent high UV intensity). The closed symbols in model D represent two potential responses to high UV intensity: more rapid decline to a minimum (circles) or a lowered minimum (triangles).

or periphytic community under test will respond to the changes in UV via a cascade of toxicity as well as recovery mechanisms that range in time scale from seconds to generation time. Each of these mechanisms is likely to respond nonlinearly to radiation dosage rate (i.e., intensity; see Cullen and Lesser 1991) and to duration of exposure (Fig. 3). The net spectral response is likely to reflect a complex balance between damage processes (most sensitive to shorter wavelengths) and repair processes (most sensitive to longer wavelengths).

The first biological response curves for phytoplankton photosynthesis have only recently been published and reveal an action spectrum that is similar to that observed for higher plant photosynthesis (Cullen et al. 1992). UV-A significantly depressed photosynthesis by a diatom and a dinoflagellate, but the effects of UV-B were more severe, with a sharp exponential gradient of increasing effect at decreasing wavelengths below 320 nm. This steep section of the response curve differed from that for inhibition of photosynthetic electron transport and was more like that for DNA; conversely, the continuation of the photoinhibition effect well into the UV-A region differed from the DNA curve as shown in Fig. 1. The latter observation is important because it reduces the predicted impact of ozone depletion on phytoplankton photosynthesis (Cullen et al. 1992).

UV-B protection and recovery strategies

Animals, plants, and especially microbes have evolved in environments exposed to solar UV (Caldwell 1979; Caldwell et al. 1989) and have developed a broad range of adaptive strategies to reduce the deleterious impacts of this waveband.

These strategies include the avoidance of brightly lit habitats, the production of UV-screening materials, and a variety of scavenging mechanisms that detoxify the highly reactive oxidants produced photochemically. Most organisms also show at least some ability to repair the damage caused by UV-B.

Avoidance

Many algal species are highly sensitive to UV-B exposure by comparison with other organisms. For example, the dosages of UV-C radiation (254 nm) required to kill the leaves of higher plants seem to be at least four orders of magnitude higher than those required to kill very resistant algae (Caldwell 1979). A comparison of DNA repair rates suggested that Antarctic marine diatoms irradiated with UV-B light are about four times more sensitive than human cells irradiated with UV-C (Karentz et al. 1991a).

In part this marked responsiveness to solar UV may reflect the predominantly dim-light regimes that characterize the natural underwater habitats of many, if not most, algal species. The marine and freshwater euphotic zone is essentially a shade environment, with an average radiation level at the midpoint of the PAR spectrum that amounts to only 22% of surface values. In clear oceanic waters this translates to 32% of surface UV-A (360 nm) and 9% of surface UV-B (300 nm). Cells that are mixed through the surface mixed layer will be intermittently exposed to toxic levels of UV-B, but their cumulative radiation dosages may remain low. Mixing below the euphotic zone is common in many aquatic environments and will further reduce the UV exposure.

Some species of algae and cyanobacteria have an ability to reduce their exposure to solar UV by vertical-migration strategies. There are many examples of vertical swimming, sinking, and floating behavior patterns whereby cells can avoid the surface zone during the hours of maximum irradiance each day. Such communities include dinoflagellate assemblages in the sea and in clear, alpine lakes (e.g., Tilzer 1973), pennate diatoms in estuarine sediments, oscillatorian (cyanobacteria) trichomes in microbial mats (Castenholz et al. 1991), and bloom-forming cyanobacteria that vary their sinking and floating rates by a combination of gas vacuoles and ballast (Reynolds et al. 1987). Of course these diurnal patterns of migration are likely to be primarily driven by other factors such as light and nutrient availability, or redox conditions, and the reduced UV exposure may only be of secondary benefit. No flagellated algal species has yet been found that exhibits positive or negative phototaxis solely in response to UV wavelengths (Häder and Worrest 1991).

It is possible that high UV dosages may impair some of these migration strategies (Ekelund 1990, 1991; Blakefield and Calkins 1992), thereby prolonging the residence time under toxic UV conditions. For example, in a test of four dinoflagellates in culture, UV-B radiation caused a reduction in swimming speeds, but the magnitude of effect differed greatly between species. Maximum inhibition occurred at 280 nm; this corresponds to the absorbance maximum for cytoskeletal proteins, and such proteins might be the response site (Ekelund 1991).

Other photosynthetic organisms may completely avoid the risk of intermittent exposure to surface UV-B by their choice of habitat. Again the habitat may have other more important advantages, such as increased nutrient supply or increased physical stability. However, algal growth rates are typically low in such habitats, and this strategy is invariably accompanied by some additional costs; for example, the need to allo-
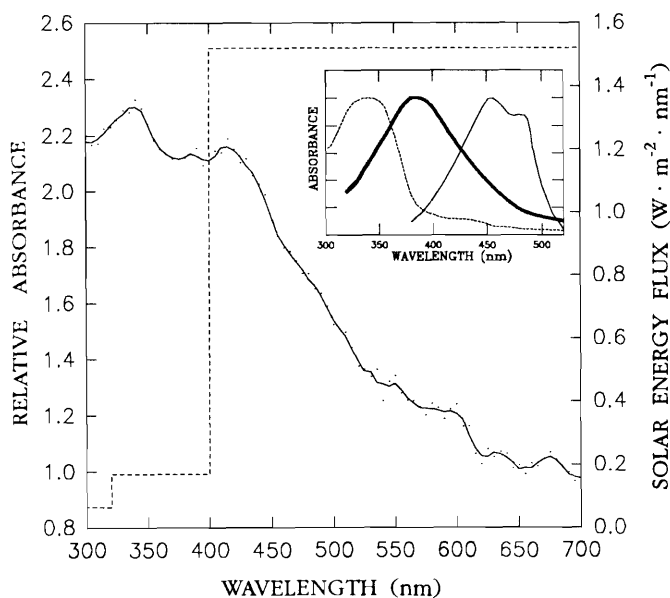
FIG. 4. Natural sunscreens. The variety of potential photoprotectants synthesized by phytoplankton and benthic communities include mycosporine-like amino acids (dotted line in inset), scytonemin sheath pigment in certain cyanobacteria (thick, solid line in inset), and carotenoids such as β-carotene (thin, solid line in inset). β-Carotene may play a more important role as an antioxidant. Each of these classes of compound probably contributes to the *in vivo* absorbance spectrum (solid line of main graph), which is for the cyanobacterium *Nostoc commune* sampled from 0.2 m depth in Toolik Lake, northern Alaska. The broken line gives the measured distribution of solar energy in the UV-B, UV-A, and PAR wavebands around solar noon, mid-June, at this site, and underscores the disproportionate absorbance of the highest energy wavelengths.

cate more cellular resources towards harvesting the low, often limiting, light supply.

Screening

An increasing number of naturally occurring compounds have been identified that absorb strongly in the UV-A or UV-B region of the spectrum. Their increase in cellular concentration under conditions of elevated UV dosages has been taken to imply that they are produced as natural sunscreens (Fig. 4), but it remains possible that they play additional, as yet unknown roles. These compounds include mycosporine-like amino acids, cyanobacterial sheath pigments, and flavonoids. Flavonoids are unknown in algae or cyanobacteria (Markham 1982) but have been reported from mosses, ferns, and higher plants, including aquatic species (Roberts and Haynes 1986; Markham and Viotto 1988).

Mycosporine-like amino acids (MLAA) appear to be especially well distributed throughout the aquatic biota, including phytoplankton, as well as invertebrate and fish species. They absorb maximally in the range 310–360 nm and are iminocarbonyl derivatives of mycosporines, water soluble compounds first identified in fungi (Favre-Bonvin *et al.* 1976, 1987). A compound extracted from corals was found to have an absorbance maximum at 320 nm, and it was suggested that such a compound might act as a UV filter to protect tropical species (Shibata 1969). Subsequent work on reef-building corals has revealed a broad range of MLAAs and a distribution consistent with the sunscreening hypothesis. Highest concentrations appear to occur in summer, and in the surface waters; for example, the concentration of the MLAA compound paly-

thine (Fig. 5) in coral samples dropped by a factor of 16 between the surface and 20 m (Dunlap *et al.* 1986).

At least six different MLAAs have been identified in benthic red algae and brown algae (Nakamura *et al.* 1982, Karentz *et al.* 1991b), but the distribution among the micro-algae and cyanobacteria is much less well known. A UV-B-absorbing compound has been identified in a terrestrial cyanobacterium (Scherer *et al.* 1988), and *in vivo* absorbance maxima in the UV-B to lower UV-A range are observed in many freshwater species of cyanobacteria (e.g., Fig. 4). The red-tide dinoflagellate *Alexandrium excavatum* also has a strong absorbance in the UV region (Carreto *et al.* 1989); HPLC analyses of cell extracts of this species have subsequently revealed at least nine MLAAs (Carreto *et al.* 1990; L. Lorrain and S. Roy, unpublished data).

There may be a close biochemical link between MLAAs and other putative sunscreens such as flavonoids. Biosynthesis of mycosporines in fungi appears to involve the shikimic acid pathway (Favre-Bonvin *et al.* 1987), which is the same pathway involved in the synthesis of higher plant photoprotectants such as phenylpropanoids (which include flavonoids) and furanocoumarins (Tevini and Teramura 1989). The UV-induced increase in flavonoids appears to be the result of increased activity and (or) biosynthesis of the enzyme phenylalanine ammonia lyase, but the biochemical regulation of cellular MLAA in algae remains completely unknown.

Many cyanobacterial species, especially benthic forms, have another pigment called scytonemin that may function as a photoprotectant against UV radiation, especially UV-A. This compound mostly occurs in the mucilaginous sheath surrounding the cells, and it has a broadband absorbance peaking at about 380 nm (Fig. 4). Scytomenin is found in high concentration in cyanobacterial communities that live in habitats exposed to direct sunlight (e.g., Turian 1985), and culture experiments have shown that its rate of synthesis can be induced to increase by exposure to UV-A or to bright PAR (Garcia-Pichel and Castenholz 1991).

Quenching

The interaction of UV radiation with oxygen and various organic compounds can result in the production of toxic intermediates that can be potentially more damaging than the UV exposure itself. Algal cells appear to have at least two quenching mechanisms that allow them to detoxify these photochemical reaction products.

All algal and cyanobacterial cells contain carotenoids, which are photosynthetic accessory pigments that play a variety of physiological roles. Certain carotenoids act as light-harvesting pigments that capture PAR in the blue–green region of the spectrum (Fig. 4), energy that is then passed on to the photosynthetic reaction centres of photosynthesis. These same molecules, however, can react with and thereby neutralize singlet-state oxygen (Jialal *et al.* 1991), confer a direct protection of photosystem II reaction centres against photooxidation (Tefler *et al.* 1991), and act as general radical-trapping antioxidants (Burton and Ingold 1984). Carotenoids also quench the triplet state of chlorophyll *a*, another major source of unwanted energy for the intracellular production of singlet-state oxygen (Moore *et al.* 1982). Certain carotenoids participate in the xanthophyll cycle, a set of reactions that plays a role in preventing photoinhibition by dissipating excess light energy (Demmig *et al.* 1987). This cycle is also active in phytoplankton (Demers *et al.* 1991).
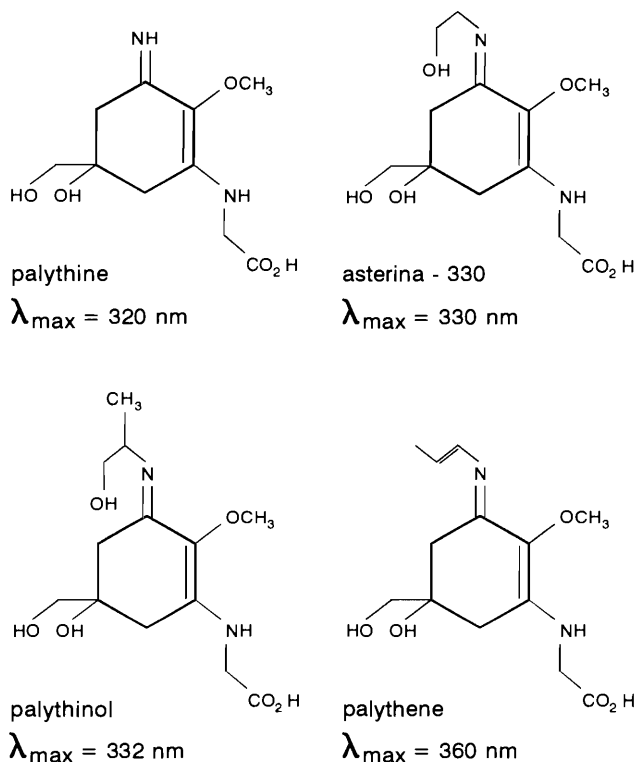
FIG. 5. Four mycosporine-like amino acids found in marine phytoplankton. λ_{max}, wavelength of maximum absorbance for each compound.

Many photosynthetic organisms in the aquatic environment also have various enzymatic defences against superoxide, hydrogen peroxide, and related oxidants. Superoxide dismutase scavenges toxic radicals inside cells and produces hydrogen peroxide, which is then consumed by a peroxidase. These enzymes typically increase under conditions of elevated dissolved oxygen tensions, but the relationship with ambient UV conditions has been little explored. UV-irradiated cultures of the cyanobacterium *Anacystis nidulans* have been observed to induce so-called shock proteins that may include superoxide dismutase and related proteins (Shibata *et al.* 1991).

Repair

The final line of defense by photosynthetic cells against UV-B damage is to have an efficient means of identifying the damage and repairing it. These repair processes have been especially well studied for DNA damage and for the photosystem II reaction centre damage that results from photoinhibition. The latter can be induced entirely by bright PAR, but is exacerbated by UV exposure.

There are three known cellular mechanisms that can restore damaged portions of DNA (Friedberg 1985); namely photoreactivation, nucleotide excision repair, and recombinational repair. Photoreactivation involves the direct monomerization of (5-6) cyclobutyl pyrimidine dimers by the action of the enzyme DNA photolyase. The enzyme requires activation by blue–green light (400–600 nm) which is absorbed by chromophoric cofactors, probably flavin derivatives (Scancar and Scancar 1984). The ratio of blue light to UV-B radiation may therefore be of considerable interest in the underwater environment. Nucleotide excision repair (also called dark repair) involves damage recognition, assembly of a DNA repair complex at the site of damage, incision of the DNA backbone on either side of the damage, and excision and resynthesis of the

damaged strand by the action of DNA polymerase. Recombinational repair has been implicated as a primary mechanism for the repair of DNA damage that has been bypassed by the replication machinery.

These mechanisms have been identified in various phytoplankton species, but little is known about their relative contribution to DNA repair in natural assemblages. Photoreactivation activities and dark repair have been observed in cyanobacteria (e.g., Asata 1972; Takao *et al.* 1989), and the gene for photolyase in *A. nidulans* has now been sequenced (Yasui *et al.* 1988). The photoreactivating enzyme has also been observed in the green alga *Scenedesmus acutus* (Eker *et al.* 1988). Diatoms collected from the ozone-depleted area in the Antarctic have recently been studied to assess UV-induced DNA damage and repair (Karentz *et al.* 1991*a*). UV-B induction of photoproducts showed a 100-fold difference between the 12 species studied, further underscoring the enormous interspecific variability in cellular UV-B protection. The smaller, chain-forming species had the highest induction densities of dimers and also had significantly greater numbers of (6-4) photoproducts per individual. Much remains to be learned about the efficacy of such repair processes, including the influence of changing spectral composition on the balance between damage and repair.

A similar balance characterizes the changes in photosystem II activity associated with photoinhibition. The primary lesion appears to be at the P680 reaction centre, but the damage then spreads throughout the photosystem II complex and causes a degradation of the oxygen-evolving system, the electron carriers, and the D1–D2 proteins to which they are bound. The cells respond to this damage by the "photoinhibition repair cycle" (see Andersson *et al.* 1992) in which the reaction centres are rebuilt de novo, a slow (time scale of hours) biosynthetic recovery process. During this "repair" phase, the synthesis of just the D1 protein may account for 10% of the total cellular protein synthesis (Raven and Samuelsson 1986). The details of how UV radiation modifies these photoinhibition responses remain unknown. For example, the repair process involves considerable transcription and translation of nucleic acids, which are themselves likely to be damaged by continuing exposure to UV-B. Evidence from experiments with the floating aquatic angiosperm *Spirodela oligorrhiza* suggests that a significant portion of the D1 protein degradation in natural sunlight is directly attributable to solar UV-B, and that different photosensitizers mediate the UV and bright PAR damage (Greenberg *et al.* 1989).

Conclusions

Solar UV-B has been a significant variable in the aquatic environment throughout evolutionary time, and photosynthetic organisms have developed a variety of defences that allow them to avoid, screen, repair, and otherwise protect their cells from long-term damage. The alarmist predictions of immediate and large-scale impairment of primary production in response to ozone depletion seem to us to be greatly exaggerated and may focus attention towards inappropriate monitoring strategies and measurement techniques.

There are major uncertainties about the time scales and assay conditions under which to assess potential UV-B impacts. The photosynthetic responses are likely to be nonlinear functions of dosage rate and dose, with possible delays in both the inhibition and the recovery phases (Fig. 3). The short-term (seconds to minutes) depression of photosystem II activity in one species, for example, may ultimately result in its replacement
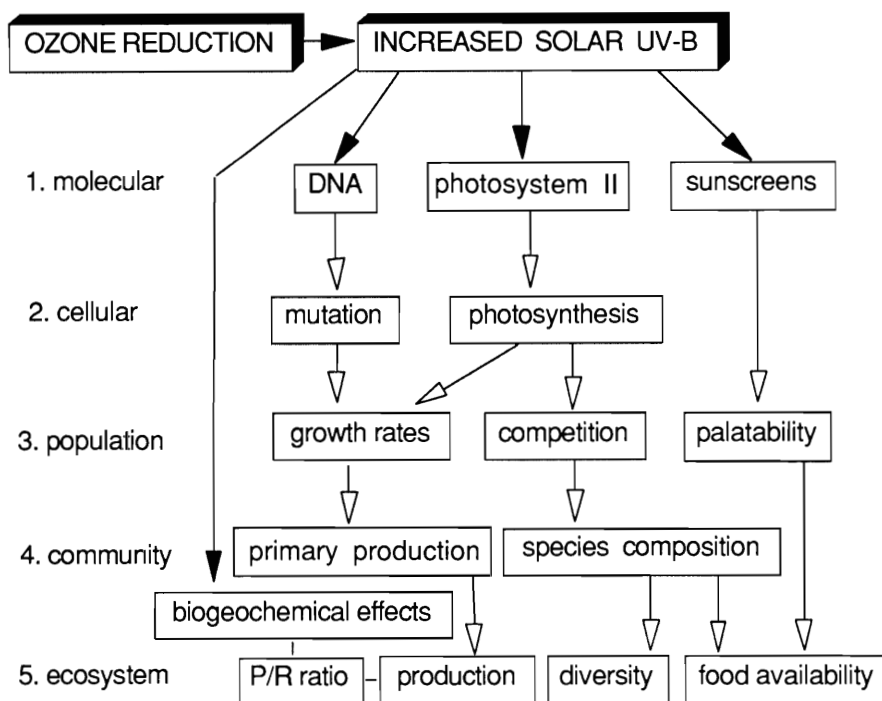
FIG. 6. UV-B has a pervasive influence, from the molecular level to community effects, on photosynthetic organisms in the aquatic environment.

by another more tolerant species over a period of hours to days. Such considerations will need to be paramount in the future development and interpretation of UV-bioassay technologies.

All photosynthetic organisms appear to have at least some resilience towards UV-B exposure, but there is an enormous variability between species. These differences mean that changes in the solar UV-B flux are likely to tip the competitive balance between species; such effects have the capacity to exert a wide-ranging, but perhaps initially subtle influence on the structure and dynamics of aquatic communities. For example, the bloom-forming algal species *Phaeocystis pouchetii*, widely distributed in polar waters, appears to produce high concentrations of UV-B-screening compounds (Marchant *et al.* 1991). If such compounds are sufficiently protective against UV damage (yet to be evaluated), they could potentially lead to the prolonged dominance of this species during periods of ozone depletion. *Phaeocystis* forms mucilaginous colonies that are unlikely to be readily grazed by zooplankton; a shift in species composition could thereby influence the efficiency of carbon transfer through to higher trophic levels.

UV-screening compounds such as furanocoumarins are known to influence the palatability of higher plants for insects (e.g., Zangerl and Berenbaum 1987). Could MLAAs, related compounds that are produced by a similar pathway, have an analogous effect on herbivores in the aquatic environment? The extent to which the UV-absorbing compounds found in aquatic plants, algae, and cyanobacteria offer a defence against UV remains uncertain, and it remains possible that they perform other ecological or physiological roles.

UV-B radiation is a highly reactive component of the solar spectrum, and it has the potential to influence biological processes at all levels, from biomolecules to whole ecosystems (Fig. 6). There are many feedback pathways, and some of these biological interactions are likely to operate in unexpected ways. Accelerated rates of photochemical degradation of dissolved

humic substances, for example, could increase the bioavailability of dissolved organic carbon in natural waters and thereby accelerate production at the base of the microbial food web. Such effects, coupled with chloroplast reduction or photobleaching (e.g., Fischer and Häder 1992; Walne 1980), might favor heterotrophy by mixotrophic phytoplankton and thereby lessen the proportional contribution of the autotrophic carbon flux to the overall ecosystem.

We conclude that aquatic ecosystems have a high level of resilience to changes in their ambient UV radiation field. They are more likely to respond by way of subtle, community-level adjustments rather than by an abrupt, large-scale deterioration in ecosystem structure and productivity. The eventual impacts of increasing UV-B remain unknown, but predicting and (or) detecting the onset of such change in the aquatic environment will require novel bioassay approaches and a commitment to long-term monitoring of community structure in representative marine and freshwater ecosystems.

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