Reports

Stratospheric Ozone, Middle Ultraviolet Radiation, and Carbon-14 Measurements of Marine Productivity

Abstract. *The effects of increased ultraviolet radiation, due to decreased stratospheric ozone, on marine phytoplankton have been investigated with the use of static bottle in situ carbon-14 productivity measurements. The relative biological efficiency for photoinhibition may be used to calculate biologically effective doses and resultant amplification factors. The carbon-14 technique (short-term incubations) is inadequate for assessment of possible large amplification factor photoprocesses that may be ecologically significant.*

Middle ultraviolet (MUV) radiation, 280 to 340 nm, can penetrate to ecologically significant depths in natural waters (*1, 2*). Thus, there is concern that reduced stratospheric ozone, and a consequent increase in MUV at the ocean surface, may have an adverse effect on phytoplankton productivity (*3*). To assess this problem, measurements of static bottle ^{14}C productivity under a variety of quantitative MUV irradiance regimes have been made (*4*). We have concluded that this widely used field technique, measuring the uptake of radioactive carbonate in incubations lasting from a few hours to 24 hours, is inadequate for accurately assessing the potential impact of increased MUV on the primary productivity of natural phytoplankton populations.

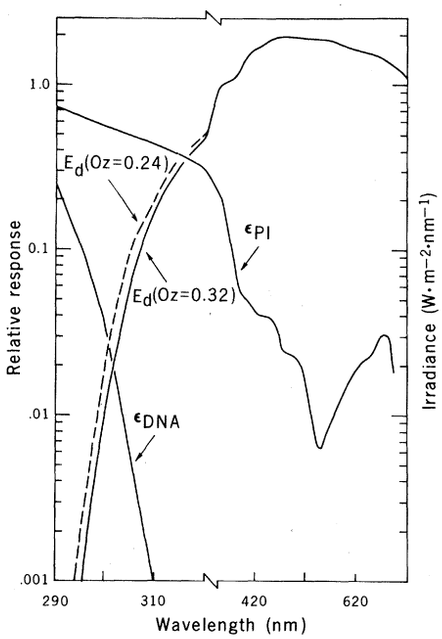

Fig. 1. Relative biological efficiencies, $\epsilon_{PI}(\lambda)$ and $\epsilon_{DNA}(\lambda)$, and downward spectral irradiance, $E_d(\lambda)$, for two stratospheric ozone concentrations plotted against wavelength. The wavelength scale is expanded below 320 nm in order to show greater detail in the MUV region of the spectrum. The effective biological dose is the product of the appropriate biological efficiency $\epsilon(\lambda)$ and the spectral irradiance $E_d(\lambda)$ summed over each infinitesimal wavelength interval.

Concerns over an anthropogenic reduction of the stratospheric ozone layer and the possible consequences of increased biologically harmful ultraviolet radiation have been widely publicized (*3*). Estimates of the amount of ozone depletion continue to be debated, with recent estimates ranging from 2 to 50 percent, and a latest estimate (August 1979) projecting a 16 percent reduction of ozone during the next several decades if 1977 input rates of stratospheric contaminants continue (*5*).

An important consideration, when discussing the potential impact of ozone reduction, is the spectral nature of biological photoeffects, which are frequently heavily weighted toward radiation in the MUV region of the spectrum. As a consequence, a 1 percent decrease in ozone may cause an A percent increase in biological effect, where A has been termed an amplification factor (*6*). More recently (*7*), this amplification factor has been subdivided into two components: (i) the ratio of the percentage change in biologically effective dose, $\Delta E_\epsilon/E_\epsilon$, to the percent change in ozone thickness, $\Delta w/w$ [the radiation amplification factor $R = (\Delta E_\epsilon/E_\epsilon)/(\Delta w/w)$]; (ii) the ratio of the percentage change in biological effect, $\Delta P/P$, to the percentage change in biologically effective dose, $\Delta E_\epsilon/E_\epsilon$ [the biological amplification factor $B = (\Delta P/P)/(\Delta E_\epsilon/E_\epsilon)$]. The product of these two components is the overall amplification factor ($A = R \cdot B$).

For a particular photoprocess the biologically effective dose is given by

$$E_\epsilon = \int E_d(\lambda) \cdot \epsilon(\lambda) \cdot d\lambda$$

where $E_d(\lambda)$ is the downward spectral irradiance and $\epsilon(\lambda)$ is the relative biological efficiency for the biological photoeffect under study. If $\epsilon(\lambda)$ and its wavelength normalization are specified, and $E_d(\lambda)$ is known, then quantitative calculation and comparison of biologically effective dose rates can be made (*2*).

The subject of marine photosynthesis and its measurement has been discussed in detail (*8*). Productivity is normally measured over relatively short periods of time, generally less than the division time of the populations under study. Ecologists are then faced with extrapolating these short measurements to growth rates and maintenance of the population. Although the ^{14}C technique is widely used to estimate the photosynthesis of natural phytoplankton populations, the interpretation of results continues to be debated (*9*).

Productivity measurements, with the static bottle ^{14}C technique, were carried out over a range from low to highly productive ocean waters. These productivity measurements were carried out for a range of quantitatively measured MUV irradiance regimes, by both excluding and enhancing natural radiation. Our results, in qualitative agreement with those of others (*3a, 10*), show that enhanced

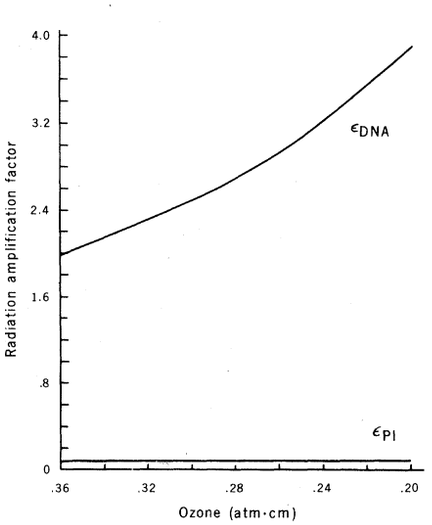

Fig. 2. Radiation amplification factor, R, plotted against the stratospheric ozone thickness, for two biological efficiencies: Setlow's (*12*) average action spectrum for biological effects involving DNA, $\epsilon_{DNA}(\lambda)$, as given in analytical form by Green *et al.* (*15*); and Jones and Kok's (*11*) action spectrum for photoinhibition as renormalized by Smith *et al.* (*4*).

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levels of MUV increase photoinhibition and that excluding MUV decreases photoinhibition in ^{14}C productivity measurements.

A quantitative analysis of our data (*4*), shows that the biological weighting function for photoinhibition of chloroplasts (*11*) allows calculation of a biologically effective dose which is consistent with the measured photoinhibition. This postulated relative biological efficiency for photoinhibition (PI), $\epsilon_{PI}(\lambda)$, is shown in Fig. 1 where we have included the DNA action spectrum (*12*), $\epsilon_{DNA}(\lambda)$, for comparison.

A distinguishing feature of $\epsilon_{PI}(\lambda)$ is that, while it has a maximum in the MUV, it continues into the visible region of the spectrum. For surface irradiance [$E_d(\lambda)$ in Fig. 1], a quantitative evaluation shows (*4*) that 25 percent of the photoinhibition weighted dose is due to radiation below 340 nm (the MUV region), 50 percent of this dose is due to radiation below 390 nm, and the remainder is due to wavelengths longer than 390 nm. In contrast, biologically effective doses, for photoprocesses such as $\epsilon_{DNA}(\lambda)$, are completely due to radiation in the MUV region of the spectrum.

In Fig. 1 we have also plotted downward spectral irradiance for two stratospheric ozone thicknesses (*13*). The effect of a diminished ozone thickness is to cause an increase in the irradiance at the ocean surface in the MUV region. The potential biological impact of this increased MUV is dependent on $\epsilon(\lambda)$, as manifest in the respective amplification factor. In Fig. 2 we have plotted the radiation amplification factor, R, versus stratospheric ozone thickness for $\epsilon_{PI}(\lambda)$ and $\epsilon_{DNA}(\lambda)$ (*14*). These curves show that R is approximately 0.1 for photoinhibition, while it ranges between 2 and 4 for photoprocesses weighted by $\epsilon_{DNA}(\lambda)$. Thus the radiation amplification factor is 20 to 40 times larger for ϵ_{DNA} than for ϵ_{PI}.

If we accept the hypothesis that $\epsilon_{PI}(\lambda)$ adequately describes the spectral weighting of photoinhibition and the effects of excluded and enhanced MUV on phytoplankton photosynthesis, as measured by the static bottle ^{14}C technique, then we can draw the following conclusions and observations: (i) possible changes in the stratospheric ozone thickness will cause only small changes in the biologically effective photoinhibition dose, E_{PI} (since $R_{PI} < 0.1$); (ii) even if the biological amplification factor, for a photoinhibition change in photosynthesis, is as large as our estimate of 5, the total amplification factor for a change in photosynthesis (ϵ_{PI} weighted) due to a change in ozone will be less than 1; (iii) if photoprocesses other than photoinhibition can potentially affect natural photoplankton populations (for example, MUV absorption and damage to DNA, which may not become evident for incubation times that are short compared to times of cell division), then the relevant $\epsilon(\lambda)$ for these alternative photoprocesses must be identified in order to estimate possible detrimental effects of increased MUV; (iv) photoprocesses having relative biological efficiencies weighted toward the MUV region of the spectrum (for example, ϵ_{DNA}) have amplification factors greater than unity which, when coupled with biological amplification factors greater than unity, gives them the potential for significant biological impact with increased MUV; and (v) conclusions regarding the possible impact of reduced ozone, hence enhanced MUV, with the use of this technique are limited since the present ^{14}C technique is not adequate to assess photoprocesses having a time frame longer than the limited incubation period of this method.

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Cogeneration of Electric Energy and Nitric Oxide

Abstract. *A solid electrolyte fuel cell operating on ammonia fuel has been constructed and tested. The yield of nitric oxide can exceed 60 percent with simultaneous electric energy production. Two dimensionless numbers have been identified which govern the product selectivity and power output of this fuel cell. The cell appears to be a promising candidate for nitric acid and electric energy cogeneration.*

The oxidation of NH_3 to NO in a fuel cell has been a long-sought goal (*1*). It is a highly exothermic reaction with a Gibbs free energy ΔG of -64.5 kcal per mole of NH_3 at 1000 K, yet it is also the basic step for the industrial manufacture of HNO_3. [More than 6.8×10^6 tons of HNO_3 are produced annually in the United States alone (*2*).] A Pt-Rh alloy is used currently as the catalyst for the conversion of NH_3 to NO. Because of the high exothermicity of the reaction, large amounts of thermal energy are generated. It would be extremely desirable from an economic as well as an energy-conservation point of view to obtain this energy as electric rather than thermal energy.

Low- and medium-temperature NH_3 fuel cells have met with no success since N_2 was found to be the only oxidation product (*3*). High-temperature fuel cells operating on H_2 or CO fuel have been developed and tested (*4*).

We have found that the primary product of the high-temperature solid electrolyte fuel cell

$$NH_3,NO,N_2,Pt/ZrO_2\ (8\ \text{percent}\ Y_2O_3)/Pt,air$$

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