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ENVIRONMENTAL EFFECTS OF OZONE DEPLETION: 1994 ASSESSMENT

Pursuant to Article 6 of the Montreal Protocol
on Substances that Deplete the Ozone Layer
under the Auspices of the
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ENVIRONMENTAL EFFECTS OF OZONE DEPLETION: 1994 ASSESSMENT

INTRODUCTION

The Montreal Protocol on Substances that Deplete the Ozone Layer requires, in Article 6, periodic assessments of available scientific, environmental, technical and economic information. The assessments shall be made at least every four years. In fact, assessments were made in 1989, 1991 and, the present one, in 1994. This 1994-Assessment on Environmental Effects is written so that it can be read without having the earlier reports at hand.

The provisions in the Montreal Protocol and its amendments in London (1990) and Copenhagen (1992) have brought about a marked decrease in production and use of ozone depleting chemicals. However, the ozone layer is still becoming thinner, and this is expected to continue until about 1998. Thereafter, a gradual recovery is predicted, but the layer will be damaged for half a century to come. These predictions were made by the Atmospheric Science Panel on the basis of a fairly optimistic scenario, including the assumptions that there will be full and worldwide compliance with the Copenhagen amendments, that no ozone depleting chemicals were overlooked, and that there will be no new threats to the ozone layer.

The present assessment deals with the consequences during the coming decades: the changes in solar ultraviolet radiation reaching the Earth's surface, and the effects on humans, animals, plants, micro-organisms, air quality and materials. A welcome new element, compared with the earlier assessments, is a special chapter on biogeochemical cycles. The main questions from a policy point of view are now: what will be the most important effects, and what can be done to prevent or mitigate these?

These questions are more difficult to answer than those posed initially when the problem of ozone depletion arose. Then the question was, will there be any effects so detrimental as to necessitate protection of the ozone layer? In principle, this could be answered by giving one or two clear-cut examples. The present questions are much broader, and require quantitative knowledge on all effects of potential importance.

Organized science recently paid special attention to the problems posed by ozone depletion. SCOPE, the Scientific Committee on Problems of the Environment (formed by the International Council of Scientific Unions) produced two reports on Effects of Increased Ultraviolet Radiation, one on Biological Systems (1992) and one on

Global Ecosystems (1993). SCOPE urges that these important and complicated problems require full utilization of existing research capacity, and a major expansion.

Reality is far from these goals. Funding for research on effects of increased UV-B radiation is so low that it does not even allow full utilization of the research capacity available. This implies that answers to urgent questions cannot be given as quickly as should be possible. We are glad that in spite of these limitations, scientific understanding of the problem is growing, as will be apparent from all chapters in the assessment.

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EXECUTIVE SUMMARY

A change in the composition of the stratosphere becomes relevant to society only if it has noticeable effects. This places the assessment of effects in a pivotal role in the problem of ozone depletion.

Decreases in the quantity of total-column ozone, as now observed in many places, tend to cause increased penetration of solar UV-B radiation (290-315 nm) to the Earth's surface. UV-B radiation is the most energetic component of sunlight reaching the surface. It has profound effects on human health, animals, plants, microorganisms, materials and on air quality. Thus any perturbation which leads to an increase in UV-B radiation demands careful consideration of the possible consequences. This is the topic of the present assessment made by the Panel on Environmental Effects of Ozone Depletion.

The assessment is given in seven chapters, summarized as follows:

Changes in Utraviolet Radiation

The quality and quantity of UV measurements has increased greatly in the last few years. Variations among measurements from different instruments are diminishing toward the 5% level. Long-term trend detection is still a problem, with little historical data available for baseline estimation.

Enhanced UV levels are clearly associated with the Antarctic springtime ozone reductions. Measurements show that maximum UV levels at the South Pole are reached well before the summer solstice, and DNA-damaging radiation at Palmer Station, Antarctica (64°S) during the springtime ozone depletion can exceed maximum summer values at San Diego, USA (32°N). UV increases at mid-latitudes are smaller. However, increases associated with the record low ozone column of 1992/93 in the northern hemisphere are evident when examined on a wavelength-specific basis.

Measurements in Argentina, Chile, New Zealand, and Australia show relatively high UV levels compared to corresponding northern hemispheric latitudes, with differences in both stratospheric ozone and tropospheric pollutants likely to be playing a role. Tropospheric ozone and aerosols can reduce global UV-B irradiances appreciably. At some locations, tropospheric pollution may have increased since pre-industrial times, leading to decreases in surface UV radiation. However, recent trends in tropospheric pollution probably had only minor effects on UV trends relative to the effect of stratospheric ozone reductions.

Global ozone measurements from satellites over 1979/93 imply significant UV-B increases at high and mid-latitudes of both hemispheres, but only small changes in the tropics. Such estimates however assume that cloud cover and tropospheric pollution have

remained constant over these years. Under the current CFC phase-out schedules, global UV levels are predicted to peak around the turn of the century in association with peak loading of chlorine in the stratosphere and the concomitant ozone reductions. The recovery to pre-ozone depletion levels is expected to take place gradually over the next 50 years.

Effects on Human and Animal Health

The increase in UV-B radiation associated with stratospheric ozone depletion is likely to have a substantial impact on human health. Potential risks include increases in the incidence of and morbidity from eye diseases, skin cancer, and infectious diseases. Quantitative estimates of risk are available for some effects. (e.g., skin cancer), but other (e.g., infectious diseases) are associated with considerable uncertainty at the present time.

UV radiation has been shown in experimental systems to damage the cornea and lens of the eye. Chronic exposure to UV-B (resulting in a high, cumulative, lifetime dose) is one of several factors clearly associated with the risk of cataract of the cortical and posterior subcapsular forms. The 1989 Report noted that a 1% increase in stratospheric ozone depletion has been predicted to be associated with a 0.6 to 0.8% increase in cataract; this estimate, although crude, has not been improved upon in the intervening years.

Some components of the immune system are present in the skin, which makes the immune system accessible to UV radiation. Experiments in animals show that UV exposure decreases the immune response to skin cancers, infectious agents, and other antigens and can lead to unresponsiveness upon repeated challenges. Studies in human subjects also indicate that exposure to UV-B radiation can suppress the induction of some immune responses. The importance of these immune effects for infectious diseases in humans is unknown. However, in areas of the world where infectious diseases already pose a significant challenge to human health and in persons with impaired immune function, the added insult of UV-B induced immune suppression could be significant.

In susceptible (light-skinned) populations, UV-B radiation is the key risk factor for development of non-melanoma skin cancer (NMSC). Using information derived from animal experiments and human epidemiology, it is estimated that a sustained 1% decrease in stratospheric ozone will result in an increase in NMSC incidence of approximately 2%. The relationship between UV-B exposure and melanoma skin cancer is less well understood and appears to differ fundamentally from that of NMSC. Epidemiologic data indicate that the risk of melanoma increases with sunlight exposure, especially during childhood. There is, however, uncertainty about the relative importance of UV-B radiation, which directly determines the magnitude of the increase in melanoma that would result from ozone depletion.

Effects on Terrestrial Plants

Physiological and developmental processes of plants are affected by UV-B radiation, even by the amount of UV-B in present-day sunlight. Plants also have several mechanisms to ameliorate or repair these effects and may acclimate to a certain extent to increased levels of UV-B. Nevertheless, plant growth can be directly affected by UV-B radiation.

Response to UV-B also varies considerably among species and also cultivars of the same species. In agriculture, this will necessitate using more UV-B-tolerant cultivars and breeding new ones. In forests and grasslands, this will likely result in changes in species composition; therefore there are implications for the biodiversity in different ecosystems.

Indirect changes caused by UV-B (such as changes in plant form, biomass allocation to parts of the plant, timing of developmental phases and secondary metabolism) may be equally, or sometimes more, important than damaging effects of UV-B. These changes can have important implications for plant competitive balance, herbivory, plant pathogens, and biogeochemical cycles. These ecosystem-level effects can be anticipated, but not easily predicted or evaluated. Research at the ecosystem level for solar UV-B is barely beginning. Other factors, including those involved in climate change such as increasing CO_2 also interact with UV-B. Such reactions are not easily predicted, but are of obvious importance in both agriculture and in nonagricultural ecosystems.

Effects on Aquatic Ecosystems

More than 30% of the world's animal protein for human consumption comes from the sea, and in many countries, particularly the developing countries, this percentage is significantly higher. As a result, it is important to know how increased levels of exposure to solar UV-B radiation might affect the productivity of aquatic systems.

In addition, the oceans play a key role with respect to global warming. Marine phytoplankton are a major sink for atmospheric carbon dioxide, and they have a decisive role in the development of future trends of carbon dioxide concentrations in the atmosphere.

Phytoplankton form the foundation of aquatic food webs. Marine phytoplankton are not uniformly distributed throughout the oceans of the world. The highest concentrations are found at high latitudes while, with the exception of upwelling areas on the continental shelves, the tropics and subtropics have 10 to 100 times lower concentrations. In addition to nutrients, temperature, salinity and light availability, the high levels of exposure to solar UV-B radiation that normally occur within the tropics and subtropics may play a role in phytoplankton distributions.

Phytoplankton productivity is limited to the euphotic zone, the upper layer of the water column in which there is sufficient sunlight to support net productivity. The position of the organisms in the euphotic zone is influenced by the action of wind and waves. In addition, many phytoplankton are capable of active movements that enhance their productivity and, therefore, their survival. Exposure to solar UV-B radiation has been shown to affect both orientation mechanisms and motility in phytoplankton, resulting in reduced survival rates for these organisms.

Researchers have measured the increase in, and penetration of, UV-B radiation in Antarctic waters, and have provided conclusive evidence of direct ozone-related effects within natural phytoplankton communities. Making use of the space and time variability of the UV-B front associated with the Antarctic ozone hole, researchers assessed phytoplankton productivity within the hole compared to that outside the hole. The results show a direct reduction in phytoplankton production due to ozone-related increases in UV-B. One study has indicated a 6 - 12 % reduction in the marginal ice zone.

Solar UV-B radiation has been found to cause damage to early developmental stages of fish, shrimp, crab, amphibians and other animals. The most severe effects are decreased reproductive capacity and impaired larval development. Even at current levels, solar UV-B radiation is a limiting factor, and small increases in UV-B exposure could result in significant reduction in the size of the population of consumer organisms.

Although there is overwhelming evidence that increased UV-B exposure is harmful to aquatic ecosystems, the potential damage can only be roughly estimated at the present time.

Effects on Biogeochemical Cycles

Increases in solar UV radiation could affect terrestrial and aquatic biogeochemical cycles thus altering both sources and sinks of greenhouse and chemically-important trace gases e.g., carbon dioxide (CO_2), carbon monoxide (CO), carbonyl sulfide (COS) and possibly other gases, including ozone. These potential changes would contribute to biosphere-atmosphere feedbacks that attenuate or reinforce the atmospheric buildup of these gases.

In terrestrial ecosystems increased UV-B could modify both the production and decomposition of plant matter with concomitant changes in the uptake and release of atmospherically-important trace gases. Decomposition processes can be accelerated when UV-B photodegrades surface litter, or retarded when the dominant effect is on the chemical composition of living tissues resulting in reduced biodegradabilty of buried litter. Primary production can be reduced by enhanced UV-B, but the effect is variable between species and even cultivars of some crops. Likewise, photoproduction

of CO from plant matter is species dependent and occurs more efficiently from dead than living matter.

In aquatic ecosystems solar UV-B radiation also might have significant impacts. Studies in several locations have shown that reductions in current levels of solar UV-B result in enhanced primary production, and Antarctic experiments under the ozone hole demonstrated that primary production is inhibited by enhanced UV-B. In addition to its effects on primary production, solar UV radiation can reduce bacterioplankton growth in the upper ocean with potentially important effects on marine biogeochemical cycles. Solar UV radiation stimulates the degradation of aquatic dissolved organic matter (DOM) resulting in loss of UV absorption and formation of disolved inorganic carbon (DIC), CO, and organic substrates that are readily mineralized or taken up by aquatic microorganisms. Aquatic nitrogen cycling can be affected by enhanced UV-B through inhibition of nitrifying bacteria and photodecomposition of simple inorganic species such as nitrate. The marine sulfur cycle may be affected by UV-B radiation resulting in possible changes in the sea-to-air emissions of COS and dimethylsulfide (DMS), two gases that are degraded to sulfate aerosols in the stratosphere and troposphere, respectively.

New research on the environmental fate and impact of the hydrofluorocarbon (HFC) and hydrochlorofluorocarbon (HCFC) substitutes for CFCs has focused on trifluoroacetate (TFA), a tropospheric oxidation product of certain HFCs and HCFCs. TFA is mildly toxic to most marine and freshwater phytoplankton. The results indicate that TFA, although it may become globally distributed with increased usage of alternative fluorocarbons, is not likely to accumulate in soils and organisms. Although resistant to chemical degradation, very recent evidence indicates that TFA can be broken down by microorganisms.

Effects on Air Quality

Reductions of stratospheric ozone and the concomitant increases of UV-B radiation penetrating to the lower atmosphere result in higher photodissociation rates of key trace gases that control the chemical reactivity of the troposphere. This can increase both production and destruction of ozone (O_3) and related oxidants such as hydrogen peroxide (H_2O_2), which are known to have adverse effects on human health, terrestrial plants, and outdoor materials. Changes in the atmospheric concentrations of the hydroxyl radical (OH) may change the atmospheric lifetimes of climatically important gases such as methane (CH_4) and the CFC substitutes.

Trends in the photodissociation rate coefficient of tropospheric O_3, of about +0.36±0.04% per year in the northern hemisphere and +0.40±0.05% per year in the southern hemisphere, have been estimated from satellite measurements of the ozone column between 1979 and 1992. The corresponding model-calculated changes in tropospheric chemical composition are non-linear and sensitive to

the prevailing levels of nitrogen oxides (NO_x). In polluted regions (high NO_x), tropospheric O_3 is expected to increase, reaching potentially harmfulä concentrations earlier in the day, and leading to more frequent exceedance of oxidant standards for air quality in urban areas where O_3 levels are routinely near such air quality thresholds. In more pristine regions (lower NO_x), O_3 increases can be lower or even negative. Other oxidants, such as H_2O_2 and OH, are projected to increase for both polluted and pristine regions. Changes to H_2O_2 concentrations may have some impact on the geographical distribution of acid precipitation. Rural regions may become more urban-like and the percentage of areas with remote tropospheric conditions may decline.

Increases in OH concentrations cause a nearly proportionate decrease in the steady state tropospheric concentrations of CH_4 and CFC substitutes such as the HCFCs and HFCs. Thus, the measured reductions in the ozone column (TOMS, 1979-92) are likely to have moderated CH_4 increases over the past decade, and may account for about 1/3 of the slowing of the global CH_4 trends.

Increased tropospheric reactivity could also lead to increased production of particulates such as cloud condensation nuclei, from the oxidation and subsequent nucleation of sulfur of both antropogenic and natural origin (e.g. carbonyl sulfide and dimethylsulfide). While these processes are still not fully understood, they exemplify the possibility of complex feedbacks between stratospheric ozone reductions, tropospheric, chemistry, and climate change.

Effects on Materials

Synthetic polymers, naturally occurring biopolymers, as well as some other materials of commercial interest are adversely affected by solar UV radiation. Application of these materials, particularly plastics, in situations which demand routine exposure to sunlight is only possible through the use of light-stabilizers and/or surface treatments to protect them from sunlight. Any increase in solar UV-B content due to partial ozone depletion will therefore accelerate the photogradation rates of these materials, limiting their service lifetimes outdoors.

The nature and the extent of such damage due to increased UV-B radiation in sunlight is quantified in action spectra. In spite of the several polymer action spectra available in the research literature the information is often inadequate to make reliable estimates of the increased damage. However, it is clear from the available data that the shorter UV-B wavelengths processes are mainly responsible for photodamage ranging from discoloration to loss of mechanical integrity. The molecular level interpretation of these changes remain unclear in many instances.

The use of higher levels of conventional light-stabilizers in polymer formulations will undoubtedly be attempted as a means of

mitigating the effects of increased UV levels in sunlight. However, such an approach assumes that a) these stabilizers continue to be effective under spectrally-altered sunlight conditions; b) they are themselves photostable on exposure to UV-rich sunlight; and c) they can be sufficiently effective at low enough concentrations to serve the purpose. Experimental data bearing on these issues is sparse. Ongoing research, particularly that relating to extreme-environment exposure of polymers, is expected to shed more light on these questions. Substitution of the affected materials by more photostable plastics and other materials also remains an attractive possibility. Both these approaches will add to the cost of plastic products in target applications.

Key Areas of Uncertainty

- Effects on human health (infectious diseases, vaccination efficacy, cataract, melanoma)
- Effects on food production (fisheries, agriculture) and on natural ecosystems (aquatic, terrestrial)
- Links between ozone depletion and global warming by interactions between atmosphere and biosphere (phytoplankton, forests)

Conclusions

The increases in UV-B radiation already observed and expected in the future will have consequences of significant magnitude in several respects. This applies to the UV-B increases predicted on the basis of the most favorable scenario of ozone depletion; it applies even more if ozone depletion would be greater, for instance, due to incomplete compliance to the phaseout agreed for ozone depleting chemicals. This strongly supports continued determination to protect the ozone layer.

In many areas the uncertainties about effects are still so great that quantitative predictions are not possible. Incompleteness of knowledge does not diminish the concerns for the consequences, e.g., an increase in infectious diseases or disturbance of natural ecosystems. Some of these consequences of ozone depletion may well be more serious than the effects now quantifiable. Further investigations are necessary in order to achieve more certainty about such effects and, if necessary, about possibilities for protection or mitigation.

CHAPTER 1

CHANGES IN ULTRAVIOLET RADIATION REACHING THE EARTH'S SURFACE

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Summary

The quality and quantity of UV measurements has increased greatly in the last few years. Variations among measurements from different instruments are diminishing toward the 5 percent level. Long term trend detection is still a problem, with little historical data available for baseline estimation.

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Measurements in Argentina, Chile, New Zealand, and Australia show relatively high UV levels compared to corresponding northern hemispheric latitudes, with differences in both stratospheric ozone and tropospheric pollutants likely to be playing a role. Tropospheric ozone and aerosols can reduce global UV-B irradiances appreciably. At some locations, tropospheric pollution has increased since pre-industrial times, leading to decreases in surface UV radiation. However, recent trends in tropospheric pollution probably had only minor effects on UV trends relative to the effect of stratospheric ozone reductions.

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Introduction

Reductions in stratospheric ozone (O_3) allow more solar ultraviolet (UV) radiation to reach the earth's lower atmosphere and surface. UV radiation affects many chemical and biological processes, and its increases are of concern because of potential adverse effects on the biosphere, on tropospheric air quality, and on materials such as wood and plastics. The UV wavelengths most affected by O_3 reductions are in the UV-B (280-315 nm) band with some effect also in the UV-A (315-400 nm) (see Figure 1.1). Radiation at shorter wavelengths is absorbed completely by even relatively small amounts of O_3 and by atmospheric oxygen (O).

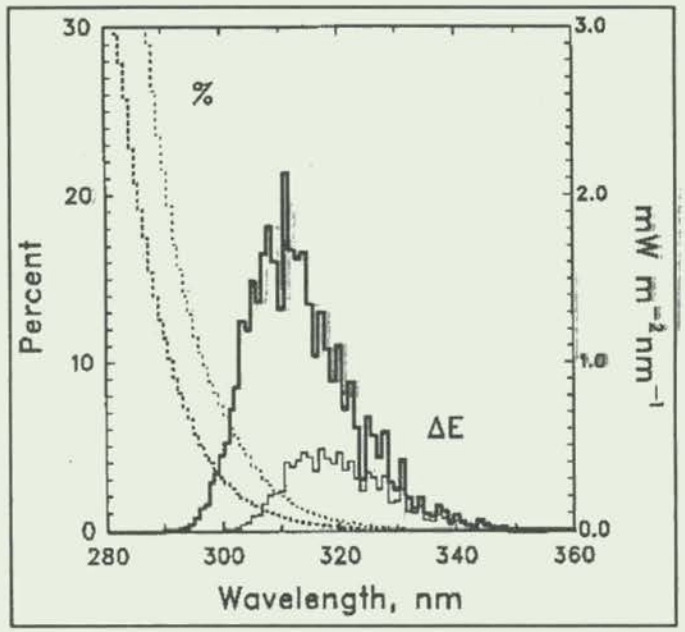


Fig.1.1. Increases in UV radiation in response to a 1 percent decrease in the total ozone column near 300 DU (1 DU = 2.69×10^{16} molec cm^{-2}). Solid lines (right scale) give spectral irradiance changes, dotted lines (left scale) give percent changes. Values are for overhead sun (thick lines) and for a solar zenith angle of 70° (thin lines). From Madronich *[1993c]*.

Accurate characterization of environmental UV radiation is difficult because of large geographical and temporal variations. However, significant progress has been made in recent years. Geographical and seasonal variations are now better understood in terms of earth-sun geometric factors, O_3 amounts, cloudiness, various local and regional pollutants, and surface elevation and reflectivity. UV increases associated with recent O_3 reductions have also been detected.

This update to the UNEP *[1989, 1991]* reports addresses the state of knowledge on environmental UV radiation as of August 1994, emphasizing the sensitivity to O_3 changes for different biological and chemical photo-processes, the measurements of UV radiation at ground level and possible causes for its variations, and the implications of measured global O_3 trends for UV radiation.

The Biological Effectiveness of UV Radiation

Weighted UV Radiation and its Sensitivity to Ozone Changes

Various biological and chemical photo-processes respond differently to different parts of the UV spectrum. The relative effectiveness of different wavelengths must be known in order to assess the responses to O_3 changes. The effective UV irradiance, E, or dose rate (exposure), is given by

$$E = \int F(\lambda)\, W(\lambda)\, d\lambda$$

where $W(\lambda)$ is the weighting function, or action spectrum, for a specific biological or chemical effect, and $F(\lambda)$ is the spectral irradiance, either computed or measured, for a given time and location. Hourly, daily, and yearly weighted doses may then be computed by time-integration of the dose rates.

The weighting procedure is required because solar UV-B increases steeply towards longer wavelengths, whereas the biological effectiveness often increases toward shorter wavelengths. As a result, weighted UV irradiances computed with different action spectra have different responses to atmospheric O_3 changes. A commonly used measure of this dependence is the radiation amplification factor (RAF), defined by

$$\Delta E/E = -RAF\ (\Delta O_3/O_3)\ \text{(percent rule)}$$

where $\Delta O_3/O_3$ is the percent change in the ozone column, and $\Delta E/E$ is the corresponding percent increase in weighted irradiance (instantaneous or an a time-integrated basis e.g., daily, yearly). The RAFs give the increase of available effective radiation in response to O_3 reductions. They do not however measure the ultimate biological response, since this often depends non-linearly on the radiation exposure, and other factors, such as repair, time in the life cycle, whether the cell is dividing, etc., may also be important.

A compilation of RAFs for different biological and chemical processes is given in Table 1.1. The RAFs are useful for comparing the sensitivity of different processes to O_3 changes. Action spectra that decrease strongly with increasing UV-B wavelengths have larger RAFs, while spectra with a significant UV-A tail tend to be less sensitive.

Several uncertainties in RAF values exist. In many cases, the original data used to derive action spectra are highly variable. For many spectra, insufficient data exist at the longer wavelengths, and if an exponential tail is used for extrapolation,

the RAFs are significantly reduced (as indicated by the bracketed values in Table 1.1). The RAFs depend somewhat on the total O_3 column, the altitude of the O_3 perturbation, and the solar zenith angle (and therefore on latitude and season). They are, however, essentially independent of cloud cover, surface albedo, or local pollution.

The simple "percent rule" given above is valid only for small O_3 changes. For large O_3 changes, a more accurate relation is

$$E_2/E_1 = [\ (O_3)_1 / (O_3)_2\ ]^{RAF} \quad \text{(power rule)}$$

where E_1 and E_2 are the weighted irradiances corresponding respectively to ozone columns $(O_3)_1$ and $(O_3)_2$. Figure 1.2 demonstrates the non-linear dependence of erythemal radiation on ozone reductions.

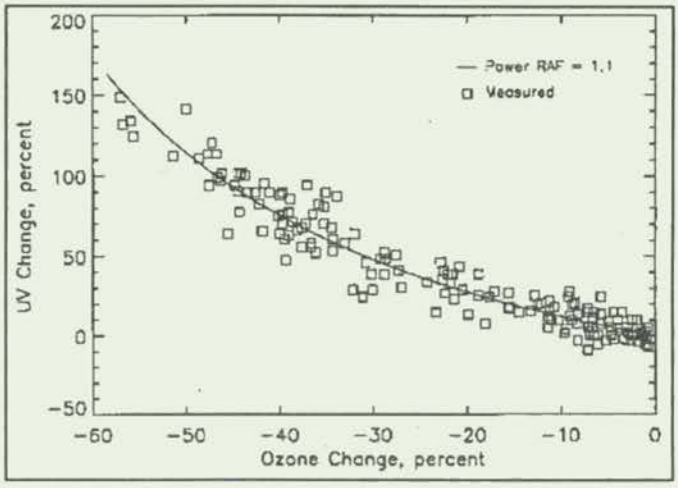


Fig. 1.2. Dependence of erythemally weighted UV radiation on O_3 column changes. Measurements from South Pole, 1 February 1991 to 12 December 1992. Adapted from Booth and Madronich *[1994]*.

Table 1.1. Radiation Amplification Factors (RAFs) at 30°N.

Effect	RAF January	RAF July	Reference
Skin			
*Erythema reference	1.1	1.2	McKinlay and Diffey, 1987
*Skin cancer in SKH-1 hairless mice (Utrecht)	1.5	1.4	deGruijl et al., 1993
*SKH-1 corrected for human skin transmission	1.2	1.1	deGruijl and van der Leun, 1994
Elastosis	1.1	1.2	Kligman and Sayre, 1991
Photocarcinogenesis, skin edema	1.6	1.5	Cole et al., 1986
Photocarcinogenesis (based on STSL)	1.5	1.4	Kelfkens et al., 1990
Photocarcinogenesis (based on PTR)	1.6	1.5	Kelfkens et al., 1990
Melanogenesis	1.7	1.6	Parrish et al., 1982
Erythema	1.7	1.7	Parrish et al., 1982
*Melanoma in fish	0.1	0.1	Setlow et al.., 1993
DNA Related			
*Generalized DNA damage	2.2	2.1	Setlow, 1974
Mutagenicity and Fibroblast killing	[1.7] 2.2	[2.7] 2.0	Zölzer and Kiefer, 1984; Peak al., 1984

Fibroblast killing	0.3	0.6	Keyse et al., 1983
Cyclobutane pyrimidine dimer formation	[2.0] 2.4	[2.1] 2.3	Chan et al., 1986
(6-4) photoproduct formation	[2.3] 2.7	[2.3] 2.5	Chan et al., 1986
HIV-1 activation	[0.1] 4.4	[0.1] 3.3	Stein et al., 1989
Eyes			
Damage to cornea	1.2	1.1	Pitts et al., 1977
Damage to lens (cataract)	0.8	0.7	Pitts et al., 1977
Other effects on animal cells			
*Occupational exposure limit	1.4	1.5	ACGIH, 1991
Immune suppression	[0.4] 1.0	[0.4] 0.8	DeFabo and Noonan, 1983
*Cell mortality in Chinese hamster			Banrud et al., 1993
*Substrate binding in Chinese hamster			Banrud et al., 1993
Membrane Damage			
Glycine leakage from *E. coli*	0.2	0.2	Sharma and Jagger, 1979
Alanine leakage from *E. coli*	0.4	0.4	Sharma and Jagger, 1979
Membrane bound K^+-stimulated ATPase inactiv.	[0.3] 2.1	[0.3] 1.6	Imbrie and Murphy, 1982
Plants			
Generalized plant spectrum	2.0	1.6	Caldwell et al., 1986
Inhibition of growth of cress seedlings	[3.6] 3.8	3.0	Steinmetz and Wellmann, 1986
Isoflavonoid formation in bean	[0.1] 2.7	[0.1] 2.3	Wellmann, 1985
Inhibition of phytochrome induced anthocyanin synthesis in mustard	1.5	1.4	Wellmann, 1985
Anthocyanin formation in maize	0.2	0.2	Beggs and Wellmann, 1985
Anthocyanin formation in sorghum	1.0	0.9	Yatsuhashi et al., 1982
Photosynthetic electron transport	0.2	0.1	Jones and Kok, 1966
Photosynthetic electron transport	0.2	0.2	Bornman et al., 1984
Overall photosynthesis in leaf of *Rumex patientia*	0.2	0.3	Rundel, 1983
*DNA damage in Alfalfa	0.5	0.6	Quaite et al., 1992
Phytoplankton			
Inhibition of motility *(Euglena gracilis)*	1.9	1.5	Häder and Worrest, 1991
*Inhibition of photosynthesis *(Phaeodactylum sp.)*	0.2	0.3	Cullen et al., 1992
*Inhibition of photosynthesis *(Prorocentrum micans)*	0.3	0.4	Cullen et al., 1992
*Inhibition of photosynthesis, in Antarctic community	0.8	0.8	Boucher and Prezelin, 1994
*Inhibition of photosynthesis (*Nodularia spumigena* cyanobacteria)	0.2	0.2	Häder et al., 1994
Tropospheric photolysis			
*$O_3 + h\nu \rightarrow O(^1D) + O_2$	2.1	1.8	Madronich and Granier, 1994
*$O_3 + h\nu \rightarrow O(^3P) + O_2$	0.1	0.1	Madronich and Granier, 1994
*$H_2O_2 + h\nu \rightarrow OH + OH$	0.4	0.4	Madronich and Granier, 1994
*$HNO_3 + h\nu \rightarrow OH + NO_2$	1.1	1.0	Madronich and Granier, 1994
*$NO_2 + h\nu \rightarrow O(^3P) + NO$	0.0	0.0	Madronich and Granier, 1994
*$HCHO + h\nu \rightarrow H + CHO$	0.5	0.5	Madronich and Granier, 1994
*$HCHO + h\nu \rightarrow H_2 + CO$	0.2	0.2	Madronich and Granier, 1994

Table 1.1. Radiation Amplification Factors (RAFs) at 30°N. (Continued)

Effect	—RAF— January (290DU)	July (305DU)	Reference
Aqueous photochemistry			
*CO production (Suwannee River)	0.3	0.3	Valentine and Zepp, 1993
*COS production (Gulf of Mexico)	0.2	0.2	Zepp and Andreae, 1994
*COS production (North Sea)	0.6	0.6	Zepp and Andreae, 1994
*Photodegradation of nitrate ions	1.1	1.0	Zepp et al., 1987
*Photodegradation of DOC (Biscayne Bay)	1.3	1.1	Kieber et al., 1990
*Photoproduction of H_2O_2 in freshwater	0.1	0.1	Cooper et al., 1988
Materials damage			
Yellowness induction in poly vinly chloride	0.2	0.2	Andrady et al., 1989
Yellowness induction in polycarbonate	0.4	0.4	Andrady et al., 1989
Other weighting functions			
Temple U. Robertson-Berger meter	0.8	0.7	Urbach et al., 1974
*Solar Light Robertson-Berger meter (Model 501)	1.2	1.1	M. Morys, priv. comm. 1994
*ozone cross section (273 K)	0.8	0.8	
*UV-A (315-400 nm)	0.03	0.02	
*UV-B (280-315 nm)	1.25	0.99	
*UV-B' (280-320 nm)	0.87	0.71	
*simple exponential decay, one decade per 14 nm.	1.00	1.00	

Updated from UNEP (1991). (*) denotes change or new entry. Values in brackets show effect of extrapolating original data to 400 nm with an exponential tail, for cases where the effect is larger than 0.2 RAF units. RAFs computed on basis of daily integral.

Limitations of Biological Action Spectra

Commonly used weighting functions are based on biological action spectra. Frequently a weighting function at the effects level is the composite of more than one spectrum at the molecular level, and is modified by absorbing molecules filtering the radiation before it reaches its target. Therefore the weighting functions, and data derived from them such as the RAFs of Table 1.1, depend on various independent factors and should be used with caution, taking into account the conditions under which the experiments were performed. When labels such as "DNA-effective radiation" are used, this simply describes the integrated irradiance potentially effective in causing effects (e.g., naked DNA damage) but does not necessarily mean that the effect (DNA damage) will ensue. The actual effect will depend on the sensitivity of the particular organism and several other factors.

Traditionally, action spectra have been developed for very different purposes than evaluating biological effects of O_3 reductions. Action spectra allow the photobiologist to draw some conclusions regarding the biological pigment or molecule that absorbs the radiation and mediates the effect within an organism. The criteria often used to develop action spectra are directed to this traditional use in photobiology and these, along with many technical constraints, limit the usefulness of action spectra as weighting functions. A photobiologist may wish to know how an absorbing molecule is acting, with as little interference by other substances in the organism as possible, e.g., how DNA is absorbing radiation and acting to mediate an effect. However, for evaluating the biological consequences of O_3 reduction it is more important to know how a

molecule such as DNA in its normal state within the organism is affected by the radiation and how its effect may be altered by the activity of other absorbing molecules.

Action spectra are usually developed by exposing the biological material to radiation of only one wavelength (or a narrow range of wavelengths) at a time and then measuring the effect. Again, for traditional photobiological purposes this is quite suitable. However, organisms in nature are exposed simultaneously to radiation at all wavelengths in the entire solar spectrum reaching the earth's surface, and the radiation in the UV-A and visible wavebands is orders of magnitude more intense than in the UV-B. Under such conditions several chromophores may be acting to cause interacting effects in the organism. For example, the UV-A and visible radiation can ameliorate the effects of UV-B in many organisms *[e.g., Caldwell and Flint, 1994]*. For practical purposes, action spectra are usually developed with only hours of irradiation at each wavelength: whereas in nature organisms are usually exposed over periods of days, months or longer to the full sunlight spectrum. This too can cause interacting effects that might not be predicted from an action spectrum.

Another limitation of UV-B action spectra is that they may be arbitrarily restricted to a certain waveband where data were collected. While these still serve the traditional photobiological purposes, they can limit the usefulness for the O_3 reduction question. For example, if data for action spectra are restricted to the UV-B, but in reality there is some, even very low, effectiveness in the UV-A, this can change the resulting radiation amplification factors when these action spectra are used as weighting functions.

These limitations and qualifications of weighting functions based on action spectra must be borne in mind when considering the significance of biologically effective radiation. Use of such weighting functions is still more appropriate than the use of unweighted UV-B radiation, but qualification is required. In this chapter, several weighting functions are employed in considering the effect of O_3 reduction on the global distribution of "effective" UV radiation. While these are illustrative, they need to be interpreted with a knowledge of the uncertainties inherent in the weighting functions.

Measurements of Environmental UV Radiation

Data Quality

Measurements of environmental UV radiation still present some difficulty, especially for the detection of long-term trends since high accuracy and stability are required. Significant advances have been made recently in assessing data quality through instrument characterizations, intercomparisons, and data re-analysis.

Several intercomparisons among different spectro-radiometers showed substantial differences among instruments *[Gardiner et al., 1993; McKenzie et al., 1993; Kirk et al., 1994]*, especially at the shortest wavelengths where the solar spectrum is steepest, and therefore

problems of dynamic range, stray light rejection, and wavelength calibration are most severe. At the present time, agreement to no better than about ±5 percent can be expected for wavelengths longer than ca. 310 nm, and the agreement is worse at shorter wavelengths.

Intercomparisons with broad-band and filter instruments are more difficult, due in part to calibration ambiguities that arise when the spectral shape of the solar spectrum changes under different solar zenith angle, O_3 column, and other atmospheric conditions *[DeLuisi and Harris, 1983]*. Extensive re-examination has been carried out for the most commonly used broad-band instrument, the Robertson-Berger (RB) meter. Its temperature coefficient (ca. 1 percent K^{-1}) has been determined *[Johnsen and Moan, 1991; Dichter et al., 1993; Blumthaler, 1993]*, and a new generation of temperature-stabilized instruments is now available. The spectral response of the RB instruments was found to be stable over more than a decade, although with some differences between different instruments *[DeLuisi et al., 1992]*. A review of calibration records by Kennedy and Sharp *[1992]* did not identify any significant problems. However, DeLuisi *[1993]* found calibration shifts in the long-term data record of the RB meter located at Mauna Loa. The magnitude, timing, and direction of these shifts are such as to produce an apparent negative trend in UV comparable to the decreasing UV trends reported by Scotto et al. *[1988]* for RB meters located in the continental USA over 1975-85. Smith and Ryan *[1993]* have also identified substantial variations between different RB instruments. Until a full re-analysis of the calibrations of the RB meter network is carried out, trends derived from RB meters must be viewed with caution.

Geographical and Seasonal Variations

High Latitudes

Very little UV irradiance data in the Antarctic are available before the discovery of the springtime O_3 hole. Baker-Blocker et al. *[1984]* reported measurements over 1979-81, but because their broad-band instrument was heavily weighted in the UV-A, no conclusions can be drawn about the pre-ozone hole UV-B record. The number of Antarctic UV measurements has increased greatly in recent years *[Lubin and Frederick, 1989, 1991; Lubin et al., 1989, 1992; Stamnes et al., 1990, 1992; Frederick and Alberts, 1991; Smith et al., 1992a,b; Beaglehole and Carter, 1992a,b; Booth et al., 1993, 1994; Roy et al., 1994; Frederick and Lubin, 1994; Helbling et al., 1994]*. The effect of the O_3 hole on UV levels is now clearly established. Figure 1.3 shows the UV radiation in two different wavelength bands, 298-303 nm (very sensitive to O_3) and 338-342 nm (relatively insensitive to O_3), measured at the south pole between early 1991 and early 1994. While the 338-342 nm band maximizes near summer solstice as expected, the 298-303 nm values reach their highest values in November, and show clearly the effects of the O_3 hole. Figure 1.4a shows that 1991 springtime DNA-damage-weighted UV radiation measured at the south pole was much higher than measurements obtained in Barrow, Alaska, for the same solar zenith angle. Visible radiation measurements at the same locations (Figure 1.4b) effectively

demonstrate that the higher UV at the south pole was not due to other atmospheric factors such as less cloud cover. Although the natural UV levels at high latitudes are usually smaller than at low latitudes, measurements now show (see Figure 1.5) that during the springtime ozone depletion the DNA-damaging radiation at Palmer Station, Antarctica (64°S) can exceed maximum summer values at San Diego, USA (32°N).

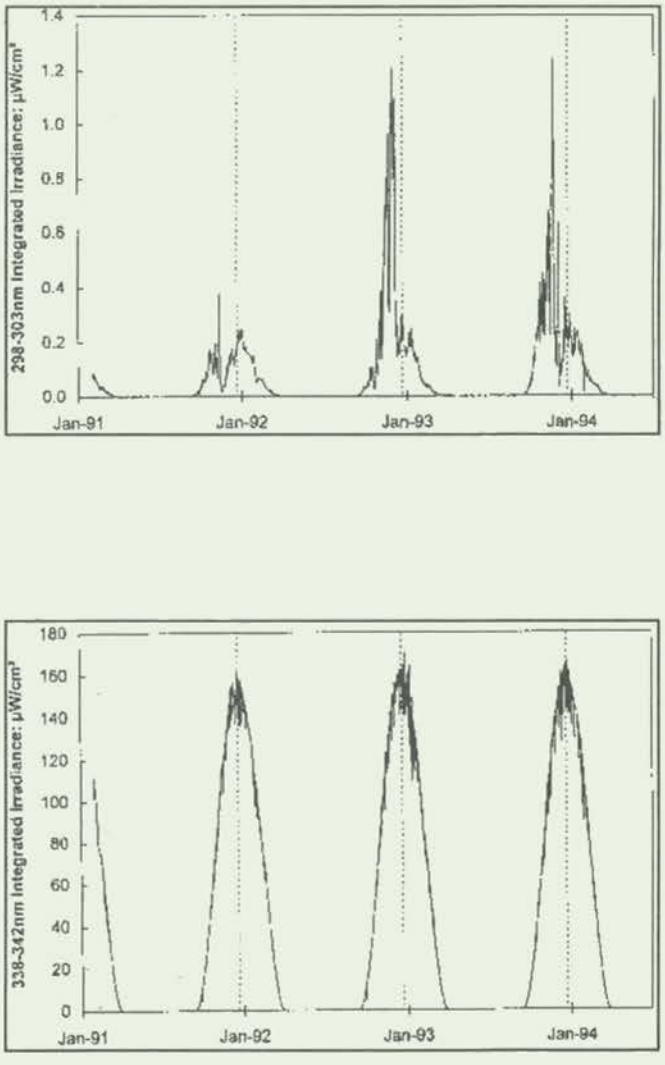


Fig. 1.3. Hourly irradiance integrated over 298-303 nm (top) and over 338-342 nm (bottom), at the South Pole between 1991 and 1994. Vertical dotted lines mark the summer solstices. From Booth et al. *[1994]*.

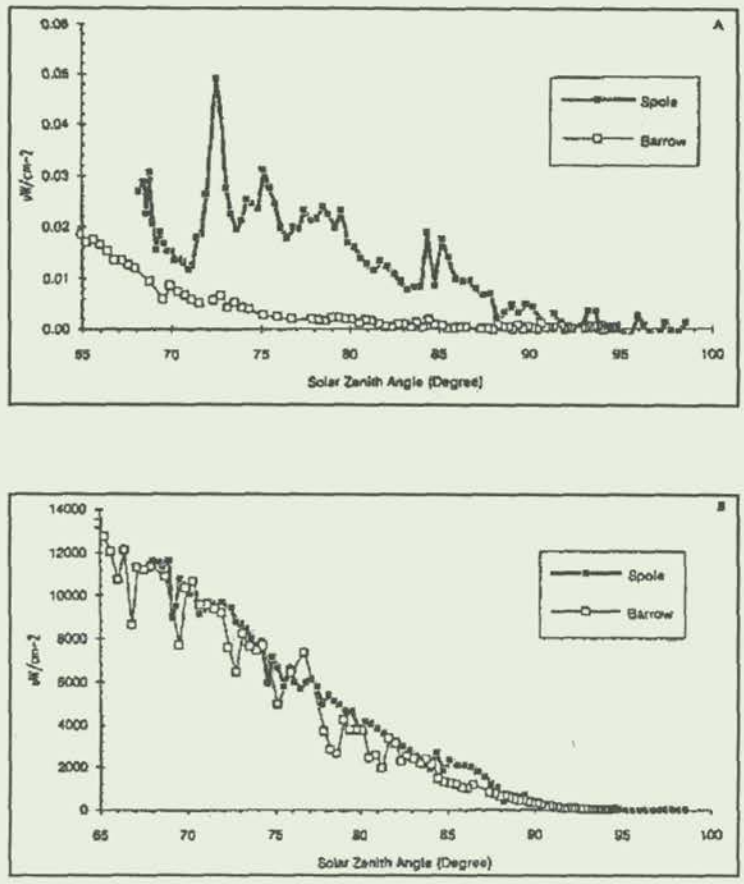


Fig. 1.4. Comparison of 1991 springtime radiation at South Pole and Barrow (Alaska). (a) DNA-weighted UV irradiance; (b) 400-600 nm integrated irradiance. From Booth et al. *[1993]*.

Northern hemisphere polar regions experienced anomalously low O_3 levels in 1992 and 1993 (see below). Spectral measurements obtained at Barrow during the spring of 1991-94 show the expected increases in UV radiation associated with low O_3, and a return to more normal levels in 1994 *[R. Booth, private communication, 1994]*.

Other Latitudes

Measurements at many locations are providing a more clear characterization of the geographical variations of ground-level UV. The RB meter network *[Scotto et al., 1975, 1988; Cotton, 1990]* has confirmed the general higher UV-B levels at lower latitudes in the US. Other RB meter measurements also confirm the broad latitudinal differences, e.g., in Russia *[Garadzha and Nezval, 1987]*, Switzerland *[Blumthaler and Ambach, 1990]*, Malaysia *[Ilyas, 1987]*, and New Zealand *[Zheng and Basher, 1993]*, though detailed comparisons of local effects (e.g., pollution, cloudiness) has not yet been carried out. Multifilter measurements at 39°N, 77°W have been made since 1975 by Correll et al. *[1992]* and are continuing, but direct comparison to other instruments is difficult because of the different spectral response.

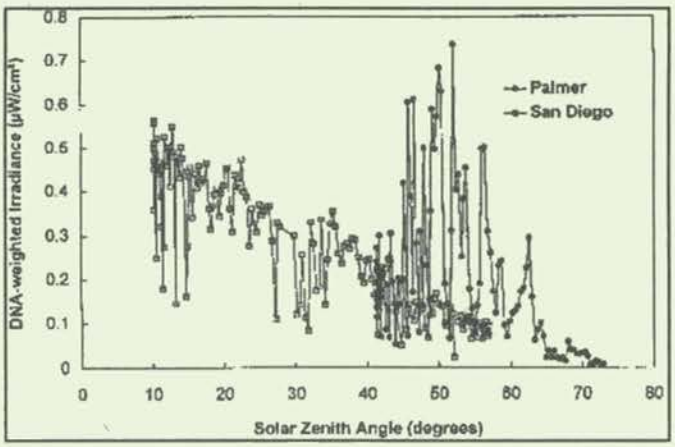


Fig. 1.5. DNA-weighted noon irradiances measured in 1993 at Palmer Station, Antarctica (64°S) and in San Diego, USA (32°N). (Courtesy R. Booth, 1994).

Spectral measurements show higher summertime values of UV-A and UV-B radiation in Lauder (New Zealand) and Melbourne (Australia) compared to Neuherberg (Germany) *[Seckmeyer and McKenzie, 1992; McKenzie et al., 1993]*, due to the yearly cycle of the sun-earth distance, and to lower stratospheric O_3 levels in the southern hemisphere and higher tropospheric pollutant levels (O_3 and aerosols) in Germany. Enhanced southern hemisphere UV-B levels are also evident from measurements in Ushuaia, Argentina (55°S) *[Diaz et al., 1991, 1994; Frederick et al., 1993b]*, where in December 1991 the average noontime clear sky radiation at 306.5 nm was 45 percent larger than calculated from the O_3 climatology of the previous decade.

Additional mid-latitude spectral measurements *[Bais et al., 1993, 1994; Gardiner et al., 1993; Blumthaler, 1993; Blumthaler et al., 1993, 1994; Seckmeyer et al., 1994; Booth et al., 1993; Ito, 1993; Kerr and McElroy, 1993; Kirk et al., 1994; Cabrera et al., 1994]* have recently contributed to a growing UV data base, and systematic compilation of the data, though not yet achieved, should provide a reasonable picture of mid-latitude UV distributions.

Other Factors Affecting UV

Clouds

The importance of clouds to surface UV is well established. Analysis of the long-term RB meter data from various locations in the US shows that monthly average UV levels are reduced by 10-50 percent, depending on season and location *[Frederick and Snell, 1990; Frederick et al., 1993a]*. Empirical parameterizations based on the fraction of occluded sky observed from the surface have been developed in Malaysia, the United States, Sweden, and Australia

[Ilyas, 1987; Cutchis, 1980; Josefsson, 1986; Paltridge and Barton, 1978; Ito, 1993]. The results are scattered and non-linear, with as much as 70-80 percent reductions at full cover, and average reductions in the 10-50 percent range. The parameterizations should be viewed as highly approximate and applicable only to the cloud types that are characteristic of the different locations of the studies.

Aerosols

Tropospheric aerosols, e.g., sulfate, reduce UV levels significantly in polluted regions *[Liu et al., 1991]*. Seckmeyer and McKenzie *[1992]* estimated that aerosols had only a minor effect in the contrast between UV irradiances in New Zealand and Germany. However, Seckmeyer et al. *[1994]* measured substantial UV-A and UV-B reductions on a day with high turbidity, compared to a day with low turbidity. Cabrera et al. *[1994]* found larger UV-A gradients with elevation in relatively polluted areas compared to pristine regions of Chile. Justus and Murphey *[1994]* analyzed RB meter data over 1980-84 for Atlanta, Georgia, and attributed the observed 10 percent decrease to local or regional aerosols. Thus, although an effect appears to exist, its magnitude is still not well defined.

The effect of stratospheric sulfate aerosols on surface UV irradiance has been of increased interest since the eruption of Mt. Pinatubo in June 1991. Scattering of the incoming UV radiation by the aerosol may decrease surface irradiance at long wavelengths, but may also change the photon pathlengths through stratospheric O_3, resulting in increased surface irradiance under some conditions (short wavelengths, large solar zenith angle *[Michelangeli et al., 1992; Davies 1993]*). The net effect on biologically weighted radiation is expected to be a relatively small decrease *[Madronich et al., 1991; Vogelmann et al., 1992]*. Spectral measurements show a marked increase in the diffuse/direct UV ratio but little effect on the total radiation *[McKenzie, 1993; Blumthaler and Ambach, 1994]*. Stratospheric aerosols also influence surface UV levels indirectly through their effects on stratospheric O_3 chemistry.

Tropospheric Ozone and other Gaseous Pollutants

Brühl and Crutzen *[1989]* suggested that tropospheric O_3 may be a somewhat more effective absorber of UV radiation than stratospheric O_3, due to enhancement of photon pathlengths by scattering in tropospheric air. Frederick et al. *[1993a]* found a negative correlation between surface O_3 concentrations and RB meter readings in Chicago (USA). Cabrera et al. *[1994]* found larger increases with surface elevation for UV-B than for UV-A, consistent with a larger tropospheric O_3 column at the lower elevations. Other tropospheric gases (especially NO_2 and SO_2) may attenuate UV in some urban areas *[Frederick et al., 1993a; Bais et al., 1993]*, but are probably not important in less polluted regions.

Surface Albedo and Elevation

Surface reflections affect UV radiation both through direct reflections toward a target, and by enhancing the diffuse down-

welling radiation. The relatively sparse measurements of surface reflectivity (albedo) in the UV range have been reviewed recently by Madronich *[1993a,b]* and Blumthaler *[1993]*. Values usually fall below 10 percent for vegetation, but are highly variable for ice (7-75 percent) and snow (20-100 percent). High reflections may be of some importance to the geographical and seasonal UV distributions because they apply preferentially to colder climates.

UV levels are expected to be increase with increasing surface elevation above sea level because of the thinner overhead atmosphere. Measurements at remote locations in Chile show increases of 4-10 percent per km *[Cabrera et al., 1994]*, in agreement with model calculations for unpolluted air *[Madronich, 1993a]*. Other locations show much larger vertical gradients, up to 40 percent per km near Santiago, Chile *[Cabrera et al., 1994]*, and 9-23 percent per km in the Swiss Alps *[Blumthaler, 1993]*, presumably because the lower elevations experience more tropospheric ozone, aerosol turbidity, and possibly lower surface albedo.

Detection of Long-Term UV Changes

Several long-term records have been obtained using RB meters, and are subject to the cautions mentioned above. In Moscow, Garadzha and Nezval *[1987]* found a 12 percent decrease in the RB meter measurements of UV radiation over 1968-83, with a concurrent 15 percent increase in turbidity and a 13 percent increase in cloudiness. RB meter measurements taken over 1974-85 at eight different sites in the USA showed UV decreases of 0.5 percent and 1.1 percent per year *[Scotto et al., 1988]*. RB meter data obtained at a station in the Swiss Alps (3.6 km above sea level, 47°N) showed increases of 0.7±0.2 percent per year over 1981-89 *[Blumthaler and Ambach, 1990]*, persisting at 0.7±0.3 percent per year over 1981-91 *[Blumthaler, 1993]*. Zheng and Basher *[1993]* have found increases of about 0.6 percent per year in RB meter data over 1981-90 in New Zealand, anticorrelated with O_3 column data. Increases at high elevations and southern latitudes, together with possible decreases in industrialized northern hemisphere regions, are consistent with a role of local pollution, although RB meter calibration shifts may have also played a role (see above).

Multi-filter measurements by Correll et al. *[1992]* over 1975-90 at a single site in Maryland (USA) indicate that the maximum monthly mean UV-B irradiance was 13 percent higher in 1983-89 than for the entire data record, with an overall increase of 35 percent from 1977/78 to 1985, much larger than expected from actual O_3 reductions. However lower values were observed after 1987, and may be indicative of the role of the atmospheric factors such as cloud variability.

Kerr and McElroy *[1993]* monitored spectral UV radiation in Toronto (Canada) from early 1989 through August 1993, a period during which ozone levels changed by -4.1 percent per year during winter (December-March) and by -1.8 percent per year in summer (May-August). The corresponding UV changes were strongly wavelength-dependent, as shown in Figure 1.6, with the greatest increments occurring at the shortest wavelengths as expected from ozone reductions. Using a

similar instrument, Zerefos et al. *[1994]* found statistically significant increases of +9.7 percent per year at 305 nm and +0.1% per year at 325 nm at Thessaloniki (Greece) between November 1990 and November 1993. These large increases span a relatively short time and are influenced by the anomalously low ozone of 1992/93, so that they are better interpreted as a perturbation rather than a trend *[Michaels et al., 1994; Kerr and McElroy, 1994]*, but they demonstrate that ozone-induced changes in UV can be detected over a period of several years despite variability due to cloudiness and local pollution, particularly at the shortest wavelengths.

Seckmeyer et al. *[1994]* found larger UV-B and simultaneously lower UV-A levels in 1993 relative to 1992 in Germany. The UV-A changes were attributed to the different average cloud cover, and the UV-B enhancements are consistent with independently measured lower O_3 values, 322 Dobson Units (DU) in 1993 compared to 342 DU in 1992, May-July averages. Enhanced peak RB meter values, measured in Innsbruck (Austria) during 1993 winter/spring, were also found by Blumthaler et al. *[1994]*.

Limited evidence for long-term changes in the spectral distribution of surface UV radiation comes also from data collected by ground-based O_3 monitoring networks (see above). Most of these determine O_3 through a measurement of the ratio of UV at several wavelengths, either from the direct solar beam or the zenith sky. Long-term negative trends in O_3 reported by such networks are therefore indicative of long-term shifts of surface UV towards shorter wavelengths.

Trend detection remains a problem due to the sparsity of reliable long-term data. It is likely that the opportunity to measure the historical natural UV baseline levels (i.e., pre-ozone depletion) has already been lost over most of the globe, and will not return until the ozone layer returns to its natural state.

Evaluation of Radiative Models

The geographical coverage possible with radiative transfer models is limited only by the available atmospheric data which, if derived from satellites, can span the entire globe. Therefore, such models are an important complement to UV measurements. Models are also an essential aid in identifying the causes of observed UV changes, to carry out sensitivity studies, and ultimately to predict future UV environments under different atmospheric O_3 reduction scenarios.

The theory of scattering and absorption of atmospheric radiation is well established, and there is no scientific doubt that, all other factors being held constant, O_3 reductions are accompanied by predictable increases in surface UV radiation. However, models require as input the optical characteristics of the atmosphere, and if these are poorly known, as is often the case with pollutants and clouds, model-calculated irradiances can be in serious error.

For cloud-free and low-aerosol sky conditions and known O_3 column, model irradiances generally fall within the experimental errors of both broad-band meters *[e.g., Jokela, 1993]* and spectroradiometers

[e.g., McKenzie et al., 1993; Kirk et al., 1994; Zeng et al., 1994; Wang and Lenoble, 1994]. The theoretical relationship between O_3 reductions and UV increases has also been confirmed in numerous studies *[Stamnes et al., 1988, 1990, 1992; Roy et al., 1990, 1994; McKenzie et al., 1991; Smith et al., 1992b; Seckmeyer and McKenzie, 1992; Bais et al., 1993; Frederick et al., 1993b; Holm-Hansen et al., 1993]*.

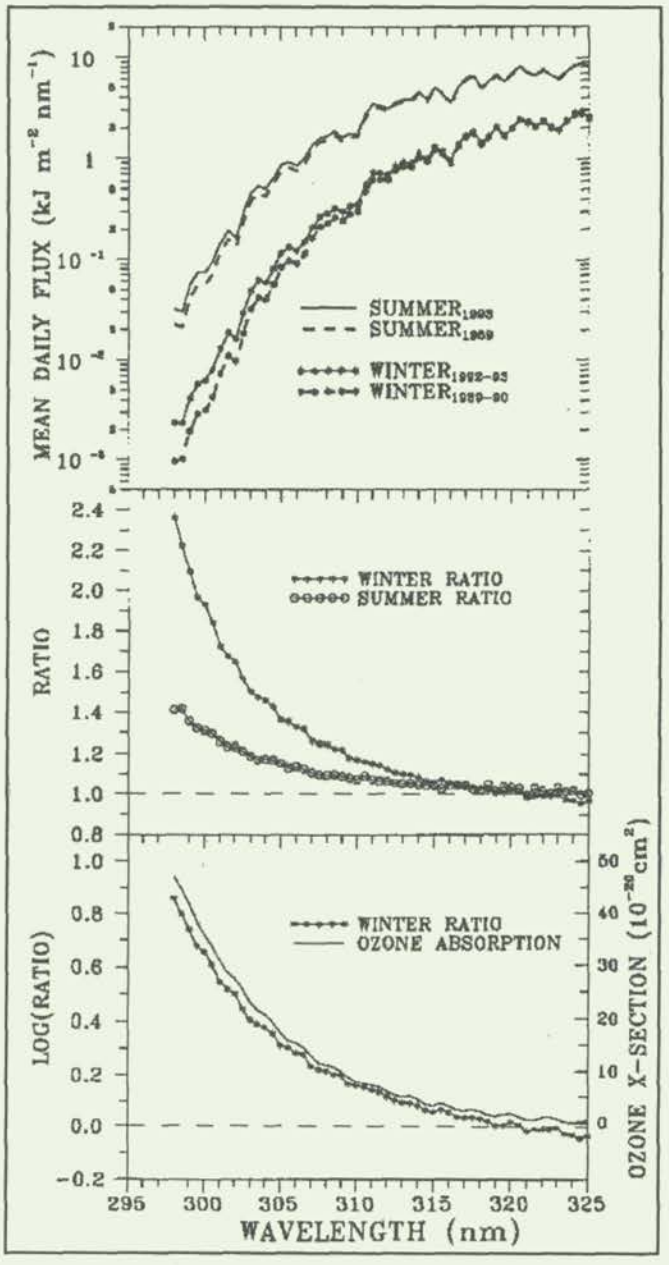


Fig. 1.6. Impact of low ozone over Toronto, Canada in 1992/1993 compared with earlier years. The top panel shows the median daily UV spectral irradiance for the summers of 1989 and 1993, and the winters of 1989-90 and 1992-93. The middle

panel shows spectral irradiance ratios for summer (1993 divided by 1989) and winter (1992-93 divided by 1989-90). The bottom panel compares the observed changes as a function of wavelength with the ozone absorption spectrum; the log of the winter ratio is used because the transmission of UV radiation depends on the exponent of the ozone absorption coefficient. Adapted from Kerr and McElroy *[1993]*.

Validation of the models is still a problem in the presence of clouds and tropospheric pollutants. Commonly used UV models are incompatible with the empirical formulations based on fractional cloud cover discussed in section above, either because they don't consider clouds at all, or idealize them as hori-zontal layers of homogeneous vertical optical depth that do not allow for partial coverage nor for realistic cloud morphology *[Frederick and Lubin, 1988; Madronich 1990, 1993a,b]*. Use of satellite images to estimate both areal coverage and optical depths is promising *[Lubin et al., 1994; Gautier et al., 1994]* but requires additional development and evaluation. Other highly variable factors such as aerosols and gaseous pollu-tants are seldom well characterized, which presents some difficulty for accurate modeling *[Liu et al., 1991]*.

Trends in Ozone and Implications for UV Radiation

Ozone Trends

The recent changes observed in atmospheric O_3 are described in the WMO *[1994]* report and summarized only briefly here. Measurements of the total O_3 column are made mainly by optical means from ground-based and satellite-based instruments. In addition, vertical profiles of O_3 concentrations are made from balloon-borne instruments. The rather large data set has elucidated the geographical and seasonal distribution of O_3. Ground-based Dobson instruments, developed in the 1920's, have increased in number and have been providing fairly wide geographic coverage since the 1960's. Other instruments, including the M-83 and M-124 filter ozonometer, the Brewer, and the SAOZ spectrometer, have shorter data records. True global coverage began in the late 1970's with the deployment of the Nimbus 7 satellite carrying the Total Ozone Mapping Spectrometer (TOMS) and the Solar Backscatter Ultraviolet spectrometer (SBUV). The SBUV instrument ceased functioning in June 1990 and the TOMS in May 1993. The Nimbus 7 TOMS data have been analyzed extensively, and the version 6 data appear to be reliable at least through May 1990, but there is concern about additional calibration drifts after that date. SBUV/2 (on the NOAA-11 satellite) was launched in January 1989 and another TOMS instrument was launched in August 1991 (on the Russian Meteor 3 satellite). Both of these instruments are still functioning. The com-bined SBUV and SBUV/2 data records appear to be suitable for trend determinations. The Meteor 3 TOMS data have not yet been properly assessed for consistency with the earlier systems. Other satellite O_3 monitoring systems (TOVS, LIMS, SAGE I and II) are at the present

time less suitable due to incomplete detection of the total O_3 column, and some still unresolved calibration issues.

Statistically significant negative trends in total O_3 are found at all latitudes except possibly in the tropics, where ground-based measurement show no trend. Recent Dobson trends are larger (more negative) than long-term trends, suggesting greater O_3 reductions in the more recent years. The years 1992 and 1993, in particular, exhibited large negative anomalies in O_3, possibly related to the eruption of Mt. Pinatubo, with record low values measured at northern mid-latitudes. Total O_3 in early 1994 has largely returned to the trends observed before the Pinatubo eruption. The springtime Antarctic O_3 loss, first observed in the late 1970's, has continued as an annual event, and record low values (for the first time less than 100 DU) were observed at the South Pole in late September and early October 1993. The 1992 and 1993 O_3 holes appeared earlier and covered larger areas than those of earlier years.

Tropospheric O_3 accounts for about 1/10th of the total O_3, and tends to be highly variable, being associated with more polluted regions. Surface O_3 concentrations in Europe may have increased 3-4 fold since last century, and doubled since the 1950's. However, surface values may not be representative of the free troposphere. Analysis of vertical profiles from O_3 sondes indicates increases of about 10 percent per decade in the northern mid-latitudes, with strong regional patterns and largest increases over European and Japanese stations *[WMO, 1994]*. There is also some evidence for a slowing of the trends during the 1980's. In the southern hemisphere, surface O_3 levels show little or no trends, except for the polar regions where a decrease of about 7 percent per decade has been reported.

Calculated UV Radiation Trends

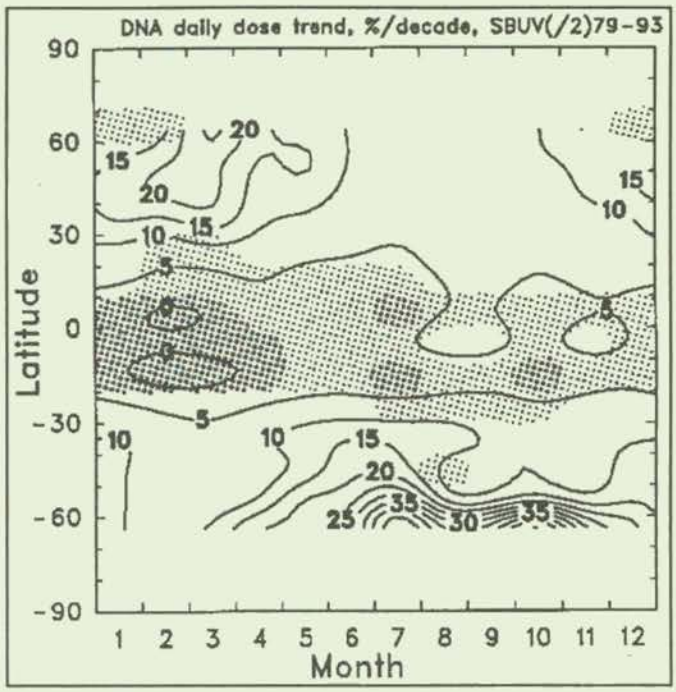
The Nimbus-7 TOMS O_3 data (version 6) over 1979/92 have been analyzed by Madronich and de Gruijl *[1993, 1994]* to infer the corresponding changes in UV radiation weighted by several biological action spectra. The TOMS data after May 1990 may be affected by a calibration drift which is not considered in the version 6 data. Here, the calculations of biologically weighted UV changes are repeated using the combined SBUV and SBUV/2 data, from January 1979 through December 1993.

The procedure to calculate trends in biologically effective doses is essentially unchanged. Briefly, the atmosphere is taken to be cloudless and aerosol-free, with 10 percent surface albedo, and standard vertical profile of O_3 scaled to the total column from SBUV(/2). The down-welling spectral irradiance is calculated at 1 nm intervals (279.5-399.5 nm), then integrated over wavelength using several biological action spectra to compute dose rates. This is repeated every 15 minutes for the 15th day of each month of the O_3 data record (January 1979-December 1993) in 10° latitude increments from 70°S to 70°N. The results are time-integrated to compute daily and yearly doses, and trends with their standard deviations are calculated by linear least-squares fitting.

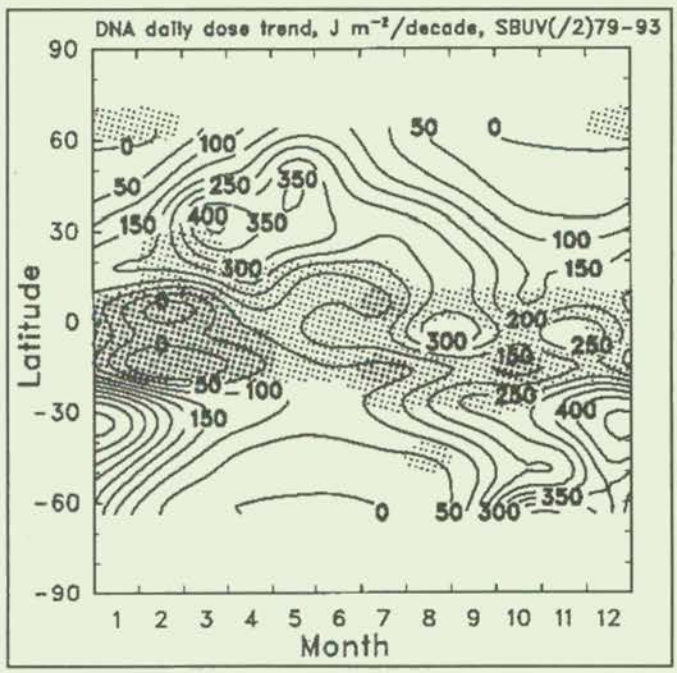
Figure 1.7 shows the trends in daily doses for UV radiation weighted by the action spectrum for *in vitro* DNA damage *[Setlow, 1974]*. The results are generally similar to those obtained with TOMS data over 1979-89 *[Madronich, 1992]* and over 1979-92 *[Madronich and de Gruijl, 1993, 1994]*. Relative increases (percent per decade, Figure 1.7a) are significant in both hemispheres at middle and high latitudes, and are largest in winter and spring. The relative increases in the tropics are small and probably not significant. Daily dose increments (J m^{-2} day^{-1} per decade, Figure 1.7b) are shifted toward summer and lower latitudes, i.e., toward higher natural UV levels.

Table 1.2 summarizes the increases over the 15-year SBUV(/2) data record for the annual doses for DNA damage, erythema induction in humans *[McKinlay and Diffey, 1987]*, and skin cancer induction in laboratory mice *[de Gruijl et al., 1993]* (see also Table 1.1). The largest increases are observed at high latitudes of the southern hemisphere. Significant increases are also found in the northern high latitudes, and the mid-latitudes of both hemispheres.

Some regions, particularly in the Northern Hemisphere, have experienced increased tropospheric pollution (mostly sulfate aerosol and ozone) during the last century. It has been estimated that the corresponding UV (DNA-weighted) could have been reduced by 6-18 percent from the sulfate aerosol increases *[Liu et al., 1991]* and by 3-10 percent from the tropospheric ozone increases *[UNEP, 1991]* in some industrialized regions. However, no direct information exists on pre-industrial stratospheric ozone, precluding accurate estimates of the net UV changes. More recent tropospheric ozone trends in industrialized regions are estimated to contribute at most 2 percent per decade to the DNA-weighted UV, compared to +5 to +11 percent per decade from mid-latitude ozone reductions *[UNEP, 1991]*. Sulfur emissions have recently decreased in some regions while increasing in others *[NRC, 1986]*, and the corresponding UV changes are expected to reflect such local variations.



a.



b.

Fig. 1.7. Trends in daily DNA-damaging radiation based on SBUV(/2) total O_3 measurements over 1979-93. Heavy shading indicates regions where trends differ from zero by less than one standard deviation (1s), light shading by more than 1s but less than 2s

(a) Fractional trends, in percent per decade relative to 1979-93 average values; (b) energy trends, J m^{-2} day^{-1} per decade with action spectrum normalization at 300 nm.

Table 1.2. Annual UV exposures estimated from stratospheric ozone measurements between 1979 and 1993[a].

Latitude	Erythema annual dose (MJ m^{-2})	Percent increase during 1979-1993		
		Erythema induction	DNA damage	Skin cancer
65 N	0.47	5.6±2.1	10.3±3.8	7.9±2.9
55 N	0.68	6.6±1.8	11.6±3.3	8.9±2.5
45 N	1.01	8.6±1.9	14.5±3.3	11.1±2.4
35 N	1.46	7.9±1.9	13.0±3.1	9.8±2.3
25 N	1.94	6.0±1.9	9.6±3.0	7.1±2.2
15 N	2.35	4.0±1.5	6.3±2.4	4.7±1.7
5 N	2.58	2.6±1.7	4.1±2.7	3.0±2.0
5 S	2.58	3.2±1.5	5.1±2.3	3.0±1.7
15 S	2.34	1.8±1.4	2.8±2.1	2.0±1.6
25 S	1.95	5.4±1.5	8.7±2.4	6.4±1.8
35 S	1.49	8.0±1.5	13.2±2.4	9.8±1.8
45 S	1.06	8.0±3.9	13.6±3.2	10.2±2.4
55 S	0.73	10.7±2.8	18.8±5.1	14.2±3.8
65 S	0.51	20.4±4.4	37.2±8.2	27.1±6.1

(a) Computed using monthly and zonally averaged ozone column data measured from SBUV and SBUV/2 satellite instruments between January 1979 and December 1993. Annual doses (only erythemal is shown) are 1979-93 averages. Percent changes are expressed relative to the 1979-93 annual averages. Uncertainties are one standard deviation.

Long term changes in cloud cover may also affect ground-level UV radiation. Surface observations at a few continental and marine locations suggest some long term cloudiness increases, but there is yet no confidence that such changes have occurred on global scales *[IPCC, 1991]*. The implications of such changes for surface UV levels have not been quantified. Global space-based observations of clouds *[e.g., Rossow et al., 1991]* are becoming available, but the record is still of insufficient length for trend detection.

Future Trends

With continued full compliance to the Montreal Protocol and its amendments, it is expected that stratospheric chlorine will peak around the year 1998, with a slow recovery over the subsequent 50 years *[WMO, 1994]*. Model simulations of stratospheric ozone indicate that the peak global ozone depletions will also occur in the next several years, with recovery over the next half-century. Relative to 1960, the maximum ozone depletion expected at northern mid-latitudes is 12-13 percent in winter/spring, and 6-7 percent in summer/fall. The depletion at southern mid-latitudes will be approximately 11 percent (all seasons). However, it should be noted that there are some differences among the predictions of different models, and between modeled and observed trends to date. Furthermore, model predictions may be altered significantly by events such as volcanic eruptions of magnitude comparable to that of Mt. Pinatubo.

The corresponding changes in biologically-weighted UV irradiances can be estimated using the RAFs in Table 1.1. The estimated UV increases for erythema induction and DNA damage are, respectively,

15-17 and 29-32 percent (northern hemisphere mid-latitudes, winter/spring), 8-9 and 12-15 percent (northern hemisphere mid-latitudes, summer/fall), and 15 and 25 percent (southern mid-latitudes, all seasons).

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CHAPTER 2

EFFECTS OF INCREASED SOLAR ULTRAVIOLET RADIATION ON HUMAN HEALTH

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Summary

The increase in UV-B associated with stratospheric ozone depletion is likely to have a substantial impact on human health. Potential risks include increases in the incidence of, and morbidity from, eye diseases, skin cancer, and infectious diseases. Quantitative estimates of risk are available for some effects (e.g., skin cancer), while for others (e.g., infectious diseases), quantitative estimates are not possible due to a lack of sufficient data.

UV radiation has been shown in experimental systems to damage the cornea and lens of the eye. Chronic exposure to UV-B (resulting in a high, cumulative, lifetime dose) is one of several factors clearly associated with the risk of cataract of the cortical and posterior subcapsular forms. Estimates of the effect of ozone depletion on cataract have been made, but are still highly uncertain. (As stated in the 1989 report, *[van der Leun, et al., 1989]* these estimates predict an approximately 0.5 % increase in cataract for each 1% sustained decrease in ozone.)

Some components of the immune system are present in the skin, which makes the immune system accessible to UV radiation. Experiments in animals show that UV exposure decreases the immune response to skin cancers, infectious agents, and other antigens and can lead to unresponsiveness upon repeated challenges. Suppressed immunity may occur either locally in sun-exposed skin or systematically, at non-exposed sites. Studies in human subjects also indicate that exposure to UV-B radiation can suppress the induction of some immune responses and may cause systemic alterations in immune function. The importance of these immune effects for infectious diseases in humans in unknown. However, in areas of the world where infectious diseases already pose a significant challenge to human health, and in persons with impaired immune function, the added insult of UV-B-induced immune suppression could be significant.

In susceptible (light-skinned) populations, the cumulative lifetime exposure to UV-B radiation is the key risk factor for

development of non-melanoma skin cancer (NMSC). This knowledge has permitted the development of quantitative risk estimates for increases in the incidence of NMSC resulting from ozone depletion. Using information derived from animal experiments and human epidemiology, it is estimated that a sustained 1% decrease in stratospheric ozone will result in an increase of NMSC incidence of approximately 2.0% The relationship between UV-B exposure and melanoma skin cancer is less well understood and appears to differ fundamentally from that of NMSC in that it is not apparently a function of cumulative lifetime dose but may be related to the accumulation impact of multiple high dose exposures such as those received in sunburns. Epidemiologic data indicate that the risk of melanoma increases with an increase in episodes of intense sunlight exposure, (i.e. sunburn) especially during childhood. There is, however, uncertainty about how the relationship between these exposures and melanoma should be modeled so that the estimates of the increase in melanoma that would result from ozone depletion are much less certain.

Introduction

As presented in detail in chapter 1, solar ultraviolet radiation (UVR) illuminates nearly everything and everyone on the earth's surface not covered or shadowed. With stratospheric ozone depletion, increases in the ambient levels of a particular type of ultraviolet radiation known as UV-B are likely to occur. In humans and animals, the primary (i.e., direct) effects of increases in UV-B on health are manifest through those organs which are exposed to sunlight, i.e., eyes and skin. These effects occur because of the absorption of UV-B photons by molecules in these organs and the resulting tranfer of energy to produce changes that may be either beneficial or adverse. A direct beneficial influence of exposure is the formation of Vitamin D in the skin, a process important to the maintenance of bone tissue. Direct adverse effects of exposure to UV-B include snow blindness, cataract, sunburn, "aging" of the skin, photodermatoses and skin cancer. Some effects may have both beneficial or adverse elements, depending on how they are expressed. This applies, for instance, to the influences of UV-B radiation on the immune system. The resulting suppression of immune reactions in the skin is beneficial in patients suffering from psoriasis, (a hyperproliferative skin disorder) but adverse when it affects the immune defense against skin tumors or infectious agents. In addition, there may be indirect beneficial or adverse effects. An example indirect adverse effect could be the increase in disease associated with the potential decrease in food production discussed in chapter 3.

The question to be addressed by the present chapter is, what will be the human health consequences of an increase in the UV-B radiation reaching the surface of the earth? One cannot simply say

that all effects of UV-B radiation will change in proportion to the increase in radiation, because in many cases, the relationship between the amount of exposure and effect is non-linear. For example, exposure of the skin to UV-B radiation results in a hyperproliferation of skin cells and increased pigment production providing the skin with efficient protection against sunburn through the increase in the UV absorbing molecules, keratin and melanin. The hyperproliferation of skin cells may, however, also render the skin more susceptible to cancer. In some instances, the modifying influences may be so strong that greater doses of radiation lead to smaller effects.

For example, photodermatoses are skin diseases where the skin lesions are caused by light. Solar UV-B radiation is the predominant causative agent for several of these diseases. Although many patients and their doctors expect an aggravation of these diseases with a decreased ozone layer, there are reasons to question this expectation. In the first place, these diseases generally occur less frequently and with less severity in sunny areas of the world. Second, many patients with photodermatoses are treated effectively by regular exposures to low-dose UV-B radiation during winter. Because depletion of the ozone layer will increase UV-B irradiance, especially in winter, this may improve the patients' condition *[van der Leun and de Gruijl, 1993]*.

Due to such complications, and due to the limited knowledge we have on some of the effects of UV-B radiation on humans, the overall consequences of an increase of UV-B irradiance on health cannot be predicted in a straightforward manner. This section, therefore, presents both qualitative and quantitative answers to the question of what the consequences of stratospheric ozone depletion and its accompanying increase in UV-B may be for human health. Quantitative estimates of UV-B effects are presented for non-melanoma skin cancer; however, the impact of UV-B exposure on other effects has been treated qualitatively. It should be stressed that the dependence on qualitative estimates for some effects does not imply that these are less significant; indeed, the quantitative estimates should be treated very cautiously because they involve many assumptions, are based on data mainly from the United States, and may not be representative of all regions of the world.

Ocular Effects

Background

Perhaps the best documented short-term ocular effect of exposure to UV radiation (especially UV-B and UV-C) is photokeratoconjunctivitis ('snow blindness' and 'welder eyes'), i.e., an inflammatory reaction (a reddening) of the surface of the eyeball. Extraordinarily painful, one episode should be sufficient to induce behavior modification to prevent recurrences, e.g., the use of proper eye protection. The effects of long-term or chronic

exposures, e.g., pterygium or cataract, are less well documented in part because they result after many years of exposure, and, in part, at least for cataract, because many other factors are known to have etiologic role. For such endpoints, as with endpoints such as NMSC, causality has to be inferred from epidemiological studies supported by animal experiments. For a much more detailed review of this subject, the reader is referred to Pitts and Kleinstein *[1993]*.

Epidemiological Data

Epidemiological data indicate that chronic sunlight exposure is associated with pterygium, an outgrowth of the conjunctiva (outermost mucous layer) over the neighboring cornea (overlying the lens), and with climatic droplet keratopathy, a degeneration of the corneal stroma (fibrous layer of tissue of the cornea) with droplet- shaped deposits *[Doughty and Cullen, 1989, and Hollows, 1989]*. Climatic droplet keratopathy can be a major cause of blindness. Both of these conditions are common in certain geographical locations, especially in snowy or sandy areas.

Sun exposure is also thought to be a contributing factor in the development of cataract, an opacity in the crystalline lens of the eye (for an extended analysis, see *Dolin 1994*). The World Health Organization (WHO) estimated in 1985 that cataract was the main cause of avoidable blindness, responsible for 17 million cases of blindness worldwide (about half of the total) *[Maitchouk, 1985]*.

The etiology of cataract in humans is multifactorial; increased relative risks are associated not only with increased exposure to UV-B, but also with increasing age, diabetes, renal failure, severe diarrhea, heavy smoking, hypertension, high alcohol consumption, excessive heat, and malnutrition *[e.g., Harding and Van Heyningen, 1987]*. The increase in relative risk associated with increased UV-B exposure is 1.3 to 3.5-fold, compared to diabetes which has a relative risk increase of approximately 10-fold. However, because of the nearly universal exposure of humans to solar UV radiation, the size of the population likely to be affected by this factor is significantly greater than for any of the other factors (except age) listed above.

In comparing epidemiological studies, two things must be kept in mind: 1) there are differences in the precise definition of cataract since the form of the disease can vary from small opacities which do not impair vision to a completely opaque lens with severe loss of vision, (furthermore, there can be variation between clinicians, and techniques; future studies would benefit from standardization of classifications) and 2) there are different types of cataract that show differing associations to the factors discussed above. Exposure to solar UV radiation appears specifically to increase the risk of cortical opacities (including opacities not impairing vision): a clear UV dose-related trend in risk was established in a well designed, cross-sectional study of

Chesapeake Bay watermen *[Taylor et al., 1988]*. This UV exposure-associated increased risk of cortical opacities was confirmed for the male population in the Beaver Dam Eye Study (an odds ratio of 1.36 between numbers with 'high versus low exposures', 95 percent confidence interval 1.07-1.79), but the risks of other types of lens opacities, i.e., nuclear and posterior subcapsular cataract, were not detectably increased by UV exposure *[Cruickshanks et al., 1992]*.

The relationship between sunlight exposure and vision-impairing cortical cataract was confirmed in a large case-control study drawn from three Italian opthalmology clinics *[Italian-American Study Group, 1991]*. Increased odds ratios for cortical cataract were found for working outdoors (1.75, 1.15-2.65) and spending leisure time in sunlight (1.45, 1.09-1.93); these increased odds ratios were also found for the mixed cataract, but not for posterior subcapsular and nuclear cataract. However, posterior subcapsular cataract is relatively rare, making detection of risk in a small population difficult. In a special case-control study in the Chesapeake Bay area on 168 surgical cases involving this type of cataract, a highly significant ($p = 0.006$) positive trend was established between risk and exposure to ambient UV radiation *[Bochow et al., 1989]*.

The relationship between geographical location (latitude) and prevalence of cataracts has also been attributed to ambient UV radiation; e.g., in Aborigines *[Hollow and Moran, 1981]* and in the North American population *[Hiller et al., 1983]*. The latter study provided the basis for the USEPA risk estimates for increases in cataract from ozone depletion *[USEPA 1987]*.

Experimental Data

There is ample experimental evidence that UV radiation can damage the lens and that in rabbits the active portion of the solar spectrum lies in the UV-B region *[Pitts et al., 1977]*. In albino mice, regular UV-B exposure (1 to 2 months of daily exposure) can disrupt the anterior (frontal) part of the lens, resulting in opacities *[Jose and Pitts, 1985]*. High dose, daily UV-A exposure also induced opacities in the anterior lens of nocturnal animals and squirrels *[Zigman et al., 1991]*. However, experimentally-induced opacities in animals are located centrally in the anterior lens (the irradiated zone), whereas human anterior cortical cataracts tend to form in the periphery (the equatorial region) of the lens. Also, microscopic examination of experimental cataract commonly shows marked disruption of the lens epithelium and inward folding of the underlying cortical fibers, which is not seen in human cataract. These differences, while possibly attributable to differences between animals and humans in geometry, level of exposure and/or ocular structure, contribute to the uncertainty associated with extrapolating from data in mice to human cataract risk.

Solar UV Exposure of the Human Eye

The exposure of the unprotected eyes to solar UV radiation is significantly influenced by the shielding from the eyebrows and eyelids (through squinting) and is strongly dependent on the direction of the line of sight. Highly reflecting surfaces increase the exposure dramatically; for example, the risk of photokeratoconjunctivitis is strongly increased over snow surfaces *[Sliney, 1987]*. This variability in exposure can seriously complicate studies in which eye exposures in different environments are compared unless careful exposure measurements are made. *[Rosenthal et al., 1991]*.

In humans, the anterior eye is not only exposed to light entering along the line of sight, but also to light impinging from very oblique angles. Coroneo *[1993]* drew attention to the phenomenon in which impinging (UV) light, especially that entering the eye at a very oblique angle, can be focussed onto the overlying periphery of the cornea and the lens; this would intensify the light while it is traversing the cornea and the lens in a direction roughly perpendicular to the line of sight. This phenomenon could explain not only the sites of preference for pterygium and climatic droplet keratopathy, but also why many cortical cataracts occur in the nasal quadrant of the lens *[Schein et al., 1994, Adamson et al., 1991, Hollow, 1989, and personal communication with Dr. B. Klein for the Beaver Dam Eye Study]*.

Impact of Ozone Depletion on Eye Conditions

In view of present data, it is prudent to consider that a depletion of the ozone layer could be associated with an increase in the incidence of cataract and other ocular effects of UV-B, e.g., pterygium and snow blindness. It is, however, difficult to estimate the magnitude of the increase without adequate information on the wavelength dependence of these effects and proper dose-response relationships. In the case of cataract, by assuming a certain wavelength dependence and with some additional assumptions, one can produce an estimate based on epidemiological data (e.g., an estimate from EPA based on Hiller et al., *[1985]*, cited in van der Leun *[1989]*, and one from van der Leun and de Gruijl, *[1993]*, based on Taylor et al., *[1988]*, and Pitts et al. *[1977]*: 0.3-0.6% and 0.5% increase in cataract, respectively, for every 1% decrease in ozone) but such an estimate has a high degree of uncertainty. A similar quantitative estimate is not yet possible for snow blindness, pterygium and climatic droplet keratopathy because of the inadequacy of epidemiologic information and experimental data. Nevertheless, it is prudent public health policy to indicate to medical personnel and the lay public that these are effects which may well increase with increased exposure to UV-B.

Immunological Effects

Background

Through a variety of complex, delicately balanced mechanisms, the immune system helps maintain health by protecting the host against infectious diseases and some cancers. The two most important of these mechanisms are 1) humoral immunity, involving the production of antibodies that can neutralize toxins, kill microorganisms, prevent infection, and assist in the elimination of infectious agents, and 2) cellular immunity, involving the production of chemical mediators (cytokines) by lymphocytes which activate other cells of the lymphoid system to kill pathogens, virus-infected cells, and cancer cells. These two arms of the immune response, humoral and cellular, are delicately balanced, and some cytokines involved in activating one pathway tend to inhibit the other. A severe imbalance in either direction can lead to pathological conditions, such as allergies and inflammatory and autoimmune diseases.

Because skin is an important immunological organ, the immune system is vulnerable to modification by environmental agents, including UV-B radiation. Demonstrations that systemic immunity can be perturbed by exposing skin to UV-B radiation raise the concern that ozone depletion might adversely influence immunity to infectious diseases.

Immunomodulatory Effects of UV-B Radiation

There is now ample evidence that exposure of humans and experimental animals to UV-B radiation from artificial or natural sources can modify the immune system both at the site of exposure (locally) as well as systemically, mainly by decreasing cellular immune responses *[Hersey et al., 1983; Morison, 1989; Kripke, 1984, 1990; DeFabo and Noonan, 1993; Cruz and Bergstresser, 1988]*. The immunosuppressive effects of UV-B radiation have been shown to play an important role in determining the outcome of both melanoma *[Donawho and Kripke, 1991]* and non-melanoma skin cancer [Kripke, 1984; 1990; Fisher and Kripke, 1982], certain infectious diseases *[Jeevan and Kripke, 1993]*, and some forms of autoimmunity *[Ansel et al., 1985]* and allergy, e.g., delayed type hypersensitivity *[Kripke, 1984; Cruz and Bergstresser, 1988, Noonan et al., 1981]* in laboratory animal models of these diseases. Furthermore, introduction of a foreign substance (antigen) during a critical period after UV irradiation can lead to immunological tolerance, rendering the host unresponsive to re-introduction of the same antigen at a later time *[Kripke, 1984]*.

In addition to these systemic effects on immune responses, UV-B irradiation can also inhibit local inflammatory responses within UV- irradiated skin; thus, the response elicited by injection of antigen into the skin of sensitized individuals (delayed hypersensitivity response) may be diminished in UV-irradiated skin *[Morison, 1989]*. Such local effects of UV irradiation can also

decrease resistance to the growth of cancer cells, including melanomas *[Donawho and Kripke, 1991]*.

Information on the UV-induced alterations in immune function in humans is fairly limited and is drawn principally from experimental studies of the impact of UV exposure on natural killer cell activity, contact allergy (e.g., poison ivy) and delayed hypersensitivity responses (e.g., the tuberculin skin test reaction) *[Hersey et al., 1983; Morison, 1989; Yoshikawa et al., 1990; Cooper et al., 1992]*.

Mechanisms

In recent years, many advances have been made in our understanding of the cellular and molecular mechanisms involved in modulation of immune responses by UV-B exposure. Studies with mice provide strong evidence that at least some of the immunomodulatory effects of UV irradiation result from the production and release of immunologically-active cytokines and other substances from cells in the skin. Interleukins 1 and 10 (IL-1, IL-10), tumor necrosis factor (TNF)-alpha, urocanic acid (UCA), and prostaglandins have all been suggested as contributors to the altered immune responses observed in UV-irradiated animals *[DeFabo and Noonan, 1983, 1993; Rivas and Ullrich, 1992, 1994a; Noonan et al. 1988; Vermeer and Streilein, 1990; Luger and Schwartz, 1990]*.

The ability of UV-irradiated keratinocytes to produce IL-10 *[Rivas and Ullrich, 1992]* is particularly noteworthy, because this cytokine preferentially decreases delayed hypersensitivity responses, leaving humoral responses undiminished *[Mossman et al., 1991]*. IL-10 is thought to alter the cells that initially take up antigens (mainly macrophages, epidermal Langerhans cells, and dendritic cells in lymphoid organs) and inhibit their ability to stimulate the subset of murine helper T lymphocytes responsible for generating delayed hypersensitivity responses (Th1 cells), while leaving intact their ability to stimulate Th2 lymphocytes, which are involved in antibody formation and suppression of Th1 cells *[Ullrich, 1994; Rivas and Ullrich, 1994]*. Figure 2.1 presents one possible model for how these various factors and events may operate in UV-B induced immunosuppression.

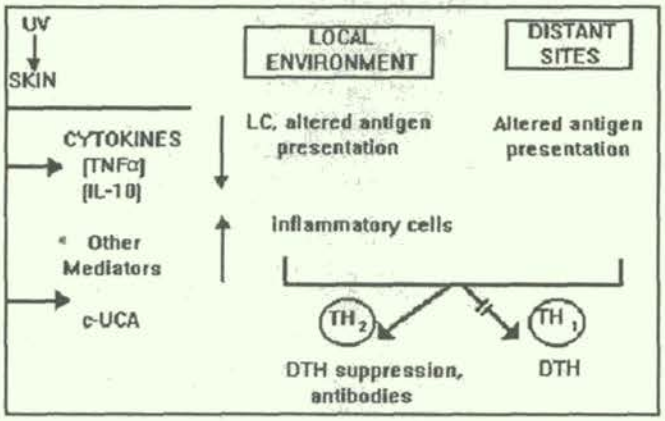

Fig. 2.1. Model for UV-B Induced Immunosuppression. (See text for details; *Cruz and Bergstresser, 1988; Kripke, 1984; DeFabo and Noonan, 1993; Luger and Schwartz, 1990; Rivas and Ullrich, 1994)*

There is also evidence that the cis-photoisomer of UCA can alter the ability of antigen-presenting cells to stimulate T lymphocytes *[Noonan et al., 1988]* and that TNF-alpha *[Vermeer and Streilein, 1990]* can alter the migration pattern of antigen-presenting cells in the skin (epidermal Langerhans cells). Direct exposure of epidermal Langerhans cells to UV-B radiation may also alter their antigen- presenting activity *[Simon et at., 1990; 1991]*, and UV irradiation of the skin induces an inflammatory response that attracts other types of antigen-presenting cells into the UV-irradiated site *[Cooper et al., 1993]*.

Thus, UV radiation appears to alter the induction of immune responses by perturbing the balance of factors that normally regulate the immune response and by altering the activity and distribution of the cells responsible for triggering these immune responses. The mechanisms involved in the local inhibition of delayed hypersensitivity and tumor resistance are unknown, but they are likely to involve local modifications of cytokines and other mediators [Luger and Schwartz, 1990] and changes in the expression of adhesion molecules on cells of various types in the skin *[Krutmann et al., 1992]*.

The molecular events that initiate photoimmunological effects are incompletely understood. Studies in the mouse *[Kripke et al., 1992; Yarosh et al., 1994]* and the opossum *[Applegate et al., 1989]* demonstrated that increasing the repair of UV-specific lesions in DNA abrogated the suppression of contact allergy and delayed hypersensitivity reactions, implying that UV-induced DNA damage is an essential initiating step. These authors hypothesized that DNA

damage may trigger the production of immunoregulatory cytokines in the skin [Kripke et al., 1992].

Another mechanism by which UV irradiation could initiate immunosuppression is by converting trans-UCA to its cis-isomer. Trans- UCA is present in large quantity in mammalian epidermis; the more soluble cis-isomer is formed upon absorption of UV radiation. There is considerable evidence that cis-UCA suppresses certain immune reactions in mice, suggesting that UCA may also mediate some of the immunomodulatory effects of UV irradiation *[DeFabo and Noonan, 1983, 1993]*.

Wavelength Dependence of Immune Suppression

The two molecular mechanisms proposed for initiating immune suppression (DNA damage and UCA isomerization) imply different wavelength dependencies, which in turn, give different Radiation Amplification Factors (RAFs); see Chapter 1). If DNA damage were the sole mechanism by which UV radiation caused immune suppression, then the percent increase in innumosuppressive UV radiation per percent ozone depletion (RAF) would be between 1.2 and 1.7. On the other hand, if UCA isomerization were the sole mechanism, the RAF would be between 0.4 and 0.8 (See Table 1, Chapter 1). The most detailed action spectrum for immune suppression was determined for systemic suppression of contact allergy in the BALB/c (albino) mouse strain, using wavelengths between 254 and 320 nm *[DeFabo and Noonan, 1983]* (See Figure 2.2). Another action spectrum for local suppression of contact allergy in a different mouse strain has also been measured *[Elmets et al., 1985]*. However, neither action spectrum can distinguish among the two proposed mechanisms or a composite mechanism with absolute certainty, partly because of a lack of detailed information concerning the effect of wavelengths >320 nm. At present, there is no information available on the action spectrum for immune suppression in humans.

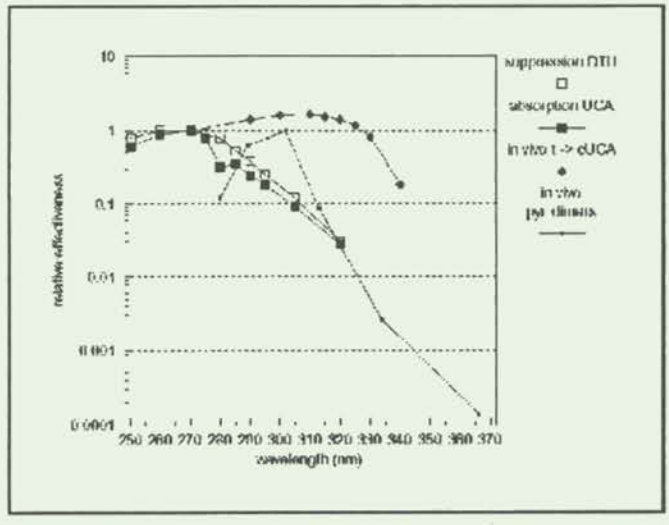

Fig. 2.2. Action spectra of possible importance to immunosuppression: suppression of CH (-◇-) and absorption UCA (....) *[DeFabo and Noonan, 1983]*, in vivo trans- --> cis-UCA (*) *[Gibbs et al., 1993]*, pyrimidine dimers in skin *[Freeman et al., 1989]*

Infectious and Other Diseases

The finding that UV-B irradiation of laboratory animals and humans could impair the induction and elicitation of certain types of immune responses raised concerns that immunity to infectious agents might also be impaired. Theoretically, UV-B irradiation could affect the pathogenesis of infectious diseases by modifying the defense mechanisms of the host to a microbial pathogen or by directly activating an infectious organism present within exposed skin. Evidence for both effects has been provided in model systems, but data in humans are still very limited.

Effects of UV in Experimental Models

Viral diseases

Because of the ability of UV radiation to activate herpes simplex virus (HSV) infection in humans *[Perna et al. 1991]*, experimental models of this infection have been studied extensively. Exposure to UV radiation triggered active disease in mice with latent HSV infection, decreased the delayed hypersensitivity response, induced suppressor T cells to HSV, and impaired resistance to initial infection *[reviewed in Jeevan and Kripke, 1993]*. UV irradiation also decreased cellular immunity to reovirus infection in mice; however, clearance of systemic virus was unimpaired, suggesting that antibody may be more important than cellular immunity in controlling this infection *[Letvin et al., 1981]*. Reports that the AIDS virus could be detected in epidermal Langerhans cells in the skin of HIV+ persons *[Tschachler et al., 1987]* raised concern that UV-B irradiation might accelerate the course of this disease. Although there is no evidence to support this possibility in humans, one study in mice suggested that the course of an AIDS-like immune deficiency was accelerated by chronic UV irradiation *[Brozek et al., 1992]*. The study showed that UV-irradiated mice developed antibodies against a murine retrovirus earlier than non-irradiated controls, suggestive of more rapid disease progression.

Virus activation by UV

In addition to decreasing host resistance to infection by means of its immunomodulatory effects, UV-B radiation has the ability to activate latent viruses contained within cells exposed directly to UV. This phenomenon, which has been demonstrated in vitro *[Zmudzka and Beer, 1990; Schmitt et al., 1989]*, would be expected to affect viruses present in cells of the skin, such as papillomaviruses, herpes simplex virus, and perhaps HIV, which can be present in

epidermal Langerhans cells *[Tschachler et al., 1987]*. In vivo activation of HIV in the skin has been demonstrated in transgenic mouse models, in which UV irradiation turned on genes involved in virus activation and replication in the skin *[Morrey et al., 1991; Vogel et al., 1992]*. These studies have raised the concern that exposure of HIV-infected persons to UV radiation early in the course of infection, when the virus is present in the skin, might accelerate the course of AIDS. However, there is at present no experimental evidence to support this possibility. Thus, the likely impact of increased UV-B radiation on HIV infection resulting from viral activation remains unknown.

Parasitic infections

UV-B induced immunosuppression has been shown to have an impact on leishmaniasis *[Giannini, 1986; Giannini and De Fabo, 1987]*, malaria (B. Ward, personal communication) and trichinosis *[Goettsch et al., 1994]*, but not on schistosomiasis *[Jeevan et al., 1992]*. Leishmaniasis, a tropical parasitical disease has been studied in some depth using a mouse model. In humans, the parasites are deposited intradermally by infected sandflies, where they induce ulcerating, cutaneous lesions. The infection may be limited to the skin or can progress to a systemic disease, which may be fatal. In different mouse strains, the organism can produce either a self- limiting disease controlled by cellular immunity or a progressive, lethal infection. The outcome depends upon what type of immune response the particular strain of mouse mounts against the parasite: a Th1 response leads to immunity, whereas a Th2 response leads to disease progression. UV irradiation of mice before and after infection through exposed tail skin improved the appearance of the resulting skin lesions, but decreased the delayed hypersensitivity (Th1-type) response to the parasites thereby decreasing clearance of the organism *[Giannini, 1986]*. The mortality rate was increased in infected and UV-irradiated mice, which also exhibited decreased resistance to reinfection with the parasite *[Giannini and DeFabo, 1987]*. Thus, in this model, although there was a reduction in the size and severity of the skin lesions in UV-irradiated mice, the pathogenicity of the disease was increased. Similar decreases in the clearance of parasites have also been observed in rodent models of both trichinosis and malaria, but not in schistosomiasis *[Goettsch et al., 1994; B. Ward, personal communication; Jeevan et al. 1992]*.

Bacterial infections

The impact of UV-B exposures on immunity to mycobacterial infection in mice has been studied extensively. Infection of UV irradiated mice in the hind footpad with *Mycobacterium bovis BCG* or *M. lepraemurium* resulted in a decreased delayed hypersensitivity response and delayed the clearance of bacteria from the lymphoid organs. Furthermore, macrophages from the spleen and peritoneal cavity of UV-irradiated mice had a reduced ability to ingest *M. bovis*. A single high dose of UV radiation given 3 days before

infection accelerated the rate of death from *M. lepraemurium* *[Jeevan and Kripke, 1993]*. Similar results were obtained in a mouse model of Lyme disease. UV-irradiated mice infected with *Borrelia burgdorferi* exhibited a decreased delayed hypersensitivity response, decreases in certain subclasses of anti-*Borrelia* antibodies, and increased numbers of organisms in the joints *[Brown et al., 1994; E. Brown, unpublished data]*.

Fungal Infections

The only model of fungal infection studied to date is systemic *Candida albicans* infection in mice. Candida is an opportunistic fungus normally present on the skin, which causes systemic disease in immunosuppressed persons. Exposure of mice to a single high dose of UV-B radiation one day before a lethal intravenous injection of Candida significantly reduced their survival time. Lower doses of UV radiation decreased the delayed hypersensitivity response to this organism, but had no effect on the outcome of systemic disease *[Denkins and Kripke, 1993; Denkins et al., 1989]*.

Autoimmune and other diseases

The possibility exists that UV-B could reduce some forms of autoimmunity, by virtue of its ability to attenuate cell-mediated immunity. However, studies in experimental models of autoimmune diseases are quite limited and only serve to underscore the complexity of the situation. In a study of the effects of UV-B irradiation on the development of autoimmune hemolytic anemia in autoimmune strains of mice, UV-B irradiation accelerated and exacerbated the disease process *[Ansel et al., 1985]*. In another study using a different strain of autoimmune mice, chronic UV irradiation seemed to have no effect on the pathogenesis of this disease *[Strickland, 1984]*.

In humans, UV-B is used therapeutically for the treatment of certain skin diseases, such as psoriasis, which seem to have an immunological component. On the other hand, one autoimmune disease, systemic lupus erythematosis is aggravated by UV exposure, and UV is involved in the pathogenesis of some photoallergic and photosensitivity diseases. Thus, increased UV-B radiation is likely to have varied, and even opposing, effects on autoimmune and other diseases, and it is presently not possible to make any predictions as to its impact.

Effects of UV on Human Diseases

Of course, the crucial question regarding the significance of increased UV-B radiation is whether the findings in animal studies apply to humans. It is clear that exposure of humans to natural or artificial sources of UV-B radiation impairs the activity of T lymphocytes, decreases the activity of natural killer cells, decreases the number of epidermal Langerhans cells, and abrogates the induction of the contact allergy response to chemicals applied

onto the irradiated skin *[Morison, et al., 1979; Hersey, et al., 1983; Yoshikawa, et al., 1990; Cooper, et al., 1992]*. Furthermore, most of these immunological effects occur even in persons with darkly pigmented skin, implying that pigmentation does not confer complete protection against UV-induced immune suppression *[Scheibner, et al., 1986; Vermeer et al., 1991]* so that the population potentially at risk for an impact on infectious diseases is far greater than that for skin cancer.

There is evidence both in murine models *[Streilein and Bergstresser, 1988; Noonan and Hoffman, 1994]* and humans *[Yoshikawa et al., 1990]* for genetic differences in susceptibility to UV-induced immune suppression unrelated to pigmentation. Such differences may be important determinants of risk for skin cancer development and susceptibility to UV-induced modifications of infectious diseases.

The effects of UV-B radiation on infectious disease processes are likely to be complex and unpredictable. Historically, UV radiation was used to treat a variety of skin diseases, most notably skin tuberculosis, and in recent years, UV-B radiation has been used to treat psoriasis, acne, and other cutaneous diseases. On the other hand, sunlight exposure was thought to aggravate pulmonary tuberculosis and scarring from smallpox *[van der Leun and de Gruijl, 1993]*. There is also considerable evidence that exposure to sunlight and to UV radiation can trigger the appearance of cutaneous lesions caused by herpes simplex virus types 1 and 2 in persons already harboring a latent infection *[Klein and Linnemann, 1986; Spruance, 1985; Wheeler, 1975]*, and exposure to UV radiation has been reported to increase the severity of skin lesions associated with herpes zoster infection *[Szigeti et al., 1976]*. UV radiation may also be a contributing factor to papillomavirus infections in immunosuppressed patients, since such individuals have a high incidence of viral warts on sun-exposed body sites *[Boyle et al., 1984; Dyall-Smith and Varigos, 1985]*. Whether these effects are a result of virus activation or immune suppression by UV or both is not clear.

One approach to addressing the effect of UV-B radiation on resistance of humans to infection is to analyze the effect of UV on a cell-mediated immune response against microbial antigens. Healthy contacts of leprosy patients often exhibit a delayed hypersensitivity response upon intradermal injection of lepromin, an antigen prepared from leprosy bacilli. Exposure of the injection site to UV-B radiation before and after inoculation of lepromin markedly reduced the size of the skin test reaction and granulomatous response and decreased the number of T lymphocytes within the reaction site, compared to the reaction site in unexposed skin of the same subject *[Cestari et al., 1994]*. This study demonstrates that exposure to UV-B radiation can diminish the cutaneous immune response to an infectious microorganism in humans; however, it does not address the question of whether UV-B

irradiation would also exacerbate the disease process in persons suffering from leprosy or other mycobacterial infections.

Obviously, it will be very difficult to assess the role of UV-B radiation on natural infections in human populations. Based on current knowledge, we would predict that an effect of UV-B radiation would manifest itself as an increase in the severity or duration of disease and not necessarily as an increase in disease incidence except possibly where reactivation of a latent virus is reflected as incidence. Since infectious diseases are influenced by many host and environmental factors, the effect of UV-B radiation on a given disease process may be difficult to discern from epidemiological studies. Clearly, more information is needed on this subject. The growing evidence that the balance of Th1- and Th2-type immune responses plays an important role in determining the outcome of various infectious diseases, and the suggestion from animal studies that UV irradiation may shift this balance toward a Th2-type response suggests that UV radiation may indeed influence the pathogenesis of some diseases. It may also influence the outcome of vaccination against infections. Whether this influence is beneficial or harmful will probably depend on what type of immune response is most effective in protecting against a particular microorganism. Thus, it is presently difficult to predict both the direction and magnitude of an effect of UV-B radiation on a particular disease process.

This possibility is borne out in a study in mice demonstrating that UV irradiation could prevent the induction of an autoimmune demyelinating disease, experimental allergic encephalomyelitis, in mice [Hauser et al., 1984] which is a Th1-dependent disease.

For example, photodermatoses are skin diseases where the skin lesions are caused by light. Solar UV-B radiation is the predominant causative agent for several of these diseases. Although many patients and their doctors expect an aggravation of these diseases with a decreased ozone layer, there are reasons to question this expectation. In the first place, these diseases agenerally occur less frequently and with less severity in sunny areas of the world. Second, many patients with photodermatoses are treated effectively by regular exposures to low-dose UV-B radiation during winter. Because depletion of the ozone layer will increase UV-B irradiance, especially in winter, this may improve the patients' condition *[van der Leun and de Gruijl, 1993]*.

UV dose-response and wavelength studies for immunosuppressive effects of UV radiation in humans are essential for making quantitative predictions. More important still is understanding the significance of these immunological effects for the pathogenesis of human diseases. In spite of its central importance to the analysis of the consequences of stratospheric ozone depletion for human health, information to address the latter issue is difficult and expensive to obtain and is thus almost totally lacking.

Skin Cancer

Background

UV radiation damages DNA (i.e., is genotoxic). This may lead to faulty replication of DNA in a daughter cell, i.e., fixation of a mutation. Mutations in certain key genes (proto-oncogenes or tumor suppressor genes) that regulate the cell cycle, cell differentiation, and cell death (apoptosis) can lead to formation of a cancer cell. Recent research is beginning to reveal how these steps relate to the course of UV-induced tumor formation.

Animal data and human epidemiologic studies clearly indicate that excessive exposure to UV radiation is associated with skin cancer in humans. (See IARC *[1992]* for a comprehensive overview). The involvement of DNA damage, for instance, was elegantly demonstrated in opossums (*Monodelphis domestica*) which have an enzyme (photolyas) that reverses certain types of UV-induced DNA damage (cyclobutane pyrimidine dimers) upon exposure to UV-A and visible light; UV-A plus visible light treatments counteracted the UV induction of skin tumors (both squamous cell carcinomas and melanomas). It is also known that xeroderma pigmentosum (XP) patients whose cells are deficient in the repair of UV-induced DNA damage have dramatically increased risks of skin cancer (both squamous and basal cell carcinomas, and melanoma). [This observation is, however, complicated by the fact that individuals with other kinds of defects in DNA repair (e.g., Cockayne's syndrome and trichothiodystrophy), do not have an increased risk of skin cancer.] One interpretation of this seeming contradiction is that deficiencies in the repair of genes that are normally inactive, e.g., XP, leads to skin cancer, whereas deficient repair of active genes, as in Cockayne's syndrome, is related to developmental and degenerative effects.

Non-Melanoma Skin Cancer

There are two main types of non-melanoma skin cancer (NMSC): basal cell carcinoma (BCC) and squamous cell carcinoma (SCC). In most countries, reporting of these tumors to a cancer registry is either not required or inadequately standardized, resulting in inadequate cancer registry data and an inability to track trends in incidence or mortality. Where good medical care is available, the overall mortality is thought to be less than 1 percent. Although BCC typically represents 80 percent of NMSC, the mortality is mainly due to SCC.

SCC has a convincing and clear-cut relationship to UV-B radiation, whereas that for BCC is somewhat less compelling. The causative role of sunlight in SCC is supported by the observations that a) SCC occurs predominantly on the most sun-exposed parts of the skin, face, neck and hands; and b) in comparable populations the incidence of SCC is highest in geographic areas with the most

sunlight. The observation that SCC occurs predominantly in fair-skinned people is consistent with this conclusion. The risk of developing SCC appears strongly related to the total dose of sunlight received in the course of a lifetime. In addition, in animal models, exposure to UV radiation is associated with the development of SCC and not BCC.

The evidence is less clear-cut with BCC, which rarely appears on the well-exposed backs of the hands, but instead occurs more on the face and neck areas, with a fair percentage developing on the trunk. Also, a person's most recent history of sun exposure (the preceding 10 to 20 years) relates better to the risk of developing SCC than BCC. *[Vitasa, et al., 1990]*. This may be interpreted to mean that UV radiation is somehow related to an "early event" in the development of BCC, after which other "events" (including growth) must occur before the tumor develops.

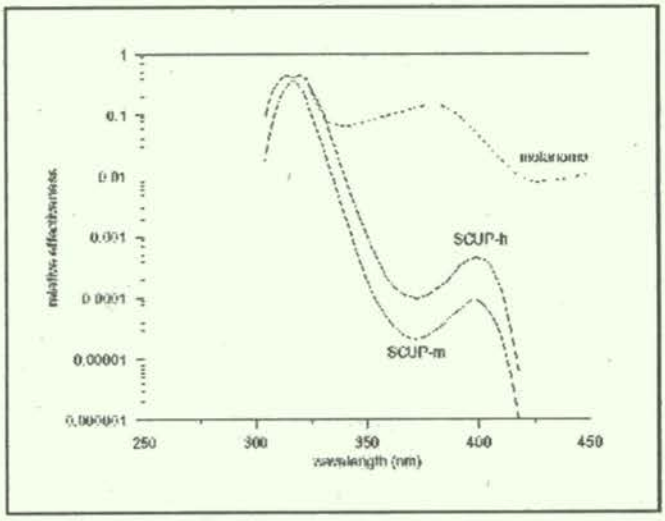

Fig. 2.3. Action spectra for cancer in animal models: Melanoma in fish *[Setlow et al., 1993]*, non-melanoma skin cancer in mice - SCUP-m *[DeGruijl et al., 1993]*, and in humans -SCUP-h *[DeGruijl and van der Leun, 1994]*

Important molecular evidence for the role of UV-B in the induction of these tumors is that large percentages (>50 percent) of SCC and BCC in humans bear UV-specific mutations (i.e., at dipyrimidine sites where cytosine is replaced by thymine, a C-to-T transition) in their p53 tumor suppressor gene. This constitutes the most direct evidence that UV radiation causes skin cancer in humans. Furthermore, it was found that in mice these types of

mutations already exist in the precursor lesions of SCC, implying that UV irradiation can be an early event in the development of the tumor. Strikingly, it has recently been shown that certain UV-related mutations (tandem transitions of CC-to-TT) can be detected in sun-exposed skin of skin cancer patients (17/24 in Australia), but are virtually non-existent in unexposed skin (1/20). *[Nagazawa et al., 1994]*.

Information on the wavelength dependence of the UV induction of cancer is crucial for quantitative risk assessments; however, it would be both impractical and unethical to derive such information from experiments in humans. Several groups have developed such action spectra based on tumorigenesis in hairless mice, with the most complete spectrum being that published by De Gruijl and his colleagues *[1993]*, and presented as the Skin Cancer Utrecht-Philadelphia (SCUP) action spectra (see Figure 2.3). The carcinogenicity for wavelengths over 340 nm was somewhat higher than expected from constructed action spectra (mutagenicity corrected for epidermal transmission), which could be due to an increased level of indirect, radical-mediated damage in vivo. More recently, the SCUP action spectrum has been corrected for differences in epidermal transmission between mouse and human, thus a SCUP-h was derived from the SCUP-m action spectrum ('h' standing for human and 'm' for murine). *[De Gruijl and van der Leun, 1994]*. This correction must be considered to represent a crude average, because the epidermal transmission will vary both in human and mouse from one individual to another, and it will decrease under regular UV exposure.

In relation to a depletion of the ozone layer, it is important to quantify how much more carcinogenic UV radiation reaches the ground level for each percent decrease in ozone. For NMSC, annual doses are assumed to be an appropriate measure, and personal doses are assumed to be proportional to ambient doses. This increase in carcinogenic dose is expressed by the Radiation Amplification Factor (RAF), which equals 1.4 for SCUP-m-weighted UV doses and 1.2 for SCUP-h-weighted UV doses (i.e., 1.4 or 1.2 percent more carcinogenic UV radiation for each percentage decrease in ozone; see also Chapter 1). Next, the relationship between skin cancer incidence and an increase in carcinogenic UV radiation must be determined. For stationary situations, this is estimated from incidence data in comparable populations living at different geographical locations under different levels of solar UV exposure comparable in genetic composition, lifestyle, etc.). Estimates for the white population in the United States predict that for every 1 percent increase in annual carcinogenic UV radiation, the SCC incidence over a human lifetime will ultimately rise by 2.5±0.7 percent, and the BCC by 1.4±0.4 percent, based on SCUP-h (for SCUP-m-weighted doses, the numbers are virtually the same). These latter numbers are referred to as the Biological Amplification Factors (BAF). Multiplying the RAF and BAF gives the overall Amplification Factor (AF), the ultimate, predicted increase in skin cancer for each percent decrease in ozone. For SCC, AF equals

3.0±0.8 percent; for BCC, AF is 1.7±0.5 percent, and for all nonmelanoma skin cancers combined, AF is 2.0±0.5 percent. With approximately 1.2 million new cases each year worldwide [Longstreth et al., 1991], this would amount to 250,000 additional cases each year from a sustained 10 percent decrease in average ozone concentration [for more detail, see Madronich and De Gruijl, 1993].

It is also worth noting here that there are subpopulations of individiuals at very high risk of developing NMSC, who will be greatly affected by an increase in ambient UV-B radiation. As noted above, persons with the rare genetic disorder XP are exquisitely susceptible to the development of UV-induced NMSC early in life and often die of this disease. A much larger population at high risk are renal allograft recipients and other immunosuppressed individuals, who tend to develop multiple, aggressive, and often fatal SCC on sun-exposed skin at a relatively young age. Increased UV-B radiation is likely to be especially hazardous for such high-risk persons [Glover et al., 1994].

In reality, the projections suggest not a sustained decrease, but rather a transient seasonal decrease in ozone that will vary substantially over the globe, reaching its maximum in early spring at the poles. The concentration of ozone in the stratosphere is projected to reach a minimum around the year 1998, and will normalize to 1980 levels around the middle of the next century (see Chapter 1). Increases in UV-B associated with these ozone losses are likely to cause a delayed transient increase in skin cancer incidence. Besides knowledge of the UV dose dependency, information on the time dependency of the response after changes in the ambient UV load is also needed. Such information is not available for human populations, and additional hypotheses must be introduced to extend the model to time-dependent responses. To a certain extent, animal experiments can assist in providing this extension of the model *[De Gruijl and van der Leun, 1991]*, however, certain assumptions as to how the animal data translate to human responses are still required. Although more work should be done in this area, a plausible model estimates that a steady increase in nonmelanoma skin cancers will occur even under the most recent international agreement with regard to the phase-out of ozone-depleting substances, reaching a 25 percent higher level in the year 2050 in comparison to 1980 at approximately 50 degrees NL *[Slaper et al., 1992]* see Figure 2.4.

Melanoma

Cutaneous melanoma (CM) is the result of the neoplastic transformation of melanocytes, the pigment-producing cells in mammalian epidermis. There are four different categories of CM in humans: 1) superficial spreading melanoma (SSM) 2) nodular melanoma (NM) 3) lentigo maligna melanoma (LMM) also known as Hutchinson's melanotic freckle) and 4) unclassified melanoma.

The etiology of LMM appears to be similar to that of NMSC in relation to sun exposure, whereas that of SSM and NM appears to be different in that it appears linked more with intermittent, intense exposures (i.e., severe sunburns) and/or exposures in childhood (for a comprehensive overview, see IARC, 1992; USEPA, 1987; IBMC, 1992; or Elwood, 1993).

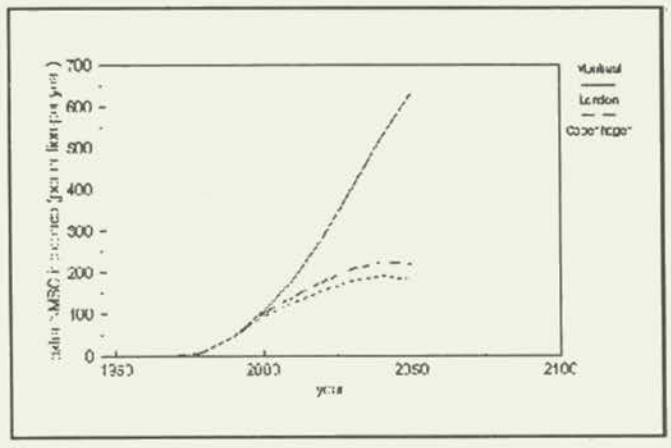

Fig. 2.4. Estimated increase in NMSC incidence under 3 CFC-phaseout scenarios. *[Slaper et al., 1993]*

In the case of SSM and NM, evidence supporting an etiologie relationship with solar (UV) radiation includes:

1) the fact that in general, people light-skinned individuals who are more sensitive to sunburn run a higher risk; in such individuals irregularities in pigmentation, i.e., freckles, a high number of moles (nevi), and/or atypical nevi, contribute especially strongly to the risk.
2) high levels of solar exposure during childhood (before ages of 15-20 years, and possibly especially intense intermittent exposures) is strongly associated with increased risk (e.g., Holman and Armstrong, 1984), and increases the number of nevi (potential precursor lesions) that a person develops (Gallagher et al., 1990).
3) the risk is often higher for indoor workers than for outdoor workers, and can be associated with (intense) intermittent exposure to the sun in leisure time.
4) positive correlations between ambient UV levels (e.g., latitudinal gradients) and CM in sensitive populations.
5) high risk in XP patients who are deficient in repairing DNA damage inflicted by UV radiation (see 2.5.1).
6) mutations in the N-ras gene at di-pyrimidine sites (the target sites of UV-B radiation in DNA) in SSM and NM occurring in sun-exposed skin (Van't Veer et al., 1989).

The hypothesis that intermittent UV exposure is important for the risk of CM was largely inferred from the locations of CM over the

body (relatively large numbers on irregularly exposed sites) and more occurences in indoor workers than in outdoor workers. Later confirmation of this hypothesis is, however, solely based on studies in which patients and control groups were retrospectively interviewed; thus, these studies are vulnerable to recall-bias--after having contracted a CM, people tend to remember more sunburns than before *[Weinstock et al., 1991]*.

In the U.S., incidence rates for CM among white-skinned populations during the decade from 1974 to 1986 increased at an average yearly rate of 34 percent (varying from -2 to -7 1/4 %. Increases in mortality during that time period showed a similar trend, although a slower rate. More recently, Scotto et al. *[1991]* have analyzed trends in skin melanoma death rates by cohort for fair-skinned ("white") males and females over a 35-year period (1950- 1984) and observed upward trends for older men and women (over 40) and downward trends for the younger cohorts. Assuming no life-style changes and constant UV radiation levels, these authors project that the 2 to 3 percent upward trend in mortality per annum observed since 1950 will discontinue and bend downward by the second decade of the 21st century.

This information is critical to assessing the risks of stratospheric ozone depletion, which would clearly need to incorporate cohort data and age-specific trend analyses into the baseline data used in such an activity. This same sort of cohort analysis information is also critical to estimating the potential increases in non-melanoma skin cancer; unfortunately most countries are not collecting sufficient data on non-melanoma skin cancer to be able to perform such trend and cohort analyses.

Animal Models for Melanoma

In the past few years, several animal models have been developed in which primary cutaneous melanomas can be induced by UV radiation alone or in combination with cancer-inducing chemicals. The most interesting of these involves the induction of melanoma by UV-B radiation in *Monodelphis domestica*, the grey, short-tailed, South American opossum *[Ley et al., 1989]; see below*.

Another animal model in which melanomas can be induced with UV radiation is the tropical fish model of Setlow *[Setlow et al., 1989]*; see below.

As described in the 1991 UNEP panel report *[Longstreth et al., 1991]*, primary melanomas can be induced in mice using a combination of UV radiation and chemicals, but UV radiation alone has so far been ineffective *[Romerdahl et al., 1989]*. These and more recent studies *[Donawho and Kripke, 1991; Hasan et al., 1992]* indicate that UV radiation may play several different roles in the induction of murine melanomas, including that of an initiator, a tumor promoter, and a co-carcinogen that contributes to melanoma development by means of its immunosuppressive effects.

The animal models are instructive because they demonstrate that UV radiation can contribute to the induction of melanotic tumors in a variety of ways. However, they are not very helpful for assessing increases in melanoma incidence in humans exposed to increased UV-B radiation. In the opossum model, the dose-response and wavelength data are inadequate for making such calculations, and extrapolation of the information from the fish model to humans is obviously fraught with difficulties.

Wavelength Dependency of Melanoma

Animal experiments have not yet yielded results that unambiguously indicate mechanism(s) by which the UV radiation may be causing CM in humans. The wavelength dependence of the induction of CM is important for risk assessments, but conclusive data are not available, and the wavelength dependence cannot be confidently constructed from presumed mechanisms.

In hybrid fish of the genus *Xiphophorus* a single, early in life UV-A exposure is quite efficient in evoking melanomas; a UV-B exposure is only 10 to 50 times more effective (per J/m^2, i.e., this action spectrum is relatively flat when compared with the SCUP action spectra, see Figure 2.3; Setlow et al., 1993). These experiments were, however, contaminated by the aquarium lighting. This lighting contributed to a high background occurrence of melanomas (in about 25% of the fish), and possibly even counteracted the induction of melanomas by UV-B radiation the fish have photolyase). In the opossum *Monodelphis domestica*, melanomas can be induced by chronic broadband combined UV-B/UV-A exposure; such tumors do not develop when the animals are kept solely under yellow light. Visible light exposure after each UV exposure counteracts the development of the UV-induced melanomas, which would indicate that UV-induced di-pyrimidine dimers cause melanomas. If these dimers are the main DNA lesions causing melanomas in human skin, then the reversal by visible light is not likely to occur (humans appear not to have photolyase, *[Li et al., 1993]* although this is a matter of some controversy). The action spectrum in humans could then follow the induction of these DNA lesions in the skin, and would presumably resemble the SCUP action spectra more than the one found for the melanomas in fish (for comparison see Figure 2.3).

It is conceivable that UV radiation may contribute in various ways to the induction of melanomas, and that the specific mechanisms differ in the two animal models. Although it is difficult to induce melanoma in mice by UV irradiation, it can be done quite efficiently with exposure to chemical carcinogens, and concomitant UV exposure can then promote the melanomagenesis.

How these experimental data should be extrapolated to humans is, of course, very much an open question. CM in humans may well have a multifactorial etiology. Although UV radiation is likely to play a dominant role, (e.g., initiating precursor lesions during youth and

suppressing immunity to the tumor cells as a result of a sunburn in the final stage of tumor development), other factors may affect expression of the UV effect.

Related Issues

The majority of this chapter has been devoted to a review of the potential human health effect of the increased ultraviolet radiation which may result from stratospheric ozone depletion. There are, however, other health issues associated with this stratospheric ozone depletion. This section addresses four such issues. First, animal populations beyond humans are potentially affected by increased UVR which can lead to impacts on agricultural productivity. Second, the effects on human health of increased UVR, can be potentially mitigated by appropriate changes in behavior. Third, although most ozone depleting substances (ODSs) are scheduled for complete phase out by 1995, methyl bromide is not yet subject to complete phase out. Its toxicity is of some concern, so has been included in this dicussion. Fourth, the chemicals which replace ODSs may themselves have toxicity, so a brief synopsis of information known about them is also presented.

Effects on Animals

Animals of several species develop skin cancer, mainly SCC, in sparsely haired, light-colored areas of the skin. This includes cows, goats, sheep, cats and dogs *[Emmett, 1973; Dorn et al., 1971; Nikula et al., 1992]*. The body distribution is consistent with sunlight as the etiologic agent; UV-B is implicated by extrapolation from studies with laboratory animals. Cancers of the eye also occur in many animal species, including horses, sheep, swine, cats, and dogs, and are particularly frequent in cattle *[Hargis, 1981]*. In rats, mice, hamster, and the opossum (Monodelphis domesticus), studies on the induction of skin cancer with mainly UV-B radiation have sometimes induced ocular tumors as well *[Ley et al., 1989]; [Blum, 1943]; [Freeman and Knox, 1964]*. Photokeratitis and cataract have been induced experimentally in rabbits, with the most effective wavelengths falling mainly within the UV-B range *[Pitts et al., 1977]*. Bovine infectious keratoconjunctivitis, an eye infection caused by the bacterium *Moraxella bovis*, is triggered and aggravated by UV-B irradiation of the eye *[Hughes, et al., 1965]*.

In animals in which these effects occur under natural conditions, an increase in UV-B irradiation would be expected to exacerbate them. However, it is not possible to estimate the magnitude of such effects because of the paucity of information on dose-response and wavelength dependence and on possible behaviorial modifications.

Mitigation/Amelioration

The effects of increased UV-B exposure on human health may, in principle, be mitigated by reducing the exposure time to sunlight. Being indoors gives a practically complete protection. Limiting exposure during the hours of maximal UV-B irradiance, that is, between 2 hours before and 2 hours after solar noon is especially effective.

Even while outdoors, there are still possibilities for protection. An important protection is offered by constitutional skin pigmentation. Dark-skinned people are better protected against skin cancer and sunburn than light-skinned individuals, but their pigment does not seem to protect them against some of the suppressive effects of UV-B radiation on the immune system.

Changes in behavior also offer many possibilities for mitigation. Many clothing fabrics give good protection. Hats are especially effective because they offer some protection of the facial skin and the eyes, two body sites at comparatively high risk. Sun glasses of appropriate material also provide good protection for the eyes. Being in the shade of buildings or trees also reduces the UV-B dose received.

Sunscreens may be a useful addition, especially for occasions when an unusually high exposure is expected, such as a holiday in a sunnier area. Sunscreens are effective against sunburn. To some extent, they may also be protective against skin cancer, as long as they are not used to prolong the exposure. Several experimental results suggest that the effectiveness of sunscreens against the effects of UV-B radiation on the immune system is limited. Continuous use of sunscreens with a high protection factor is sometimes advocated, but it may be counterproductive; such "sunblocks" also block both the formation of Vitamin D3 in the skin and the body's own defense systems, such as adaptation to the UV environment by thickening of the outer skin layers and tanning.

Methyl Bromide

Methyl bromide (MeBr) is discussed here because of its potential contribution to ozone depletion and its adverse effects on living organisms. Despite its ozone-depletion potential, current revisions to the Montreal Protocol do not require phase-out of MeBr, rather production is limited to the amount produced in 1991. A variety of countries have taken unilateral action which range in level of severity; for example, the Netherlands banned all soil uses in 1992, Denmark and Italy plan a total phase out in 1998 and 2000, respectively, the US will ban production and importation in January 2001, and Canada plans a 25% reduction in 1998 *[US EPA, 1994]*.

MeBr is a colorless, generally odorless, ozone-depleting gas which is widely used for fumigation of soil (77%), commodities and quarantine facilities (12%) and sub-surface structures (5%). Current uses result in significant releases to the atmosphere. Methyl bromide is toxic by all routes of exposure. Immediate

effects from acute exposures show a dose-dependent increase in severity ranging from dizziness, headache, nausea, contact burns to the eyes and skin, respiratory irritation, venticular fibrillation, pulmonary edema (sometimes delayed for several days), convulsions, coma and death. The Time-Weighted Average occupational limit recommended in the United States by the American Conference of Government Industrial Hygienists is 5 ppm. Signs of toxicity in humans following chronic exposure have included persistent numbness in the hands and legs, impaired superficial sensation, muscle weakness, unsteadiness of gait, and depressed or absent distal tendon reflexes; however, once exposure has ceased, symptoms generally disappear and recovery is complete *[HSDB 1994]*.

Animals show similar signs of toxicity. Studies on horses, goats, cows and cattle fed hay or food contaminated with various levels of MeBr (ranging from 170 to 8400 ppm) displayed symptoms which ranged in a dose-dependent fashion and included difficulty in walking, incoordinated movement and gait, listlessness, inability to rise, and even death. MeBr is also toxic to aquatic species with acute and chronic toxicity to salt water species occurring at levels as low as 11 and 6.4 mg/l, respectively. A similar level for acute toxicity was found for fresh water species *[HSDB 1994]*.

Toxicity of CFC Substitutes

As the production of fully halogenated chlorofluorocarbons (CFCs) ceases pursuant to the provisions of the Montreal Protocol and the London and Copenhagen Amendments, a variety of potential CFC substitutes are likely to be introduced into the environment. The toxicity of these chemicals is of interest: clearly, we do not want to introduce chemicals as replacements which are more problematic than those we are replacing. Table 2.1 summarizes what is currently known about the toxicology of the more common CFC substitutes: hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs), and terpenes. Most of this information has been drawn from references found either in the open literature or submitted to EPA under the requirements of TSCA. In those cases with a sufficient database, EPA has derived a Reference Concentration (RfC), which is the concentration, at which exposure for a lifetime should be without adverse effect. The process of deriving these numbers basically involves selection of a No Observed Adverse Effect Level (NOAEL) and dividing it by an uncertainty factor that reflects differences in individual sensitivity, differences in species responsiveness, and inadequacies in the database (such as the lack of a two-generation reproduction study or a Lowest Observed Adverse Effect Level [LOAEL]).

Several chemicals have been the focus of extensive animal studies. The conclusions of such studies can promote a basis for determining the adverse human effects of these compounds. For example, HCFC-141b was determined to decrease reproductive performance; HCFC-124 has had transient central nervous system (CNS) effects; and HCFC-22 exposure has increased liver, kidney,

adrenal, and pituitary weights. On the other hand, HFC-134a, HCFC-142b, and HCFC-152a have shown no signs of adverse effects.

TABLE 2.1. Update on Potential CFC Substitutes

CHEMICAL	ADVERSE EFFECTS according to the EPA documentation and review of the inhalation RfC
d-Limonene CASRN: 5989-27-5	EPA reviewed the data for this chemical and determined that the requirements for the minimal database necessary to develop an inhalation reference concentration (RfC) have not been met (EPA 1993). The compound is listed on FDA's Generally Regarded as Safe (GRAS) list and is approved for use as a food additive (Opdyke 1975). A chronic bioassay involving exposure via oral administration resulted in kidney damage in the male rats (NTP 1990); however, the mechanism involves alpha2μglobulin which has been judged an inappropriate endpoint for effects occurring in humans (USEPA 1991)
alpha-Pinene CASRN: 80-56-8	EPA reviewed the data for this chemical and determined that the requirements for the minimal database necessary to develop an inhalation reference concentration (RfC) have not been met (EPA 1993). The compound is listed on FDA's Generally Regarded as Safe (GRAS) list and is approved for use as a food additive (Opdyke 1975). EPA has judged that there are no chronic studies by inhalation or oral routes of exposure which are adequate to the development of an RfC. Contact hypersensitivity studies in humans suggest that this compound is a contact allergen. (Cachao et al. 1986)
beta-Pinene CASRN: 127-9193	EPA reviewed the data for this chemical and determined that the requirements for the minimal database necessary to develop an inhalation reference concentration (RfC) have not been met (EPA 1993). The compound is listed on FDA's Generally Regarded as Safe (GRAS) list and is approved for use as a food additive (Opdyke 1975). EPA has judged that there are no chronic studies by inhalation or oral routes of exposure which are adequate to the development of an RfC. Contact hypersensitivity studies in humans suggest that this compound is a contact allergen. (Cachao et al. 1986)
1,1-Dichloro-2,2,2-trifluoroethane HCFC-123 CASRN: 306-83-2	EPA reviewed the data for this chemical and derived a verified inhalation reference concentration (RfC) of 10 mg/cu m (1.6 ppm)(EPA1992) based on a chronic inhalation bioassay in which rats were administered the compound at 0, 300, 1,000 or 5,000 ppm 6 hours/day 5 days/week for 2 years (Malley 1990). The study identified a NOAEL (1,000 ppm) and a LOAEL (5,000 ppm) with the critical effects being increased relative liver weight, focal histopathology in the liver, an effect on lipid metabolism, and at high concentrations (5,000 ppm), CNS depression. The European Center for Ecotoxicology and Toxicology has completed a review of this chemical (ECETOC 1994).
Chlorodifluoromethan e HCFC-22 CASRN: 74-45-6	EPA reviewed the data for this chemical and derived a verified inhalation reference concentration (RfC) of 50 mg/cu m (14 ppm)(EPA1992; EPA1994) based on a chronic inhalation bioassay in which rats were administered the compound at 0, 1,000, 10,000 or 50,000 ppm 5 hours/day 5 days/week for slightly more than 2 years (Tinston et al. 1981). The study identified a NOAEL (10,000 ppm) and a LOAEL (50,000) with the critical effects being increased liver, kidney, adrenal and pituitary weights.

2-Chloro-1,1,1,2-tetra fluoroethane HCFC-124 CASRN: 2837-89-0	EPA reviewed the data for this chemical and derived a verified inhalation reference concentration (RfC) of 300 mg/cu m (143 ppm)(EPA1992; EPA1994) based on a subchronic inhalation bioassay in which rats were administered the compound at 0, 5,000, 15,000 or 50,000 ppm 6 hours/day, 5 days/week for 90 days (Malley 1991). The study identified a NOAEL (15,000 ppm) and a LOAEL (50,000 ppm) with the critical effects being transient CNS effects. The European Center for Ecotoxicology and Toxicology has completed a recent review of this chemical (ECETOC I994).
1,1,1,2-Tetrafluoro- ethane HFC-134a CASRN: 811-97-2	EPA reviewed the data for this chemical and derived a verified inhalation reference concentration (RfC) of 100 mg/cu m (71 ppm)(EPA1992; EPA1994) based on a chronic inhalation bioassay in which rats were administered the compound at 0, 2,500, 10,000 or 50,000 ppm 6 hours/day, 5 days/week for 2 years (Hext and Mould 1991). The study identified a NOAEL (50,000 ppm) but not a LOAEL.
1 ,1-Dichloro-1-fluoroethane HCFC-141b CASRN: 1717-00-6	EPA reviewed the data for this chemical and derived a verified inhalation reference concentration (RfC) of 100 mg/cu m (21 ppm)(EPA1992; EPA1994) based on the interim report of a 2 generation reproduction study in which rats were administered the compound by inhalation at 0, 2,000, 8,000 or 20,000 ppm 6 hours/day, 7 days/week for 10 weeks prior to first mating, unexposed for a short interval around parturition, then exposed with the same regiment through a second mating and delivery until the F1B offspring were 4 days old (Brooker et al. 1992). The study defined a NOAEL (8,000 ppm) and a LOAEL (20,000 ppm) with the critical effect being decreased reproductive performance.
1-Chloro-1 ,1-difluoroethane HCFC-142b CASRN: 75-68-3	EPA reviewed the data for this chemical and derived a verified inhalation reference concentration (RfC) of 50 mg/cu m (12 ppm)(EPA1992; EPA1994) based on a chronic inhalation bioassay in which rats were administered the compound at 0, 1,000, 10,000 or 20,000 ppm 6 hours/day, 5 days/week for 80 weeks (Seckar et al. 1986). The study identified a NOAEL (20,000 ppm) but not a LOAEL.
1 ,1-Difluoroethane HCFC-152a CASRN 75-37-6	EPA reviewed the data for this chemical and derived a verified inhalation reference concentration (RfC) of 40 mg/cu m (15 ppm)(EPA1992; EPA1994) based on a chronic inhalation bioassay in which rats were administered the compound at 0, 2,000, 10,000 or 25,000 ppm 6 hours/day, 5 days/week for 2 years (McAlack and Schneider 1992). The study identified a NOAEL (25,000 ppm) but not a LOAEL.
Pentafluoroethane HFC-125 CASRN: 354-33-6	EPA reviewed the data for this chemical and determined that the requirements for the minimal database necessary to develop an inhalation reference concentration (RfC) have not been met (EPA 1993). The acute inhalation toxicity of pentafluoroethane is very low with a 4 hour LC50 of 709,000 ppm (Panepinto 1990). Developmental toxicity studies in rats and rabbits have revealed no toxicity at 15,000 ppm and only slight anesthetic effects in rats at 50,000 ppm (Masters et al. 1992; Masters et al. 1992) The compound is a cardiac sensitizer in dogs at concentration above 100,000 ppm (Hardy et al. 1992). The European Center for Ecotoxicology and Toxicology of Chemicals has completed a recent review of this chemnical (ECETOC I994).

1,3-Dichl oro-1,1,2,2,3-pentafluoropropane HCFC 225cb CASRN: 507-55-1	EPA reviewed the data for this chemical and determined that the requirements for the minimal database necessary to develop an inhalation reference concentration (RfC) have not been met (EPA 1993). Several short-term inhalation studies either of HCFC-225cb in rats at concentrations as high as 41,216 ppm for four hours (Jackson et al. 1992) or of the mixed isomers (HCFC-225cb;HCFC-225ca) in mice at concentrations as high as 13,000 ppm for four weeks (Frame et al. 1992) induced changes in lipid and carbohydrate metabolism at several concentrations. However, these effects were reversible after a 14 day recovery period.
1,1-Dichlor- 2,2,3,3,3-pentafluoropropane HCFC 225ca CASRN: 507-55-1	EPA reviewed the data for this chemical and determined that the requirements for the minimal database necessary to develop an inhalation reference concentration (RfC) have not been met (EPA 1993). Several short-term inhalation studies either of HCFC-225cb in rats at concentrations as high as 46,527 ppm for four hours (Jackson et al. 1992) or of the mixed isomers (HCFC-225cb;HCFC-225ca) in mice at concentrations as high as 13,000 ppm for four weeks (Frame et al. 1992) induced changes in lipid and carbohydrate metabolism at several concentrations. However, these effects were reversible after a 14 day recovery period.
Trifluoromet hane HFC-23 CASRN: 75-46-7	EPA reviewed the data for this chemical and determined that the requirements for the minimal database necessary to develop an inhalation reference concentration (RfC) have not been met (EPA 1993). A subchronic inhalation study in rats at 10,000 ppm or dogs at 5,000 ppm 6 hours/day 7 days/week for 90 days showed no adverse effects in either species (Leuschner et al. 1983). Cardiac sensitization testing in dogs at concentrations as high as 300,000 ppm revealed no activity (Hardy 1992)
Difluoromethan e R-32; FC-32 CASRN: 75-10-5	EPA reviewed the data for this chemical and determined that the requirements for the minimal database necessary to develop an inhalation reference concentration (RfC) have not been met (EPA 1993). Exposure of rats to 200,000 ppm 6 hours/day, 5 days/week for 2 weeks revealed no treatment related effects (Moore 1976). Cardiac sensitization testing in dogs revealed that rare individuals were sensitive at concentrations of 250,000 (1/12) (Mullin 1993).
1,1,1-Trifluoroethane HCFC 143a CASRN: 420-46-2	EPA reviewed the data for this chemical and determined that the requirements for the minimal database necessary to develop an inhalation reference concentration (RfC) have not been met (EPA 1993). Exposure of rats to 1, 2,000, 10,000, or 39,000 ppm 6 hours/day 5 days/week for 4 weeks showed testicular effects in animal exposed nose-only but no effects in animals given whole body inhalation exposures leading to the conclusions that the finding with nose-only exposures may be related to stress (Warheit et al. 1991, 1992)
1,1,1,2,3,3,3-Heptafluoropropane (HCF-227ea) CASRN: 43-89-0	EPA reviewed the data for this chemical and determined that the requirements for the minimal database necessary to develop an inhalation reference concentration (RfC) have not been met (EPA 1993). No data were found.

Perfluorobutane FC-3-1-10 CASRN: 355-35-9	EPA reviewed the data for this chemical and determined that the requirements for the minimal database necessary to develop an inhalation reference concentration (RfC) have not been met (EPA 1993). A subchronic (90 day) inhalation exposure of rats to 0, 5,000, 15,000 or 50,000 ppm 6 hours/day, 5 days/week induced no exposure related adverse effects (Kenny et al. 1992) suggesting that 50,000 ppm is a NOAEL for this compound. Cardiac sensitization testing in dogs at concentrations as high as 170,000 ppm reveal no activity as a sensitizer (Hardy and Kieran 1992)
Perfl uorohexane FC-5-1-14 CASRN: 355-42-0	EPA reviewed the data for this chemical and determined that the requirements for the minimal database necessary to develop an inhalation reference concentration (RfC) have not been met (EPA 1993). Acute exposures as high as 79,000 ppm for 4 hours were not lethal to rats (Jackson et al. 1992) nor is the compound a cardiac sensitizer in dogs at levels as high as 400,000 ppm (Hardy and Kieran 1992).
Bromodifluoromethane FM-100 CASRN: 1511-62-2	EPA reviewed the data for this chemical and determined that the requirements for the minimal database necessary to develop an inhalation reference concentration (RfC) have not been met (EPA 1993). However, in a developmental toxicity study of rats exposed to 0, 1,000, 4,000, or 10000 ppm 6 hours/day on gestation days 6-15, a NOAEL of 4,000 and a LOAEL of 10,000 ppm were observed for both developmental and maternal toxicity (Nemec 1991b). A similar NOAEL for rabbits can be derived from Nemec (1991c). Cardiac sensitization potential testing in dogs revealed a NOAEL of 3,000 ppm.

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CHAPTER 3

EFFECTS OF INCREASED SOLAR ULTRAVIOLET RADIATION ON TERRESTRIAL PLANTS

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Summary

Physiological and developmental processes of plants are affected by UV-B radiation, even by the amount of UV-B in present-day sunlight. Plants also have several mechanisms to ameliorate or repair these effects and may acclimate to a certain extent to increased levels of UV-B. Nevertheless, plant growth can be directly affected by UV-B radiation. Response to UV-B also varies considerably among species and also cultivars of the same species. In agriculture, this will necessitate using more UV-B-tolerant cultivars and breeding new ones. In forests and grasslands, this will likely result in changes in species composition; therefore there are implications for the biodiversity in different ecosystems. Indirect changes caused by UV-B (such as changes in plant form, biomass allocation to parts of the plant, timing of developmental phases and secondary metabolism) may be equally, or sometimes more, important than damaging effects of UV-B. These changes can have important implications for plant competitive balance, herbivory, plant pathogens, and biogeochemical cycles. These ecosystem-level effects can be anticipated, but not easily predicted or evaluated. Research at the ecosystem level for solar UV-B is barely beginning. Other factors, including those involved in climate change such as increasing CO_2 also interact with UV-B. Such reactions are not easily predicted, but are of obvious importance in both agriculture and in nonagricultual ecosystems.

Introduction

Since the first reports of potential stratospheric ozone reduction over 20 years ago (e.g., *[Johnston, 1971; Crutzen, 1972]*), UV-B (280-315 nm) effects on higher plants have been the subject of considerable research. Approximately 350 papers have appeared, but the majority of these deal with herbaceous, agricultural plants under laboratory or glasshouse conditions. Fewer than 5% of the studies have been conducted under field conditions, and fewer still with plants from forests and other nonagricultural systems. While the laboratory and glasshouse studies provide information on mechanisms and processes of UV-B action, only the field studies can provide realistic assessments of what will happen as the stratospheric ozone layer thins.

Several reviews of this literature have appeared in the last five years *[Bornman, 1989; Caldwell et al., 1989; Tevini and Teramura, 1989; Krupa and Kickert, 1989; Tevini, 1993; Bornman and Teramura, 1993; Caldwell and Flint, 1993, 1994a, 1994b; Tevini, 1994; Teramura and Ziska,*

1994; Teramura and Sullivan, 1994]. The present chapter provides an overview with interpretation of the results for both agriculture and other ecosystems such as forests, grasslands, etc. It also includes a brief consideration of the potential effects of the breakdown products of new man-made chemicals being brought into use which are less offending to the ozone layer.

Figure 3.1 shows some of the effects of UV-B radiation on plant processes.

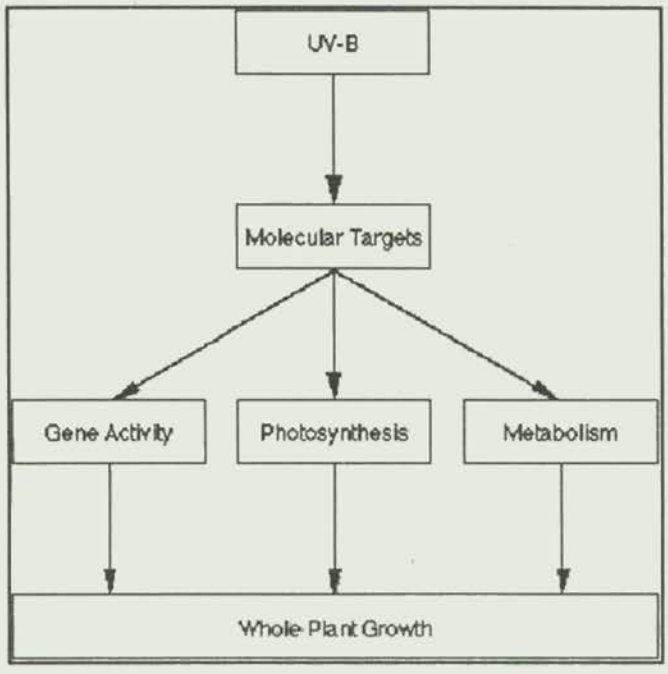

Fig.3.1. The influence of UV-B radiation on plant processes.

The Biological Effectiveness of Changes in Sunlight

As explained in Chapter 1, the biological effectiveness of UV-B solar radiation needs to be considered in assessing what ozone reduction, and the resulting changes in solar radiation, potentially mean for plants and other organisms. The biological weighting functions used for this purpose often come from action spectra. Action spectra assumed to be relevant for plants (Figure 3.2) all indicate that the shorter UV-B wavelengths are the most important. However, the relative importance of shorter vs longer UV-B wavelengths (the slopes in Figure 3.2) vary considerably. Depending on these slopes, the Radiation Amplifications Factors (discussed in Chapter 1) vary enormously. Action spectra that do not decrease sharply with increasing wavelength result in small RAF values. Thus, the evaluation of weighting functions (and therefore action spectra) is critical. There is evidence that action spectra for many plant functions are steep indicating that ozone reduction translates into large increases in effective solar UV-B *[Caldwell, 1971; Setlow 1974]*. Some more recent spectra developed specifically for evaluating the ozone reduction problem show flatter slopes (and therefore lower RAF values) than the

earlier work *[Caldwell et al., 1986; Steinmueller, 1986; Quaite et al., 1992]*. Still, these spectra are sufficiently steep so that ozone reduction must be taken seriously. Biological weighting functions also are needed to relate solar UV to UV from artificial sources used in experiments.

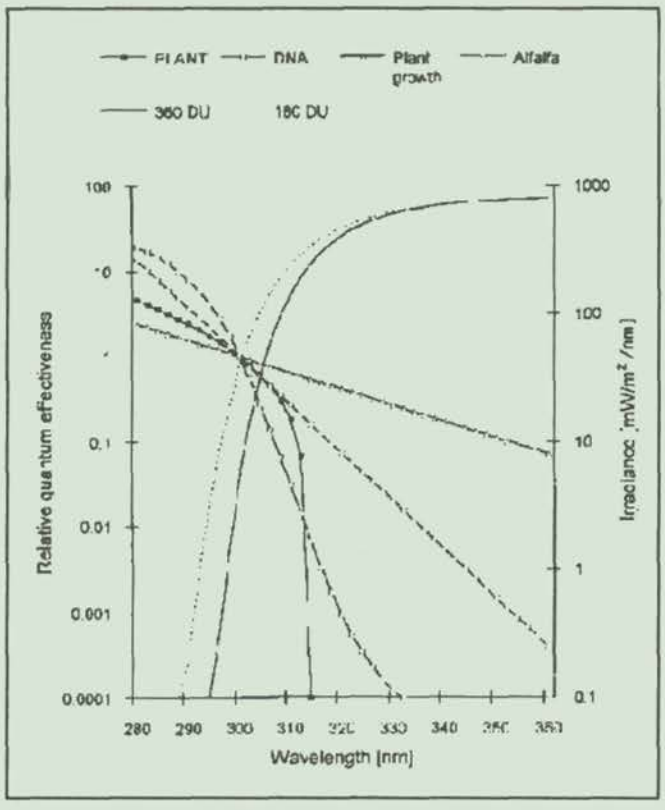

Fig.3.2. Action spectra for DNA damage *[Setlow, 1974]*, DNA dimer formation (a type of DNA damage) in alfalfa seedlings *[Quaite et al., 1992a]*, growth inhibition in seedlings *[Steinmüller, 1986]*, and generalized plant responses *[Caldwell, 1971]*. The generalized plant action spectrum was developed from action spectra available in 1971 for several processes of higher and lower plants. It has been widely used for calculating UV irradiance in experiments with higher plants. Solar spectral irradiance at 360 and 180 Dobson Units (DU) of atmospheric ozone is also shown. (A Dobson Unit is an expression used for describing thickness of the ozone layer at standard temperature and pressure; 1 mm ozone layer thickness is equivalent to 100 DU.) The solar irradiance is calculated for latitude 49°N at solar noon on Julian date 173 using the model of Green et al., *[1980]*.

Apart from action spectrum considerations, it is important in experiments to maintain a realistic balance between different spectral regions since both UV-A (315-400 nm) and visible (400-700 nm) radiation can have strong ameliorating effects on responses of plants to UV-B *[Caldwell et*

al., 1994]. In growth chamber and greenhouse experiments, the visible and UV-A radiation is usually much less than in sunlight. Thus, even if realistic levels of UV-B are used in simulating ozone reduction, the plant response may be exaggerated relative to field conditions. Even under field conditions, if applied UV-B is not adjusted downward during cloudy periods, the UV-B sensitivity may be unduly pronounced. Unfortunately, the most expensive and difficult experiments, i.e., those conducted in the field with UV-B supplements adjusted for cloudiness and other atmospheric conditions, are seldom undertaken.

As indicated in subsequent sections, another approach which achieves appropriate spectral balance is to filter existing solar radiation to modify the UV-B component. This has been done either with materials such as plastic filters or using ozone gas as a filter *[Tevini et al., 1990]*. For the latter system, in identical growth chambers, different UV-B levels can be achieved by filtering sunlight using ozone (the ozone gas is passed through an envelope of UV-transparent Plexiglas). In these growth chambers other factors such as temperature and CO_2 can be controlled. This is a considerable technical improvement on other UV-B modification experiments using filtering materials such as glass, plastic films, etc. Growth and other responses of intact seedlings can be evaluated in these chambers, but they are too small for larger plants. Of course, all these UV-B filtering approaches can only result in lowering, but not increasing, solar UV-B under the particular conditions experienced.

Plant Growth Responses

General Effects in Individual Plants

Enhanced UV-B radiation can have many direct and indirect effects on plants including inhibition of photosynthesis, DNA damage, changes in morphology, phenology, and biomass accumulation. Most of the work to date has concentrated on crop plants from temperate regions, whereas little has been done on tropical and nonagricultural plants. Sensitivity to UV-B radiation, defined as the relative change induced by UV-B on plant growth, morphology, or yield, depends on plant species, cultivar, developmental stage and experimental conditions.

Plant Growth

In many plant species reduced leaf area and/or stem growth have been found in studies carried out in growth chambers, greenhouses and in the field *[Tevini and Teramura, 1989; Johanson et al., 1994]*. Studies where the ozone filter technique with special growth chambers under solar radiation (in Portugal at 39° latitude) showed that higher solar UV-B (close to ambient levels) can result in smaller plants with reduced leaf area compared with plants under reduced UV-B levels *[Tevini et al., 1990, 1991a; Mark, 1992]*. These observations correspond with results obtained in other studies with artificial UV-B in greenhouses, growth chambers *[Tevini and Iwanzik, 1986]* and in the field *[Teramura and Murali, 1986]*. To provide differently filtered solar UV-B on a relatively larger scale, different thicknesses of UV-transparent Plexiglas have been used in greenhouses. The greenhouses (also located in Portugal) were covered with either 3 or 5 mm Plexiglas, providing a 10% difference in weighted solar UV-B. Even with this small difference in solar UV-B attenuation, reductions in growth of different cultivars of bean were observed under the higher level of solar UV-B (with the 3-mm Plexiglas).

Two studies on rice cultivars from different geographical regions were carried out in greenhouses with an enhanced daily dose of UV-B radiation using lamps *[Teramura et al., 1991]*. Of 16 rice cultivars native to the Philippines, India, Thailand, China, Vietnam, Nepal and

Sri Lanka, about one third showed statistically significant decreases in total biomass and leaf area. Tiller number, correlated with yield, was reduced in 6 of the cultivars (Figure 3.3). The Sri Lanka cultivar, Kurkaruppan, however, showed increases in both total biomass and tiller number, indicating that selective breeding might be a successful tool for obtaining UV-B tolerant cultivars *[Teramura et al., 1991]*. In another study with rice cultivars from the Philippines, total biomass changes were different among cultivars, with IR74 being the most sensitive and IR64 the least sensitive *[Figure 3.3; Barnes et al., 1993]*. Field experiments are currently underway in the Philippines using modulated UV-B lamp systems which should provide some realistic estimates of rice cultivar response to UV-B radiation.

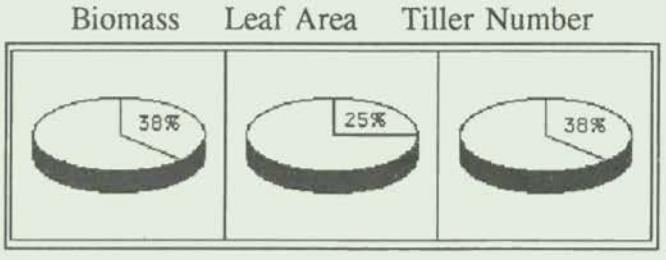

Fig. 3.3.A. Summary of a greenhouse study examining 16 rice cultivars grown with and without UV-B radiation simulating a 20% ozone depletion over the equator. The proportion of cultivars which has significantly reduced biomass, leaf area, and tiller number are shown in percents *[Teramura et al., 1991]*.

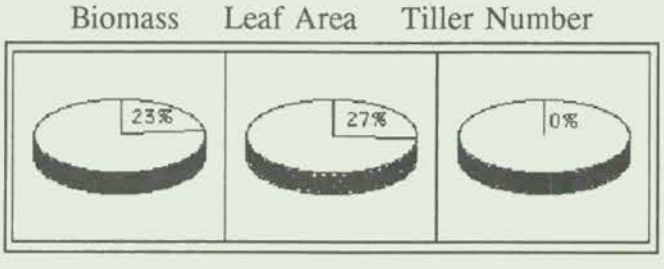

Fig. 3.3 B. Selected data from a study examining 22 rice cultivars grown with and without UV-B radiation simulating a 5% reduction in stratospheric ozone in Spring for the Philippines. The proportion of cultivars with significantly reduced total weight, leaf area, and tiller number are shown in percents [Barnes et al., 1993].

The molecular basis for many of the changes observed following UV-B exposure is not yet well defined. Responses may result from direct damage to essential cell components and by UV-B absorbed by specific photoreceptors or growth regulators *[Ensminger and Schäfer, 1992; Ballaré et al., In press]*. Preliminary experiments suggest that flavins may function as UV-B photoreceptors for the induction of pigment synthesis and inhibition of elongation *[Ensminger and Schäfer, 1992; Ballaré et al., In press]*. Elongation growth is influenced by the auxin, indole acetic acid, which absorbs in the UV-B range and could be photodegraded by high levels

of UV-B radiation. Oxidative enzymes, such as the peroxidases, are increased by enhanced UV-B radiation, and may be involved in plant hormone regulated growth responses, as shown in sunflower *[Ros 1990]*. The levels of another plant hormone, ethylene, which causes greater radial growth and less elongation, are increased after irradiation with UV-B in, e.g., sunflower seedlings *[Ros 1990]* and cultured shoots of pear plants [*Predieri et al. 1993]*.

Flowering

Ultraviolet-B radiation can alter both the time of flowering *[Caldwell, 1968; Ziska et al., 1992; Saile-Mark, 1993; Staxén and Bornman, 1994]* as well as the number of flowers in certain species. For example, Rau et al., *[1988]* found substantial decreases in flowering from UV-B irradiation. Differences in timing of flowering may have important consequences for the availability of pollinators. The reproductive parts of plants, such as pollen and ovules, are rather well shielded from solar UV-B radiation. For example, anther walls can absorb more than 98% of incident UV-B *[Flint and Caldwell, 1983]*. In addition, the pollen wall contains UV-B absorbing compounds affording protection during pollination. Only after transfer to the stigma might pollen be susceptible to solar UV-B radiation. Germinating pollen can be sensitive at this time to UV-B *[Flint and Caldwell, 1984]*. The overall significance of this in the context of the ozone reduction problem is unclear and needs to be assessed.

Limitation of Growth Chamber Studies

In growth chambers and greenhouses the radiation conditions are usually quite different from those in the field. For example, the visible radiation which is used in photosynthesis (400 to 700 nm, photosynthetically active radiation, PAR) and the UV-B/UV-A/PAR ratios are different from those in the field. As mentioned earlier, if UV-A and PAR are low, the effects of UV-B may be much more severe (see above). In addition, other factors, such as temperature, water and nutrients differ from conditions in the field and this can alter response to UV-B radiation. However, experiments in controlled conditions are usually necessary as a first step in defining plant response to specific combinations of UV-B and other environmental factors. It is, however, important that these studies conducted under controlled conditions be verified as much as possible under field conditions.

Translating Whole-Plant Reactions to Ecosystem Responses

Plants compose most of the living mass in terrestrial ecosystems. Although there can be effects of UV-B directly on microbes and animal life (e.g., *[Blaustein et al., 1994; Gehrke et al., In press]*, see also Chapters 2 and 4), most of the ecosystem-level responses of solar UV-B are anticipated to be mediated through the effects on plants. As shown in Figure 3.4, the major anticipated effects of increased solar UV-B on agricultural and nonagricultural ecosystems (such as forests, grasslands, savannahs, deserts, tundra, etc.) may result from changes in plant growth and form and secondary chemical composition. Although the principal processes may be the same in highly managed agroecosystems and in nonagricultural ecosystems, their importance is thought to be different. Therefore, different schemes are presented for each in Figure 3.4. Some forest systems, such as plantations, can be considered as agricultural systems for these purposes.

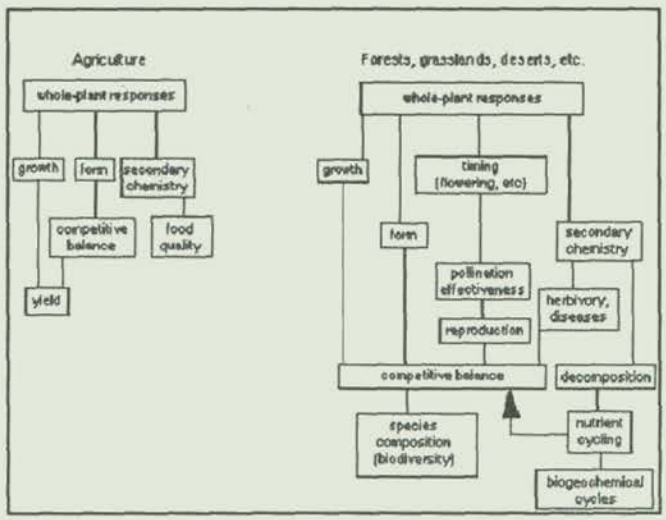

Fig. 3.4. Possible important consequences of increased solar UV-B in highly managed systems such as agricultural and forest plantation systems and in nonagricultural, less intensively managed ecosystems.

Competitive Balance

In forests, grasslands, etc., overall primary plant productivity may not be greatly affected by ozone reduction even if the growth of some plants is diminished. However, since plant species differ greatly in growth responsivity to UV-B, it is anticipated that a productivity reduction of one species will probably lead to increased productivity of another, more UV-tolerant species. This is conceivable because more resources (e.g., light, moisture and nutrients) will be available to the tolerant species. Thus, the overall productivity of the system may well remain about the same while species composition may change. However, a change in the balance of species could have far-reaching consequences for many ecosystems.

Another mechanism whereby the competitive balance of plant species can be changed by increased UV-B is through changes in plant form. Even if plant production per se is not affected by increased UV-B, changes in plant form can result in changes in which species can more effectively compete for sunlight. This phenomenon has been demonstrated in several experiments. For example, in a five-year field study using modulated UV-B lamp systems, the competitive balance of two species (wheat and a common weed, wild oat) could be changed even though the increased UV-B had no effect on production and growth of these species if grown by themselves *[Barnes et al., 1988]*. A quantitative analysis of competition for sunlight in the mixed stands with and without supplemental UV-B showed that subtle changes in plant form of the two species were sufficient to change the balance of competition for sunlight which is necessary for photosynthesis *[Ryel et al., 1990]*. Therefore, one species can achieve some advantage over the other because one captures more sunlight for photosynthesis. In these experiments, the wheat benefited from increased UV-B and the weed suffered. However, in other mixtures of crop and weeds, the situation could well be reversed. Also, other changes in plant form, such as greater allocation of biomass to roots, might change competitive effectiveness of individual species for soil moisture and nutrients.

In grasslands and forests that are not managed intensively, similar changes in species composition may be experienced. Of course, in forests this would take a long time to be realized. Also, if there are only a few tree species present and they all are sensitive to solar UV-B and experience growth reduction, overall forest productivity could decrease. Ecosystem-level experiments with nonagricultural systems are only beginning *[Johanson et al., In press]*.

Timing of Life Phases

The timing of life phases of plants is a combination of response to environmental factors and the genetic constitution of the plant. This timing of events such as flowering, entering and breaking of dormancy, and even senescence is important not only to the individual plant, but also in how plants interact with other plants and animals. For example, a shift in the timing of flowering can mean that a plant species might not have sufficient insect pollinators available at the new time of flowering either because the insects are not present or because other plant species are attracting these pollinators. Such changes could also conceivably be important in agricultural systems, but intervention with management options may make these changes less important. As indicated earlier in this chapter, increased UV-B has been shown to advance or delay (depending on species) the time of flowering in plants. There is little work at present on flowering responses and virtually nothing on other potential effects of UV-B on life phase timing.

Plant Secondary Metabolism

Another pathway by which increased solar UV-B can have an influence at the ecosystem level is through changes in secondary metabolism of plant tissues. Increased UV-B can alter secondary chemical composition. It has been shown repeatedly that flavonoids and related phenolic compounds increase when plants are exposed to increased UV-B. Apart from the UV-B protection afforded by increases of these compounds, there are many other ecological implications of changes in these and related compounds. These compounds are important for plants in deterring insects and other herbivores from consuming plant tissues and they play a role in resistance to pathogens. For example, McCloud and Berenbaum *[1994]* have shown that UV-B can increase furanocoumarin content of plant tissue which, in turn, results in slower development of certain insect larvae during early life stages of the larvae. In some legume, conifer and in one woody dicotyledon (*Vitis vinifera*) UV-B has been shown to induce phytoalexin synthesis *[Beggs and Wellmann 1994];* some phytoalexins are considered to be toxic to humans and many animal species, e.g., coumestol a compound with estrogenic properties which is induced in bean plants exposed to UV-B *[Beggs et al. 1985]*.

Secondary compounds that are important as structural materials in plants, such as lignin, are also related to flavonoids and phenolic compounds. If the ratio of lignin to cellulose in plant tissues changes, it can alter the rate of decomposition. This has very important implications for biogeochemical cycles as discussed in Chapter 5.

Overall, the consequences of increased solar UV-B in forests, grasslands and other nonagricultural ecosystems may involve several complex pathways (Figure 3.4) rather than simply a reduction in overall ecosystem primary productivity. However, the effects of these more involved pathways are difficult to predict without conducting experiments with assemblages of plant species and long-term study of ecosystem responses. This has, thus far, received very little attention in actual research. Further discussion of implications for specific types of ecosystems follows later in this chapter.

UV Protection and Adaptive Responses

UV Penetration

Structural and biochemical changes induced by enhanced levels of UV-B radiation ultimately modify the penetration of UV radiation into the plant. For example, the induction of UV-screening pigments, typically flavonoids and certain other phenolic compounds, will reduce the penetration of UV-B radiation to underlying tissues. Increased wax on leaf surfaces also can contribute to reduced penetration of UV due to increased reflection from the leaf surface, although reflection for most leaves is usually not more than 10% *[Robberecht et al., 1980]*. At the structural level, increased length of inner leaf cells or increases in cell number, both palisade and spongy mesophyll, influence the penetration and spectral distribution of UV radiation across a leaf. Direct measurements of UV penetration have been done using a fibre optic microprobe *[Bornman and Vogelmann, 1988; Day et al., 1992, 1993; see also Bornman and Teramura 1993; DeLucia et al., 1992; Cen and Bornman, 1993]*. Ultraviolet radiation penetration varies among different plant species and this should be reflected in the sensitivity of these species. Penetration of UV-B was found to be greatest in herbaceous dicotyledons (broad-leaved plants) and was progressively less in woody dicotyledons, grasses and conifers *[Day et al. 1992]*. The UV penetration also changes with leaf age; younger leaves attenuate UV-B radiation less than do the more mature leaves, as was shown for some conifers *[DeLucia et al. 1991, DeLucia et al. 1992]*.

Protection and Repair

Although different species exhibit different UV-B attenuation depending on pigments (such as flavonoids) and leaf structure, the level of attenuation can also change as more UV-B-absorbing pigments are synthesized in response to UV-B exposure. Species also differ in their ability to increase UV-B-absorbing pigment levels. Increased levels of flavonoids have been shown to directly reduce the levels of damage by UV-B *[Tevini et al., 1991b]*. The link between flavonoid levels and UV-B sensitivity is most vivid in extreme cases. For example, Li et al. *[1993]* showed that mutants of a mustard species, *Arabidopsis thaliana*, that lacked flavonoids were extremely sensitive to the UV radiation. An anthocynanin-deficient mutant of maize was found to be more sensitive to DNA damage by UV-B than the normal plants *[Stapleton and Walbot 1994]*. In cabbage leaves, flavonoids were shown to accumulate in the epidermal layers in response to mild UV-B exposure. The flavonoids protected the underlying tissues from DNA damage in the form of thymine dimer formation *[Beggs and Wellmann 1994]*. In addition to adaptive responses involving pigment induction, changes in surface waxes and certain leaf structural characteristics may also contribute to reducing penetration of UV into the plant tissues. Increases in scavengers of free radicals and active oxygen species may also mitigate the negative effects of UV radiation *[see Bornman and Teramura, 1993]*.

Another characteristic of plants is the ability to repair damage. This may be exemplified by the replacement of damaged components, e.g., proteins, or by the light and dark processes involved in repair of DNA damage. Under illumination, the enzyme DNA photolyase repairs the UV-induced production of pyrimidine dimers. Both visible and UV-A radiation drive this repair, underlining again the importance of a balanced spectral regime for experiments not conducted in the field. A very effective repair capacity by DNA-photolyase in several plant systems (cell cultures, isolated leaves, seedlings and mature plants of several species) has been demonstrated *[Buchholz et al., In press; McLennan 1987]*. To date, little research has been done on induction

of pyrimidine dimers in plants; a recent exception is the work of Quaite et al. *[1992 a,b]* on alfalfa seedlings.

Interaction of UV-B and Other Factors

Plants in nature seldom are affected by only a single stress factor, such as UV-B radiation. Instead, plants typically respond to several factors acting in concert. Therefore, it is important to keep in mind that the effectiveness of UV-B radiation can be greatly modified by some of these other factors, in some cases aggravating, and in some cases ameliorating the overall UV effect.

Water stress commonly occurs in nature. In a field study specifically designed to test the interaction between UV-B radiation and water stress, Sullivan and Teramura *[1990]* demonstrated that UV-B mediated reductions in photosynthesis and growth were observed only in well-watered soybeans. When soybeans were water stressed, the same UV-B dose produced no significant effect on either photosynthesis or growth. The interpretation of these observations was that water stress produced a large reduction in photosynthesis and growth that thereby masked the UV-B effect. Furthermore, water stressed plants produced a higher concentration of leaf flavonoids, which in turn, provided greater UV-B protection.

Increases of atmospheric CO_2 and global warming are anticipated in scenarios of future climate change. Model calculations predict that the average global temperature will rise by 1.5 - 4.5° and that atmospheric CO_2 concentration will double by the latter part of the next century *[Intergovernmental Panel on Climate Change 1992]*. When studied independently, plant growth responses to changes in UV-B radiation and atmospheric CO_2 concentration generally are thought to be in opposite directions, thereby leading some to the hypothesis of a canceling of effects. To date, only a few experiments have been specifically designed to examine this important interaction. The first such study *[Teramura et al., 1990b]* included two cereal crops (rice and wheat) and one legume (soybean). In that study, the increase in growth and seed yield resulting from a CO_2 enrichment was eliminated by UV-B radiation in rice, reduced in wheat and unaffected in soybean. This suggests that overestimates in production may be made for cereal crops if CO_2 enrichment is considered without UV-B radiation.

In loblolly pine, Sullivan and Teramura *[1994]* reported that the combined effects of UV-B and CO_2 produce changes in the proportion of dry matter in roots compared with aboveground shoots. At present-day levels of CO_2, UV-B caused more shoot production than roots, while the same UV-B dose resulted in more roots at elevated levels of CO_2. The implications of these changes is that plant competition and, therefore, ultimately community composition might be altered by these changes in allocation patterns, as described earlier.

As mentioned above, global climate change will likely include increased global mean temperatures in addition to increased UV-B radiation. Unfortunately, only very limited information is available on the consequences of these combined effects. In a study with sunflower and maize seedlings in the ozone-filter cuvette system mentioned earlier, Tevini et al. *[1991b]* found that photosynthesis was unaffected (maize) or declined (sunflower) with higher temperature when the UV-B in sunlight was attenuated with the ozone filter. In contrast, overall seedling production was greater at higher temperatures in both species under conditions approaching ambient solar UV-B. This observation might be attributed to accelerated plant development at the higher temperature.

Many metals such as cadmium, nickel, copper and lead, which can accumulate to high concentrations from human activities, are toxic to plants. The stress imposed by high levels of metals may be further compounded with increased UV-B radiation. Dubé and Bornman *[1992]* showed that in spruce (*Picea abies*) with low levels of supplemental UV-B, the effect of the addition of cadmium was greater than for either stress alone for some of the parameters measured. Mobilization of the essential trace element zinc can be reduced by UV-B radiation *[Ambler et al., 1975]*.

The degree of susceptibility of plants to disease and insect attack may change under elevated levels of UV-B radiation. These effects will vary among species, cultivar and plant age. For example, certain diseases may be less damaging to the plant under conditions of high UV-B, while the severity of others may be increased. The latter was shown in a study where sugar beet grown under elevated levels of UV-B radiation was infected with a fungus *Cercospora beticola* leading to a deleterious additive effect from the two stress factors *[Panagopoulos et al., 1992]*. The timing of infection is also of importance. Plants first exposed to UV-B radiation may be more susceptible to subsequent infection as shown in a study of cucumber infected with *Colleotrichum lagenarium* and *Cladosporium cucumerinum* prior to UV-B exposure *[Orth et al., 1990]*. Infection after UV exposure had no effect on the severity of the disease.

Interaction of UV-B with tropospheric air pollutants is also of concern although little work has been thus far conducted in this area. One field study of soybean plants showed them to be sensitive to ozone in the air. However, they were not sensitive to UV-B supplements from lamps under the particular test conditions and there were no significant interactions of supplemental UV-B and ozone *[Miller et al., 1994]*.

Implications for Agriculture, Forests and Other Ecosystems

Crops

One of the primary concerns of future increases in solar UV-B radiation is its potential effect on global agriculture. Despite the enormous potential consequences, we cannot yet make a quantitative prediction of anticipated effects resulting from stratospheric ozone depletion. This results from the limitation in the controlled-environment studies as discussed earlier and the overall paucity of experiments performed in field trials. Even in comparisons of field studies, there are large differences in temperature, precipitation, soil types, etc. from year to year and in different locations. This adds to the difficulty in making generalizations about the effects.

A six-year field experiment was conducted to evaluate the effects of UV-B supplementation in two commercially grown soybean cultivars *[Teramura et al., 1990a]*. These cultivars were specifically selected for their contrasting UV-B sensitivity previously determined by screening over 50 soybean cultivars under greenhouse conditions. (For perspective, nearly 2 out of 3 of the cultivars screened for UV-B sensitivity in the greenhouse exhibited sensitivity to UV-B.) In the field experiments, artificial lamps with selected filters were used in addition to the normal solar radiation. Plants were exposed to either ambient levels of solar UV-B or ambient radiation supplemented with UV-B emitted by the lamps. When evaluated over the entire six-year period, yield in the sensitive cultivar was reduced by 19 to 25%, in four of the six years (Figure 3.5). The other two years were characterized as hot and dry and all plants in the field experienced considerable water stress. As shown in subsequent field and greenhouse studies, the effectiveness

of UV-B radiation is masked when the plants were subjected to other stresses such as drought (see section above).

In the same study, while the sensitive soybean cultivar exhibited decreased yield, production increased by 4 to 22% in the tolerant soybean cultivar. Such cultivar differences in the response to UV-B radiation may be important in future plant breeding considerations, since it suggests that UV-B tolerance already naturally exists in the modern soybean germplasm. A number of studies have shown that in addition to the wide range of sensitivity found among species, an impressive array of cultivar responses also have been observed. Figure 3.3 shows the proportion of sensitive rice cultivars screened under greenhouse conditions. Note that in this example, UV-B radiation elicits both positive as well as negative responses in rice. Similarly, wide-ranging cultivar differences have been reported in a number of plant ranging from crops such as soybean to forest tree species such as loblolly pine.

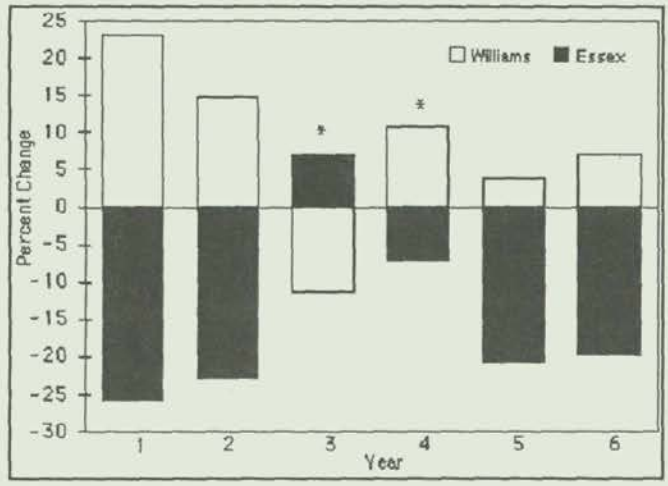

Fig. 3.5 Summary of yields in a 6-year field study using two soybean cultivars: Essex previously identified as UV-B sensitive and Williams, UV-B tolerant. The studies utilized filtered fluorescent sun lamps to simulate a 25% ozone depletion over College Park, Maryland (39° N latitude). Values presented above represent percent changes from control plants receiving only ambient levels of UV-B radiation *[Teramura et al., 1990a]*. Asterisks represent years with drought.

In addition to quantitative changes in crop yield, evidence exists for qualitative changes as well. For instance, in the study mentioned above, UV-B radiation also resulted in small changes on the order of 1 to 5% in the protein and oil content of the soybean seed.

A wide range of experimental protocols and methodologies have been used by different investigators which complicates the assessment of overall effects of elevated UV-B on crops. Several experiments reveal effects of UV-B and several do not. Because of the relatively few field studies that have been conducted, a quantitative prediction of the potential consequences for global food production resulting from increased solar UV-B is not now possible.

Forests

Despite the fact that over two thirds of global terrestrial productivity occurs in forest ecosystems, little information exists on the effects of UV-B radiation on forest tree species. Tropical forests, though representing nearly one half of global productivity and much of the total tree species diversity, have received very little attention thus far in respect to the ozone reduction problem. Although little ozone reduction has thus far occurred in the tropics, only a small decrease of ozone at these latitudes results in an absolute increase of UV-B since solar UV-B is already very intense (see Chapter 1). One recent study showed that excluding existing solar UV-B with filters can result in increased growth of some tropical tree species *[Searles and Caldwell, in press]*. However, for the most part, the effects of UV-B radiation on tropical tree species have been largely ignored.

Fortunately, there is some information for midtemperate latitude tree species. Because they are long lived, trees present a unique opportunity to observe the longer-term accumulative aspects of UV-B exposure. In one field study using loblolly pine *[Sullivan and Teramura, 1992]*, seedlings from several different geographic regions were grown for three consecutive years under UV-B lamps in a field experiment. Seedlings were exposed to either ambient solar UV-B or ambient levels supplemented with the UV-B from lamps, similar to the soybean study above. After only the first year of UV-B exposure, reductions were observed in biomass of seedlings derived from several geographic areas. By the end of the third year, these biomass reductions were several-fold larger. These overall growth reductions were generally associated with small decreases in both roots and shoots, but not necessarily accompanied by reductions in photosynthesis. This may be due to changes in needle growth or shifts of allocation as has been found for some crop species. Therefore, these results suggest that the UV-B effects may be accumulative in long-lived plants such as trees, and that even small changes in UV-B radiation might have significant effects over the life time of the trees. Even in the absence of direct UV-B effects on tree biomass, UV-B radiation may still have ecological implications. Changes in plant architecture or biomass allocation could result in alterations in tree seedling competition, ultimately affecting patterns of forest succession.

Other Ecosystems

Although absolute UV-B irradiance is naturally very low in subarctic and Arctic ecosystems such as tundra, there is experimental evidence that the plants in such a system react to increases in UV-B associated with realistic levels of ozone depletion. In a recent field study in northern Sweden, natural dwarf shrub vegetation containing two evergreen species *(Empetrum hermaphroditum* and *Vaccinium vitis idæa)* and two deciduous species *(V. myrtillus* and *V. uliginosum)* was exposed to artificially enhanced UV-B radiation. Leaf thickness was increased *(V. vitis idæa)* or decreased (the deciduous species) while stem growth over a two-year period was retarded more in evergreen species than in deciduous species. This suggests that a UV-B increase over an extended time could result in species composition changes *[Johanson et al. In press]*. Not only growth inhibitions, but also species-specific morphological changes have been observed, which, with time, may result in altered community composition.

Chemical Effects of Ozone Depleting Substances and Breakdown Products of Replacement Substances

Trifluoroacetic acid (TFA) is a breakdown product of HFC134a, HCFC123 and 124 *[WMO/UNEP 1994]* that is anticipated to achieve a final average concentration less than one thousandth of that required for toxicity of plants, making general impacts on the earth's vegetation by TFA unlikely. Substantially higher concentrations of TFA may occur in areas with low precipitation since the same quantity of TFA would be concentrated in less rainfall. Toxic concentrations in soils could conceivably build up in areas with high evaporation rate or lacking runoff, where salt stress excludes vegetation except for very specialized species. Although plants in such areas are of minor importance both economically and for global primary production, some are essential for migratory birds and other wildlife. Further investigations should therefore be focused on such areas and species.

Conclusion

Mechanisms of UV-B action on plant systems are reasonably well understood when compared with our ability to assess potential consequences of enhanced UV-B at the level of ecosystems. As global change involves not only increased solar UV-B, but also increased atmospheric CO2 concentrations and temperature changes, realistic assessments of the effect of stratospheric ozone reduction need to consider interacting factors. Effects of enhanced UV-B on terrestrial ecosystems are anticipated, both in agriculture, and in nonagricultural areas such as forests, tundra, etc., but prediction of exact consequences, and sometimes even the direction of these changes, is not currently possible.

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CHAPTER 4

EFFECTS OF INCREASED SOLAR ULTRAVIOLET RADIATION ON AQUATIC ECOSYSTEMS

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Summary

Aquatic systems supply humans with vast amounts of food, primarily in the form of finfish, shellfish and seaweed. More than 30% of the world's animal protein for human consumption comes from the sea, and in many countries, particularly the developing countries, this percentage is significantly higher. As a result, it is important to know how increased levels of exposure to solar UV-B radiation (280-315 nm) might affect the productivity of aquatic systems.

In addition, the oceans play a key role with respect to global warming. Marine phytoplankton are a major sink for atmospheric carbon dioxide, and they have a decisive role in the development of future trends of carbon dioxide concentrations in the atmosphere. The relative importance of the net uptake of carbon dioxide by the biological pump in the ocean and by the terrestrial biosphere is a topic of much current research.

Phytoplankton form the foundation on which the very survival of aquatic food webs depends. Marine phytoplankton are not uniformly distributed throughout the oceans of the world. The highest concentrations are found at high latitudes while, with the exception of upwelling areas on the continental shelves, the tropics and subtropics have 10 to 100 times lower concentrations. In addition to nutrients, temperature, salinity and light availability, the high levels of exposure to solar UV-B radiation that normally occur within the tropics and subtropics may play a role in phytoplankton distributions.

A major loss in primary biomass productivity may have significant consequences for the intricate food web in aquatic ecosystems and affect food productivity. It has been estimated that a 16% ozone depletion could result in a 5% loss in phytoplankton, which equals a loss of about 7 million tons of fish per year. Biological effects of small changes in UV-B exposure may be difficult to determine because the biological uncertainties and variations are large, and the baseline productivity for pre-ozone-loss eras is not well established.

Phytoplankton productivity is limited to the euphotic zone, the upper layer of the water column in which there is sufficient sunlight to support net productivity. The position of the organisms in the euphotic zone is influenced by the action of wind and waves.

In addition, many phytoplankton are capable of active movements that enhance their productivity and, therefore, their survival. Like humans, phytoplankton cannot perceive, and thereby avoid, UV-B radiation. Exposure to solar UV-B radiation has been shown to affect both orientation mechanisms and motility in phytoplankton, resulting in reduced survival rates for these organisms.

Researchers have directly measured the increase in, and penetration of, UV-B radiation in Antarctic waters, and have provided conclusive evidence of direct ozone-related effects within natural phytoplankton communities. Making use of the space and time variability of the UV-B front associated with the Antarctic ozone hole, researchers assessed phytoplankton productivity within the hole compared to that outside the hole. The results show a direct reduction in phytoplankton production due to ozone-related increases in UV-B. One study has indicated a 6 - 12 % reduction in the marginal ice zone.

In recent years, there has been an increased interest in UV-B effects on macroalgae and seagrasses. In contrast to the phytoplankton, most macrophytes are attached to their growing site, thereby restricting them to specific growth areas and the resultant exposure to UV-B radiation. Recent studies have demonstrated that photosynthesis is inhibited in many red, brown, and green benthic algae.

Solar UV-B radiation has been found to cause damage to early developmental stages of fish, shrimp, crab, amphibians and other animals. The most severe effects are decreased reproductive capacity and impaired larval development. Even at current levels, solar UV-B radiation is a limiting factor, and small increases in UV-B exposure could result in significant reduction in the size of the population of consumer organisms. At high latitudes (over 40°N) the late-spring increases in UV-B exposure may affect some species because the UV-B enhancement occurs at critical phases of their development. Even small increases or temporary fluctuations in UV-B may affect relatively sensitive species.

Recent studies have addressed the potential impact of chlorofluorocarbon substitutes and their degradation products. Some HFCs and HCFCs, notably HFC134a, HCFC123, and HCFC124, are degraded generating trifluoroacetic acid (TFA) as their main product. TFA is mildly toxic to most marine and freshwater phytoplankton. It is still speculative if TFA is concentrated in the food web. Even if produced well into the next century, TFA is unlikely to reach toxic levels for oceanic phytoplankton; however, it could reach toxic levels in restricted aquatic systems.

Although there is overwhelming evidence that increased UV-B exposure is harmful to aquatic ecosystems, the potential damage can only be roughly estimated at the present time.

Introduction

Aquatic ecosystems balance terrestrial ecosystems in biomass production which are assumed to incorporate large amounts of atmospheric carbon into organic material with estimates between 90 and 100 gigatons (Gt, 10^9 tons) annually *[Houghton and Woodwell, 1989; Siegenthaler and Sarmiento, 1993]*. Therefore it is important to know what effect increased solar UV-B irradiation has on marine productivity and on the whole ecosystem depending on this productivity as well as climatological processes linked with it *[Smith, 1989; Prézelin et al., 1993]*. As only 0.5 % of the water surface is freshwater, the marine systems are by far the most important in the context of global carbon cycles. On the other hand, a recent workshop on freshwater ecosystems convincingly demonstrated that lakes are excellent model systems for studying larger marine environments, and many of these systems are locally important.

Since most macroalgae are restricted to coastal areas, the largest share in biomass production can be attributed to phytoplankton. Phytoplankton constitute the basis for the intricate food web in the oceans and thus are a prerequisite for the crop of fish, crustaceans and mollusks. Furthermore, as they are responsible for the uptake of half of the carbon dioxide from the atmosphere, any reduction in the uptake capacity would result in an increase in the greenhouse effect, with subsequent impacts on global climate change. Recent investigations indicate that many aquatic ecosystems are under considerable UV-B stress even at current levels *[Häder, 1993a; Cullen and Lesser, 1991; Smith et al., 1992]*. Being dependent on solar energy for photosynthesis, phytoplankton are restricted to the upper layers in the water column where they are exposed to high levels of short wavelength radiation. The subject of UV-B effects on aquatic ecosystems has been covered in a number of recent reviews *[Häder, 1993b; Acevedo and Nolan, 1993; Weiler and Penhale, 1994; Cullen and Neale, 1994; U.S. DOE, 1993; SCOPE, 1992a,b; Holm-Hansen et al., 1993a,b; Tevini, 1993; Biggs and Joyner, 1994; Williamson and Zagarese, 1994; Karentz et al., 1994; Smith and Cullen, 1995]*.

Primary producers

Solar UV-B radiation has been found to affect DNA, to impair photosynthesis, enzyme activity and nitrogen incorporation, to bleach cellular pigments and to inhibit motility and orientation *[Döhler et al., 1991; Häder et al., 1989, 1991; Worrest and Häder, 1989; Häder and Worrest, 1991]*. DNA is one of the targets of radiation, but in addition a host of other chromophores and proteins are affected. Thus, UV-B does not damage one key target in phytoplankton but has many deleterious effects which differ in their action spectra. The action spectra are further complicated by antagonistic and repair processes stimulated by UV-A and visible radiation. Figure 4.1 shows the action spectrum based on irradiance response curves of UV inhibition of photosynthetic oxygen production in a mass biomass producer, the cyanobacterium *Nodularia spumigena*, isolated from the Baltic Sea.

In order to evaluate the effects of solar UV-B radiation on aquatic ecosystems a number of basic questions need to be answered:

- What is the expected spectral distribution at the surface of the water on a global basis as a function of important physical, chemical, bio-optical, biological and environmental parameters, e.g. time of day, season, ozone concentration, during the decades to come?
- What is the spectral penetration of solar short wavelength radiation as a function of depth in different water types?
- What is the vertical distribution of the aquatic organisms in the water column for major water types?
- What is the biologically and spectrally weighted sensitivity of the organisms affected by solar UV-B?
- What are the extent and limits of UV repair and adaptation as well as the effects of other environmental factors in mitigating or augmenting UV effects?

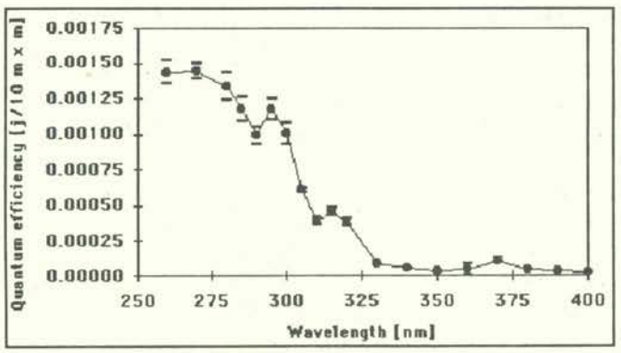

Fig. 4.1. Action spectrum for the inhibition of photosynthesis in the cyanobacterium *Nodularia spumigena*.

Global distribution

Phytoplankton are not uniformly distributed in the oceans of the world (Figure 4.2); the highest concentrations are found in the high latitude regions while the tropics and subtropics show 10 to 100 times lower concentrations (with the exception of the upwelling areas on the continental shelves and near the equator). In addition to other factors including nutrients, light availability and water column stability, UV-B radiation may play a role in this, as irradiance here is about several times higher than in circumpolar areas *[Häder, 1993b]*. In temperate oceans phytoplankton blooms occur in spring and are reduced during summer. Sometimes there is a second bloom in autumn. Judging from this general pattern, significant increases in solar UV-B irradiation are expected to have detrimental effects on phytoplankton productivity. Field studies conducted under the Antarctic ozone hole have demonstrated some impact on primary productivity. Since depletions in global

stratospheric ozone are expected to continue at all latitudes well into the next century *[Stolarski et al., 1992]* the effects of increased UV-B on marine primary productivity may also be relevant outside polar regions. The influence of UV-B on the abundance and distribution of phytoplankton remains a key uncertainty.

In the last few years the role of nano- and picoplankton have been investigated. In the past their existence was grossly underestimated because of their small size and technical problems during harvesting; today their contribution to the total biomass is estimated to be at least 40 %. A similarly important role and significant biomass productivity has been found for bacterioplankton which are responsible for degradation and cycling of organic matter in the sea. UV-B has been shown to strongly affect both bacterioplankton, as well as the extracellular enzyme activity of bacteria in subsurface waters *[Herndl et al., 1993]*. There are also indications of large populations of viral particles (10^7 per ml) in the oceans, the significance of which is not yet clear. The work of several workers *[Karentz et al., 1994]* suggests that small organisms (bacterial and microalgae), because of their size and short generation times, are likely to be more susceptible to UV stress than larger organisms. As a consequence, UV-B may play a key role in niche separation, lower food web processes and species composition shifts.

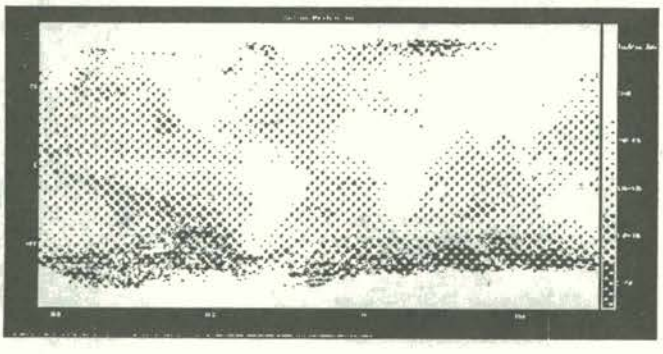

Fig. 4.2 Geographical distribution of global oceanic primary production based upon an optical model and satellite derived data (Byers, 1994).

Vertical distribution

The transparency of the water strongly depends on the water type *[Piazena and Häder, 1994]*: in coastal waters with high seston (particulate substances) and gelbstoff (yellow dissolved organic substances) concentrations UV-B may penetrate less than 1 m to the 1 % level; in contrast, in clear oceanic waters penetration to several tens of meters has been shown (Figure 4.3) *[Smith and Baker, 1979; Smith et al., 1992]*. Several recent papers contain information on bottom-ice algae and transmission of UV through ice *[Ryan et al., 1992; Weiler and Penhale, 1994]*. Until recently there were few in-water optical sensors capable of accurately measuring

UV-B as a function of depth in aquatic systems. Recent comparisons by Kirk et al. *[1994]* suggest that several commercial instruments can, with care, be used to obtain quantitative underwater UV-B information. This is an important advance in studying the effects of solar short wavelength irradiation on aquatic ecosystems as it will permit more accurate estimates of the UV-B exposures that aquatic organisms receive.

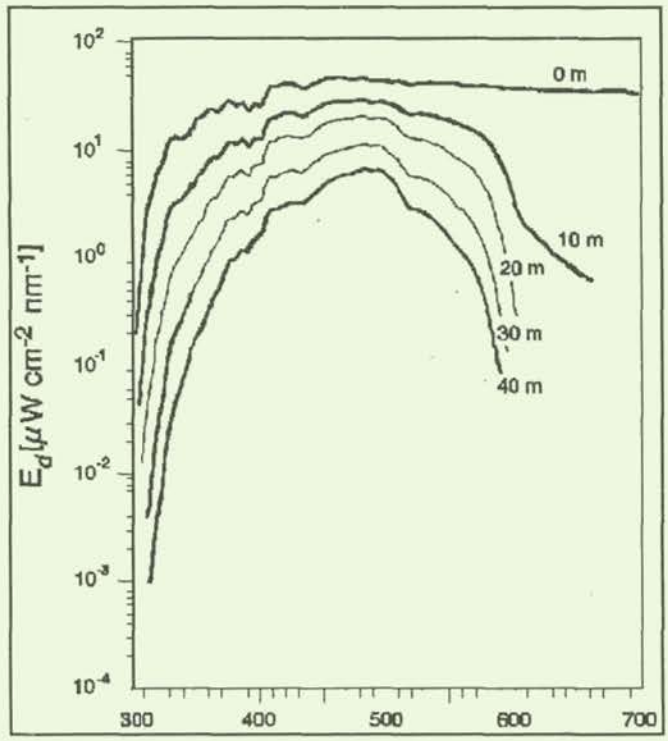

Fig. 4.3. Penetration of solar radiation in Antarctic waters (65° 20′ S, 73° 37′ W) under thin overcast, solar zenith angle 49.2°, ozone concentration 275 DU (Smith et al., 1992)

Phytoplankton productivity is limited to the euphotic zone, the top layer of the water column, the lower limit of which is defined as the depth where photosynthesis balances respiration (typically the depth to which incident PAR (photosynthetic active radiation) irradiance is reduced to the 0.1 % level of surface radiation). The position of the organisms in the euphotic zone is influenced by physical processes, e.g., wind, waves and mixing. In addition, many phytoplankton are capable of active movements, and daily vertical migrations of up to 15 m have been measured. Light and gravity are employed to guide the organisms to depths of optimal irradiation resulting in typical vertical distribution patterns found in both freshwater and marine ecosystems *[Lindholm, 1992; Eggersdorfer and Häder, 1991a,b]*. Solar UV-B irradiation has been shown to affect both motility and the orientation mechanisms in phytoplankton *[Häder, 1993a,b]*. Organisms not actively motile, such as cyanobacteria, diatoms and even bacteria employ buoyancy to control their vertical position in the water column by producing gas

vacuoles or oil droplets *[Walsby, 1987; Walsby et al., 1992; Gosink et al., 1993]*.

Phytoplankton use various bands in the visible and UV-A range to orient with respect to light while UV-B is not used for photoorientation; thus, they are in a situation similar to humans. Phytoplankton are not able to perceive the detrimental radiation and cannot escape over-exposure if UV-B levels increase.

Field studies in Ghana showed that the percentage of motile filaments and linear velocity of several cyanobacteria as well as their orientation mechanisms with respect to light are affected within minutes by solar radiation. The damage was only partially repaired and only after short exposure times. In contrast, longer exposure times even resulted in increasing damage over a 24-h period *[Donkor et al., 1993a,b]*. Work carried out in India has indicated that solar UV-B affects the nitrogenase activity and carbon dioxide uptake in rice paddy cyanobacteria *[Tyagi et al., 1991, 1992]*. Some cyanobacteria, however, characterized by a brown color, seem to be better adapted to high solar radiation than closely related green forms.

Carbon dioxide uptake and its role in global warming

The oceans play a key role with respect to global warming. A long-term global warming of surface air temperature by 1.5 - 4.5°C is predicted for a doubling of the CO_2 concentration accompanied with a 1-m rise in sea level by 2080 *[IPCC, 1990, Weaver, 1993]*. As marine phytoplankton are a major sink for atmospheric CO_2 they have a decisive role in future trends of carbon dioxide concentrations in the atmosphere as well as in terrestrial and aquatic ecosystems (Figure 4.4) *[Bowes, 1993; Melillo et al., 1993]*.

Before the onset of anthropogenic carbon release the uptake and release of atmospheric carbon were balanced and the concentration of CO_2 in the atmosphere was constant for extended periods of time. The increase in fossil fuel burning and deforestation results in an additional release of about 7 Gt of carbon into the atmosphere. However, long-term measurements indicate an annual deposit in the atmosphere of only 3 Gt. It can be assumed that the remaining 4 Gt are taken out of the global atmosphere by a net uptake by the biological pump in the ocean, a net uptake of CO_2 by the terrestrial biosphere or a combination of both. The relative importance of the two uptake modes is the topic of much current research *[Lampitt et al., 1993; Toggweiler, 1993]*.

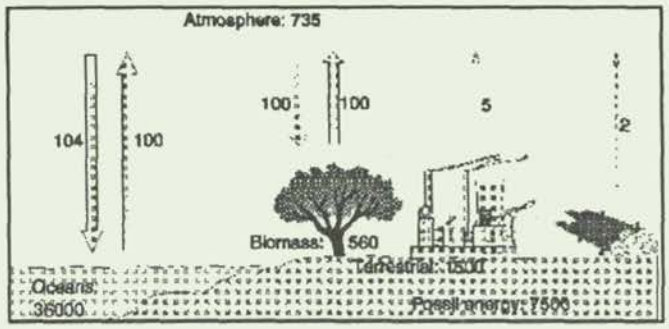

Fig. 4.4. Annual carbon fluxes (in Gt) of natural and anthropogenic origin and the sizes of major reservoirs *[after Houghton and Woodwell, 1989]*

Historical Secchi disk measurements (qualitative estimate of light transmission in the water) in the North Pacific show no evidence of a significant increase in phytoplankton biomass during this century *[Falkowski and Wilson, 1992]*. Though Secchi disk measurements are a surprisingly sensitive measure for phytoplankton biomass they do not reflect phytoplankton productivity. In contrast to terrestrial systems phytoplankton possess a very low standing crop with a high productivity. Under optimal conditions daily productivity may even equal the existing biomass. Therefore it is difficult to exactly predict the loss in carbon sink from decreases in phytoplankton biomass, and this remains a key uncertainty.

Antarctic productivity

Smith et al. *[1992]* directly measured the increase in and penetration of UV-B into Antarctic waters and provided the first conclusive evidence of direct ozone-related effects on natural phytoplankton communities. Making use of the space and time variability of the UV-B front *[Smith and Baker, 1989]* associated with the polar vortex-driven ozone hole, they quantitatively evaluated phytoplankton production inside (ozone column thickness as low as 150 Dobson units, DU) compared to outside (300 DU) the hole. These workers suggest that the ozone-related damage to phytoplankton result in reduction in primary productivity by 6 - 12 % within the marginal ice zone of the Southern Ocean, and other estimates of different Antarctic areas range from 6 - 23 % *[Weiler and Penhale, 1994; Holm-Hansen et al., 1993a]*. The work of Smith and coworkers is distinguished by the inclusion of direct *in-situ* measurement of both incident and in-water UV-B so that quantitative evaluation of biological dose as a function of depth and time could be made *[Smith et al., 1992; Prézelin et al., 1994]*. An important result from this work is the quantitative measurement of a direct ozone-related negative impact on phytoplankton production in the Southern Ocean which is directly linked to human activities in the Northern Hemisphere. Recently, there has also been increasing interest in the Arctic as there are indications for a potentially developing Arctic ozone hole *[Manney et al., 1994]*.

In situ incubations of natural phytoplankton assemblages in Antarctic waters indicated that UV-B under the ozone hole (150 DU) impaired photosynthesis by about 4.9 % while UV-A was responsible

for about 6.2 % inhibition *[Holm-Hansen et al., 1993a]*. Similar ratios were found for tropical waters *[Helbling et al., 1992]*, and screening of most UV <378 nm results in an increase in photosynthesis by 10 to 20 %. However, no significant decreases in stratospheric ozone have been detected in the tropics. Phytoplankton from below the mixing layer in tropical waters were very sensitive to solar radiation while surface plankton showed a high adaptation.

Recently McMinn et al. [1994], using high-resolution stratigraphic sequences from anoxic basins in Antarctic fjords, present findings suggesting that there have been no compositional changes in diatoms during the past 20 years of ozone hole development. They add that their findings are not necessarily applicable to the marginal ice edge and sea-ice communities nor are they relevant to non-diatom components of Antarctic phytoplankton communities. The ecological consequences of UV-B on phytoplankton communities remains a key uncertainty, and high latitude regions with relatively large decreases in ozone provide opportunities to quantitatively explore these consequences.

Screening pigments

The induction of screening pigments has been found in marine and freshwater organisms *[Karentz et al., 1991]*. The pigment scytonemin has been isolated from cyanobacteria where it is induced by UV *[Garcia-Pichel and Castenholz, 1991]*. In addition, cyanobacteria as well as eukaryotic phytoplankton use several water soluble, UV-absorbing mycosporines as screening pigments. Other phytoplankton use carotenoids to dissipate the excess radiation energy from the photosynthetic pigments, and some have been found to even tolerate the unfiltered solar radiation at the water surface in tropical oceans.

Macroalgae and seagrasses

In recent years there has been an increased interest in UV-B effects on macroalgae and seagrasses. In contrast to the phytoplankton, most macrophytes are attached to their growing site; therefore they are restricted to certain depth zones above, below or within the tidal zone. It is thought that this zonation is mainly caused by the visible light penetrating to this depth *[Lüning, 1985]*. If the UV-B/PAR ratio increases, the algae will be exposed to enhanced short wavelength radiation to which they may not be adapted. In recent studies no effect on respiration was found while photosynthesis was inhibited in many red, brown and green benthic algae. When using PAM (pulse amplitude modulation) fluorescence measurements, deep-water benthic algae were most sensitive while intertidal algae were least sensitive *[Häder et al., 1994a,b; Larkum and Wood, 1993; Maegawa et al., 1993]*. As in phytoplankton, the occurrence and induction by UV of screening pigments has been recorded in tropical red algae [Wood, 1989].

Primary and secondary consumers

Food webs

Phytoplankton are the basis for the intricate marine food webs; thus, any losses in biomass production necessarily cause decreases in biomass at the next higher trophic levels. Eventually these losses are relayed through all levels of the food web, ultimately leading to losses in fisheries yield *[Nixon, 1988; Gucinski et al., 1990]*. In addition to these indirect effects, solar UV-B radiation has been found to cause damage to early developmental stages of fish, shrimp, crab and other animals. The most severe effects are decreased reproductive capacity and impaired larval development *[U.S. Environmental Protection Agency, 1987]*. Even at current levels, solar UV-B radiation is a limiting factor, and small increases in UV-B exposure could result in significant reductions in the size of the consumer community *[Damkaer, 1982]*.

In a recent ecosystem study an interesting effect was encountered: After some lag time, algal growth in an artificial stream was higher under UV-B than in the control. The explanation of this surprising result was that the grazers, larval chironomids, were more sensitive to UV-B than their food, the algae *[Bothwell et al., 1994]*. The result of this experiment reinforces the fact that predictions of responses by ecosystems to elevated UV-B exposure should not be based solely on single-species assessments.

Invertebrates

Marine invertebrates differ greatly in their sensitivity to UV-B radiation *[Hunter et al., 1982]*. One crustacean has been found to suffer about 50 % mortality at current UV-B irradiances at the sea surface. Other shrimp larvae tolerate irradiances higher than those predicted for a 16 % ozone depletion *[Damkaer and Dey, 1983]*. The adult crustacean *Thysanoessa raschii* has a threshold sensitivity exceeding levels expected for anticipated ozone levels in spring. However, in summer a 50 % mortality cumulative radiation dose for about half the species examined would be reached in less than 5 days assuming a 16 % ozone depletion. UV-B kills most individuals of the common copepod *Acartia clausii* in culture and also reduces fecundity in the survivors. Similar inhibitions have been found in shrimp-like crustaceans and crab larvae in the Pacific Northwest. At high latitudes (over 40°N) the recently recorded late-spring increases in UV-B may affect some species as the UV-B enhancement occurs at critical phases of their development. Even sustained small increases or temporary fluctuations in UV-B may affect especially sensitive species.

Benthic organisms are also affected by UV-B radiation: cleavage in sea urchin eggs is impaired by ultraviolet radiation *[El Sayed, 1988a]*. Marine organisms associated with coral reefs, such as sponges, bryozoans and tunicates are similarly impaired. Melanins seem to serve as absorbing pigments since, e.g., several colored corals withstand high levels of radiation by production of the protective pigment S-320. Corals differ in their UV-B sensitivity depending on the depth at which they grow *[Siebeck and Böhm, 1987]*; also, the amount of the UV absorbing pigments decreases with depth

[Maragos, 1972; Jokiel and York, 1982]. UV-B radiation seems to exert an oxidative stress on these invertebrate organisms as shown in sea anemones and octocorals *[Shick et al., 1991]*.

Gleason and Wellington *[1993]* observed coral bleaching in the Bahamas that is not explained by increases in seawater temperature. Instead they showed that UV radiation under calm, clear water column conditions induced bleaching of reef-building corals. With increasing depth, colonies of *Motastrea annularis* showed a gradual reduction in mycosporine amino acids, indicating that deeper water colonies may be particularly vulnerable to sudden increases in UV radiation. Transplant experiments indicated that the organisms could not adapt to higher UV levels within a period of 21 days.

Freshwater crustaceans are also affected by solar UV-B. It is interesting to note, however, that *Daphnia* species from an alpine lake, where UV-B radiation is higher than in lowland lakes, are more intensely colored and tolerate higher UV-B doses *[Siebeck and Böhm, 1987; Hessen, 1994]*.

Vertebrates

Enhanced solar UV-B radiation directly reduces the growth and survival of larval fish *[Hunter et al., 1982]*. Based on these data for a region of the North American Pacific coastal shelf in June, a 16 % ozone reduction would result in increases in larval mortality of 50 %, 82 % and 100 % at the 0.5-m depth for anchovy larvae of ages 2, 4 and 12 days, respectively. Anchovy larvae occur in many regions coincident with high radiation levels between June and August with a peak in July. Because virtually all anchovy larvae in the shelf areas described occur within the upper 0.5 m, a 16 % ozone reduction level could lead to large increases in larval mortality.

Little and Fabacher *[1994]*, comparing the sensitivity of rainbow trout and two threatened salmonids to UV-B radiation, have shown that UV-B is an additional, and often important, environmental stress. Inhabiting shallow headwater streams and lakes in high altitude locations, these fish showed considerable variability in response to simulated increases in UV-B with some showing skin injury as well as apparent suppression of their immune system.

Williamson et al. *[1994]*, studying the impact of short-term exposure to UV-B radiation on zooplankton communities in north temperate lakes, suggest that UV-B in relatively clear lakes may prevent some species of zooplankton from fully exploiting warmer surface waters during periods of summer stratification. As a consequence, UV-B may be responsible for altering their ecological interactions with food resources, predators and other environmental variables.

Increased UV-B radiation may be responsible for recent population declines of some amphibians *[Blaustein et al., 1994]*. Species of amphibians differ in their ability to repair UV-B induced damage to their eggs or oocytes. The eggs of some frog species withstand exposure to sunlight better than those of some other frog species. The populations of certain species that lay their eggs in open

water, strongly exposed to sunlight, have suffered drastic declines [Blaustein et al., 1994]. The egg-laying behavior and enzymatic repair activities suggest that certain amphibian species have become adapted in such a way as to minimize exposure of their eggs to UV-B radiation.

Effects of substitutes and their degradation products

Some HFCs and HCFCs, notably HFC134a, HCFC123 and HCFC124, are degraded generating trifluoroacetic acid (TFA, CF_3COOH) as their main product. TFA is neither photolyzed nor does it undergo any other physicochemical degradation. It is apparently not metabolized by plants, but microorganisms such as methanogens, sulfate reducers and aerobic soil bacteria have been shown to degrade TFA *[Visscher et al., 1994]*. Thus, TFA may be a global contaminant persistent over long times. Current levels in an industrialized area are 0.01 - 0.05 ng/m^3 in air (Southern Germany) and 40 times these values are predicted for the year 2010. Further research is currently being conducted to determine whether these results reflect the global situation. Even with the event of continued production well into the next century, TFA is unlikely to reach toxic levels for phytoplankton in the oceans. In environmental niches such as vernal pools, TFA could be expected to accumulate to higher levels than elsewhere. The magnitude of this concentration effect should be similar to that observed for other solutes, which is in the range of 5 - 10 fold *[Chumley, 1994]*.

TFA is mildly toxic to most marine and freshwater phytoplankton tested so far (EC_{50} 1200 to 2400 mg/l). However, the freshwater green alga, *Selenastrum capricornutum*, showed an EC_{50} of 4.8 mg/l *[Groeneveld, 1992]*. Bioaccumulation factors have not been established for phytoplankton organisms; thus, it is still uncertain whether or not TFA is concentrated in the food web.

Consequences

Though there is overwhelming evidence that increased UV-B is harmful to aquatic ecosystems, quantitative estimates are rudimentary at this stage. There is pressing need to increase our efforts to understand the possible long-term effects on aquatic ecosystems on a global scale. In order to evaluate the current productivity in the oceans and a possible decrease in the future, combined satellite and surface data are important tools. Additional focus on important biomass producers such as diatoms, dinoflagellates and cyanobacteria is necessary. A major loss in primary biomass productivity may have significant consequences for the intricate food web in aquatic ecosystems and affect food productivity. It has been estimated that a 16 % ozone depletion could result in a 5 % loss in phytoplankton which would cause a reduction in fishery and aquaculture yields of about 7 % which equals a loss of about 7 million tons of fish per year *[Nixon, 1988]*. Consequences of increased solar UV-B levels may be further complicated by unpredicted feedback loops and other changing factors such as temperature, salinity, CO_2 concentration and different irradiation patterns caused by changing cloud cover.

However, biological effects of small changes in UV-B may be difficult to determine because the biological uncertainties and variations are large and furthermore the baseline productivity for pre-ozone-loss eras is not well established. Figure 4.5 summarizes the effects of UV-B on phytoplankton with their expected ecosystem consequences.

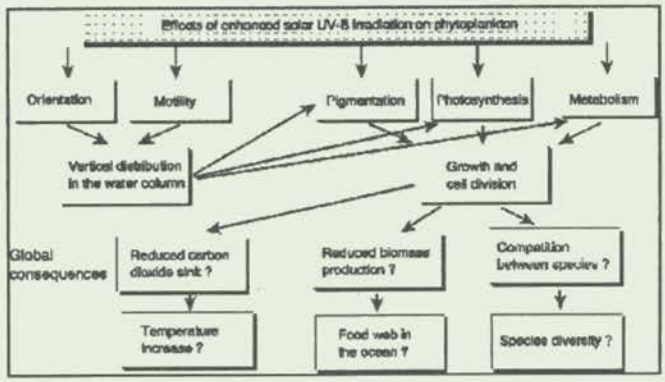

Fig.4.5. Effects of enhanced solar UV-B on phytoplankton.

The second major impact of decreased phytoplankton productivity may be a reduced sink capacity for atmospheric carbon dioxide which results in a faster development of the greenhouse effect and global climate change.
Prokaryotic microorganisms such as cyanobacteria and root nodule bacteria are capable of fixing atmospheric nitrogen in contrast to higher plants which can only utilize ammonia, nitrate or nitrite. Decreased nitrogen assimilation by prokaryotic microorganisms may lead to a nitrogen deficiency for higher plant ecosystems, such as rice paddies. Consequently, losses in nitrogen fixation due to increases in UV-B radiation may need to be compensated for by artificial nitrogen fertilization.

Both macroalgae and phytoplankton release organic sulfur compounds such as dimethylsulfide (DMS) which enter the atmosphere and serve as cloud condensation nuclei. Changes in DMS production may affect the atmospheric radiation balance. The time frame of the predicted changes in the ozone layer may not be sufficient for genetic adaptation to higher UV-B levels. Since different species differ in their sensitivity toward solar short wavelength radiation, shifts in species diversity may be a consequence. As a general rule, UV seems to affect smaller phytoplankton more than larger organisms. As primary feeders prey by size and not by

species preference, this effect may also alter the subsequent links in the food web.

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CHAPTER 5

EFFECTS OF INCREASED SOLAR ULTRAVIOLET RADIATION ON BIOGEOCHEMICAL CYCLES

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Summary

Increases in solar UV radiation could affect terrestrial and aquatic biogeochemical cycles thus altering both sources and sinks of greenhouse and chemically-important trace gases [e.g., carbon dioxide (CO_2), carbon monoxide (CO), carbonyl sulfide (COS) and possibly other gases]. These potential changes would contribute to biosphere-atmosphere feedbacks that attenuate or reinforce the atmospheric buildup of these gases. Current research discussed here focuses on effects of enhanced UV-B on biological and geochemical processes in terrestrial and aquatic ecosystems.

In terrestrial ecosystems increased UV-B could modify both the production and decomposition of plant matter with concomitant changes in the uptake and release of atmospherically-important trace gases. Decomposition processes can be accelerated when UV-B photodegrades surface litter, or retarded when the dominant effect involves changes in the chemical composition of living tissues that reduce the biodegradability of buried litter. These changes in decomposition can affect microbial production of carbon dioxide and other trace gases, and also may affect the availability of nutrients essential for plant growth. Primary production can be reduced by enhanced UV-B, but the effect is variable between species and even cultivars of some crops. Likewise, the effects of enhanced UV-B on photoproduction of CO from plant matter is species dependent and occurs more efficiently from dead than living matter. The often-individualistic response of plant species to enhanced UV-B can result in changed competitive balances between co-occurring species such as crops and weeds. Long-lived species in natural ecosystems that can accumulate UV-B damage may be slow to acclimate/adapt and replacement by immigration may be restrained.

In aquatic ecosystems other investigations have shown that solar UV-B radiation also might have significant impacts. Studies in several different locations have shown that reductions in current levels of solar UV-B result in enhanced primary production, and Antarctic experiments under the ozone hole demonstrated that primary production is inhibited by enhanced UV-B. In addition to its effects on primary production, solar UV radiation can reduce bacterioplankton growth in the upper ocean with potentially important effects on marine biogeochemical cycles. Decomposition processes can be retarded when bacterial activity is suppressed by enhanced UV-B radiation or stimulated when solar UV radiation

photodegrades aquatic dissolved organic matter (DOM). Photodegradation of DOM results in loss of UV absorption and formation of dissolved inorganic carbon (DIC), CO, and organic substrates that are readily mineralized or taken up by aquatic microorganisms. The marine sulfur cycle may be affected by UV-B radiation resulting in possible changes in the sea-to-air emissions of COS and dimethylsulfide (DMS), two gases that are degraded to sulfate aerosols in the stratosphere and troposphere, respectively. UV-B radiation induces the photoreaction of marine DOM to form COS, and it potentially can affect fluxes of COS and DMS through effects on phytoplankton that produce organosulfur precursors, on bacteria that consume DMS, and on photooxidation of DMS. Early modeling efforts to simulate these interactions have appeared during the past two years.

New research on the environmental fate and impact of the hydrofluorocarbon (HFC) and hydrochlorofluorocarbon (HCFC) substitutes for CFCs has focused on trifluoroacetic acid (TFA), a tropospheric oxidation product of certain HFCs and HCFCs. These results indicate that TFA, although it may become globally distributed with increased usage of alternative fluorocarbons, is not likely to accumulate in soils and organisms. Although resistant to chemical degradation, very recent evidence indicates that TFA can be broken down by microorganisms.

Introduction

The term "biogeochemical cycles" is used here to refer to the complex interaction of biological, chemical, and physical processes that control the exchange and recycling of matter and energy at and near the Earth's surface. Research on biogeochemical cycles focuses on the transport and transformation of substances in the natural environment. Global biogeochemical cycles strongly influence atmospheric composition through their effects on the biospheric uptake and release of greenhouse gases and gases that actively participate in atmospheric chemical reactions. The latter will be referred to as "chemically-active" gases in this chapter. On the other hand, the Earth's climate and the nutrients derived from atmospheric deposition are of great importance to the sustainability of the biosphere. Atmospheric composition, climate, and the biosphere are coupled by strong interactions, including feedbacks that reinforce or attenuate climate change. A large fraction of most greenhouse and chemically active gases in the atmosphere is derived from biogeochemical processes in terrestrial and aquatic ecosystems [*IPCC,1992*].

Solar radiation, directly or indirectly, provides the primary driving force for biogeochemical cycles. Most of the solar radiation that reaches land or water is converted into thermal energy, but a significant part, especially that in the ultraviolet and visible region, is diverted into photochemical and

photobiological processes that affect global biogeochemical cycles. Therefore, these processes are sensitive to changes in ground-level solar radiation that result from global changes in stratospheric ozone, cloud cover, aerosols, and other factors. Declines in stratospheric ozone and, by implication, increases in solar UV-B radiation reaching the Earth's surface have been particularly pronounced during the past few years. These changes, coupled with a number of recent findings that document the effects of UV-B radiation on biogeochemical cycles, have prompted this new section in the UNEP report on Environmental Effects of Ozone Depletion.

The principal goals of this section are to describe recent investigations of the effects of changing solar UV-B radiation on terrestrial and aquatic biogeochemical cycles, but we note review papers in the text that provide useful background information on this subject. Research related to biogeochemical cycles -- such as effects of UV-B radiation on photosynthesis, plant physiology, and aquatic trophic dynamics -- are reviewed elsewhere in this report. In addition, excellent overviews of global biogeochemical cycles are available as background to this section [*Butcher et al., 1992; Schlesinger, 1991*]. The cycles of various elements are discussed separately within this report, but it should be emphasized that biogeochemical cycles are tightly interwoven and are subject to significant feedback interactions, including those that affect ozone concentrations and ground-level UV-B radiation.

Terrestrial Ecosystems

Carbon and Nitrogen Cycles

Plant responses

Given the central role of plant biology in biogeochemical cycling, understanding UV-B effects on plants is of critical importance. Here we briefly consider aspects of these effects that are relevant to biogeochemical cycles; a much more detailed discussion of plant responses appears in Chapter 3. Most studies of the interactions of UV-B and plants have been conducted under artificial light conditions in growth chambers or greenhouses [*Tevini and Teramura, 1991; Krupa and Kickert, 1989; SCOPE,1992;1993*] that may not mimic the spectral characteristics of ozone-dependent UV-B changes occurring in solar radiation that reaches the ground. However, these studies have provided insights into general UV-B effects on physiological responses of higher plants and on alteration of growth rates and yields of crop plants. Fewer studies address growth responses of long-lived species or primary production and phytomass in natural ecosystems. As discussed in more detail in Chapter 3 of this report, responses to UV-B radiation are variable between species and even between cultivars of the same species. In general, however, it seems that those species experiencing naturally high fluxes of UV-B radiation

(e.g., alpine and tropical) are better adapted to withstand increases in UV-B than those from regions currently exposed to low levels of UV-B. For example, growth chamber studies of various plants from the Arctic and lower latitude alpine regions indicated that the arctic species, living where UV-B radiation is lower, exhibited significantly higher photosynthetic inhibition than the low-latitude species where solar UV-B flux is high [*Caldwell, et al., 1982*].

The few field studies that have been conducted indicate lower plant sensitivity to UV-B than that observed under growth chamber and greenhouse conditions [*SCOPE, 1993*], probably in part because of the higher flux of photorepairing solar radiation in the UV-A and other spectral regions and the plant development effects that are prevalent in the field. Multi-season field studies of loblolly pines, however, have shown statistically significant reductions of growth under enhanced UV-B radiation that corresponded to 16% and 25% decreases in total ozone [*Sullivan and Teramura, 1991*]. Moreover, the UV-B effects on growth accumulated over 3 years of exposure. Photosynthesis quantum yields were generally reduced in the loblolly experiments and the effect was attributable to direct effects on photosystem II. Field studies on Swedish subarctic heath vegetation indicated greater reductions in growth of shoots in two dominant evergreen dwarf shrubs which accumulated damage, than in two deciduous dwarf shrubs [*Johanson et al., 1994*].

Reviews of UV-B radiation effects on plants [*Tevini and Teramura,1991; Krupa and Kickert, 1989; SCOPE, 1993*] refer to publications that show these effects to be on plant morphology and flowering as well as growth and photosynthesis. Particular effects vary among species, among cultivars of a species and among local populations of a species. These changes can alter the competitive balance in mixed species stands, resulting in significant changes in species composition and thus in primary productivity. Rapid global warming is predicted to cause similar effects. Changes in primary production affect the flow of CO_2 through the biosphere, but do not necessarily affect carbon storage. However, any changes in the composition of species in plant communities driven by increased UV-B -- particularly in the representation of different life forms -- could significantly affect the amount of carbon stored in phytomass. For example, any shift from UV-B sensitive evergreens to deciduous dwarf shrubs [*implied from work by Johanson et al. 1994*] or trees could reduce carbon storage during winter while decreasing growth in general and would increase the amount of CO_2 circulating in the atmosphere. Any sensitivity of the ground layer to UV-B, particularly mosses [*Gehrke, 1992; Sonesson and Callaghan, 1994*], would alter their carbon storage and could also increase the temperature of soil, which they insulate, thereby stimulating microbial activity and CO_2 release to the atmosphere. Stresses caused by increased UV-B radiation, in combination with climatic change, may affect species composition and herbivory and enhance

susceptibility of plants to insects, disease and fire. Because high latitudes are experiencing particularly large increases in solar UV-B radiation, UV-B stresses of high-latitude forests may reinforce their transient release of carbon to the atmosphere in response to climate change [*Smith and Shugart, 1993*].

Likely UV-B increases due to stratospheric ozone depletion are not the only environmental changes. Increases in concentrations of atmospheric CO_2 are well documented and, as they generally stimulate plant productivity, at least in the short term, the balance between UV-B and CO_2 interactions could possibly be a particularly important determinant of carbon cycling.

Very little is known about the effects of enhanced solar UV radiation on the terrestrial nitrogen cycle. This lack of information is of concern because changes in terrestrial nitrogen cycling would likely affect the release of N_2O, a gas that is predominantly derived from terrestrial systems [*IPCC, 1992*]. N_2O is an important greenhouse gas and it also participates in stratospheric processes that control the ozone layer. The changes in species composition that are discussed above and in Chapter 3 would likely affect nitrogen cycling in terrestrial ecosystems, *e.g.*, possibly via UV-B effects on symbiotic association between higher plants with mycorrhizae and nitrogen fixing bacteria in root nodules. In the above-cited study of the subarctic dwarf shrub, *Vaccinium uliginosum* [*Gehrke et al., 1994*], it was found that plants exposed to enhanced UV-B had much higher levels of leachable ammonia in the litter than the controls, indicating possible effects on ammoniafication.

Litter decomposition

For many systems, site fertility is largely dependent on decomposition processes that release nutrients bound within non-living organic matter (NLOM). Therefore, changes in plant litter production and/or subsequent degradation of litter, resulting from higher UV-B levels, may have significant impacts on nutrient cycling. Decomposition of NLOM is carried out by saprophytic fungi and bacteria.

UV-B can potentially affect litter decomposition in several ways: (1) by changing the quantity of litter that is available for decomposition; (2) by altering root/shoot ratios that determine where, i.e., below ground or on the surface, and how efficiently plant matter is decomposed ; (3) by photoinhibition of biota that decompose surface litter; (4) by photodecomposition of surface litter and; (5) by changes in chemical composition of litter that alter its microbial decomposition. In comparison to studies of effects of enhanced solar UV-B radiation on plant morphology and flowering, growth and photosynthesis, little is known about the effects on decomposition.

Recent field studies in northern Sweden confirmed that enhanced UV-B radiation had significant effects on the quality and decomposition of litter from the subarctic dwarf shrub, *Vaccinium uliginosum* [*Gehrke et al., 1994*; *Jones et al., 1994*]. The leaves of the shrub were richer in soluble carbohydrates and tannins than in the controls and the initial decomposition rate of the leaves mixed with soil from the field site [expressed as micrograms CO_2 per gram dry weight (g DW) per hour] was reduced (Figure 5.1). Additional studies in microcosms further showed that leaf litter obtained from the shrubs grown under enhanced UV-B contained more leachable ammonia and less cellulose and lignin than did the litter from the control shrubs. Fungal communities were affected and fungal and microbial activity was also significantly reduced on the plant leaves that were exposed to enhanced UV-B, such that less CO_2 was emitted to the atmosphere, i.e., soil carbon storage was increased. The changes in chemical composition of leaves may involve photoreactions of lignocellulose materials. UV irradiation of lignocellulose materials results in dimerization, oligomerization, and quinone formation through photoreactions that involve carbonyl and phenolic functional groups [*see Heitner and Scaiano, 1993 for review*].

In contrast to the inhibiting effects of UV-B radiation on biotic decomposition of litter, other studies indicate that direct exposure of litter to enhanced UV-B increases its decomposition rate [*see Moorhead and Callaghan, 1994 for review*]. Moorhead and Callaghan [*1994*] have used the CENTURY model to simulate potential effects of UV-B induced litter degradation on nutrient dynamics and soil carbon storage. Results of the simulations indicated that the increased surface litter degradation rate substantially decreased the surface litter and lignin pool sizes. The simulations indicated, however, that these changes had little effect on pool sizes of the passive and slow-cycling organic matter in the soil. It was concluded, therefore, that enhanced UV-B may have little effect on long-term nutrient cycles since it is through formation of resistant soil organic matter (SOM) complexes that nutrients are sequestered.

In summary, decomposition processes can be accelerated when UV-B photodegrades surface litter, or retarded when the dominant effect involves changes in the chemical composition of living tissues that reduce the biodegradability of buried litter. These changes in decomposition can affect microbial production of carbon dioxide and other trace gases, and also may affect the availability of nutrients essential for plant growth. Factors that determine the net effect are poorly understood. In those ecosystems where decomposition is retarded by increased UV-B, any additive or synergistic interactions with increasing levels of CO_2 which have also been shown to retard decomposition [*Couteaux et al. 1991*] could lead to increased carbon storage in soils but lower primary

production. Such effects are often overlooked when feedbacks from warming soils due to climate change are calculated.

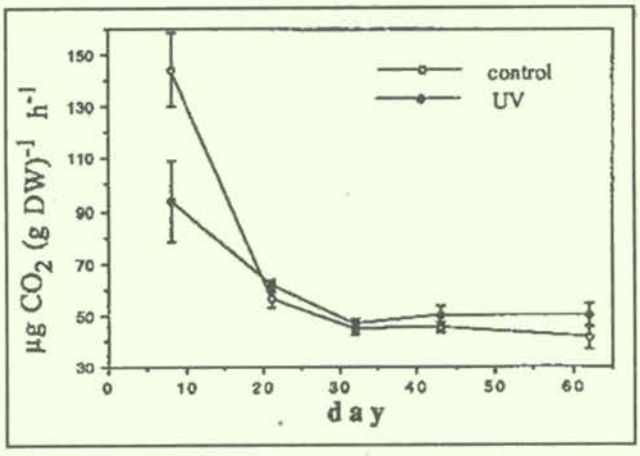

Fig. 5.1. Respiration rates of microorganisms feeding on plant litter from *Vaccinium uliginosum* leaves grown under enhanced vs. ambient UV-B radiation in the field [*Gehrke et al., 1994*]. Data represent 12 replicates of experiments. Results indicate that enhanced UV-B exposure reduced the litter decomposition rate.

Trace Gas Exchange Dynamics

In the above discussions, effects of enhanced UV-B on the exchange of carbon dioxide between terrestrial ecosystems and the atmosphere were emphasized. In addition to uptake of CO_2, plants are known to release the chemically important gases CO and non-methane hydrocarbons (NMHCs), to the atmosphere and to take up nitrogen oxides (NO_x) and COS [*IPCC, 1992*].

Isoprene and other NMHCs react in the troposphere to produce ozone, other oxidants and aerosols. In addition, CO and NMHCs are important scavengers of OH radicals in the troposphere (Chapter 6) and changes in OH concentrations may affect the concentration of the greenhouse gases, methane and CFCs. The direct effects of UV-B on release of NMHCs, such as isoprene, are unknown, but it is known that biogenic emissions from vegetation are species dependent. Thus, even if direct effects of UV-B radiation have little effect, changes in the species composition of plant communities, driven by increased UV-B and climatic stressors, could affect net fluxes of these chemically-important gases.

Laboratory studies have shown that senescent and dead leaves from temperate deciduous plants and tropical grasses photoproduce CO much more rapidly than living plant leaves [*Tarr et al.,1994*]. Wavelength studies (>300 nm) indicate that UV-B radiation produces CO from the leaves with the highest efficiency, although UV-A radiation also induces CO formation. The action spectra vary significantly from one species to another. The flux of CO from living and non-living plant matter is sufficiently great that it may be a major global source of this chemically active gas *[IPCC, 1992]*. As discussed below, UV-B radiation also affects the production of CO in aquatic ecosystems.

Current research indicates that uptake by terrestrial plants is the major global sink for COS [*Bates et al., 1992*]. Moreover, within-canopy uptake of the NO_x from soils occurs in tropical humid forests. Based on the known effects of UV-B on plant growth and photosynthesis that are discussed above, it is likely that changes in UV-B radiation would selectively affect plant uptake of COS and NO_x. To date, however, there are no experimental data that confirm this possibility. COS, a gas that is considered to be one of the major sources of sulfate aerosols in the stratosphere during periods of quiescent volcanic activity [*Crutzen, 1976*], is discussed in more detail below. NO_x, like NMHCs and CO, also participates in tropospheric chemical processes that affect concentrations of tropospheric ozone, methane, and CFCs (see Chapter 6). Thus, both COS and NO_x, like CO, may be involved in feedbacks that affect ground-level UV-B radiation and climate change.

Aquatic Ecosystems

Carbon and Nitrogen Cycles

Responses of photosynthetic organisms

Upper ocean carbon cycling is intimately tied to both the UV-B induced stresses to extant phytoplankton communities as well as the complicated interaction of DOM with UV-B radiation. The most direct effect of increased UV-B fluxes on upper ocean carbon cycling would be through changes in phytoplankton community fecundity and structure. Other indirect effects involving trophic level interactions may also affect ecosystem productivity [*Bothwell et al., 1994*]. In this section we discuss the possible role of these changes in aquatic carbon cycling. Phytoplankton responses are considered in much greater detail in Chapter 4.

Laboratory and field studies with photosynthetic organisms obtained from aquatic ecosystems in different locations indicate that reductions in current levels of solar UV-B result in enhanced primary production [*for recent review see Karentz et al., 1994*]. Antarctic experiments under the ozone hole demonstrated that

primary production is inhibited by enhanced UV-B. Figure 5.2 shows the observed decreased phytoplankton production associated with a 33% decrease in column ozone abundance during austral spring of 1990 in Antarctica [*Smith et al., 1992*]. The net impact of a reduction in primary production on the ocean sink for atmospheric CO_2 is uncertain. Most primary production is recycled in the upper layer of the sea. Only a fraction of the upper ocean particulate organic carbon (POC) and dissolved organic carbon (DOC) actually is exported from the upper ocean into intermediate and deep water. On a global basis this "new production" is estimated to be about 10 Gt C [1 gigaton (Gt) of carbon equals 10^{15} g] and it is believed that most of this POC and DOC is remineralized in the top km of the sea [*Siegenthaler and Sarmiento, 1993*]. About 0.2 Gt C of POC reaches the bottom sediments annually where long-term carbon storage takes place. Taking into account biological removal as well as vertical water transport of the dissolved inorganic carbon (DIC), the amount of anthropogenic CO_2 taken up by the ocean annually has been estimated to be about 2 Gt in recent years [*Siegenthaler and Sarmiento, 1993*]. Additional field and modeling studies are required to come up with reliable estimates of the impacts of enhanced UV-B radiation on this oceanic sink.

As in the case of terrestrial plants, aquatic photosynthetic organisms (algae, cyanobacteria) differ substantially in their tolerances to UV-B exposure and changes in the ratio of UV-B:UV-A:PAR [*UNEP, 1991; SCOPE, 1993; Prezelin et al., 1994; Weiler and Penhale, 1994*]. Evidence has been presented that the balance between photosynthesis, photoinhibition, and photorepair processes for natural communities of photosynthetic organisms has been perturbed by ozone depletion over Antarctica. This perturbation may result in changes in the competitive balance of species over time [*Prezelin et al., 1994; Weiler and Penhale, 1994*]. A recent study has indicated, however, that compositional changes in the diatom component of the Antarctic phytoplankton community over the past 20 years have cannot be differentiated from natural variability [*McMinn et al., 1994*].

Marine phytoplankton produce NMHCs [*Bonsang et al., 1988; Donahue and Prinn, 1990*], but the effects of UV-B radiation on their photoproduction is unknown. As noted earlier in this chapter and elsewhere in this report, these compounds interact with the hydroxyl radical [*Donahue and Prinn, 1990*] which in turn plays a dominant role in maintenance of the oxidizing capacity of the atmosphere. Phytoplankton, as well as higher plants and bacteria, produce other non-volatile hydrocarbons that are highly resistant to biodegradation [*for review see de Leeuw and Largeau, 1993*], but the effects of enhanced UV on production of these biomacromolecules have not been examined.

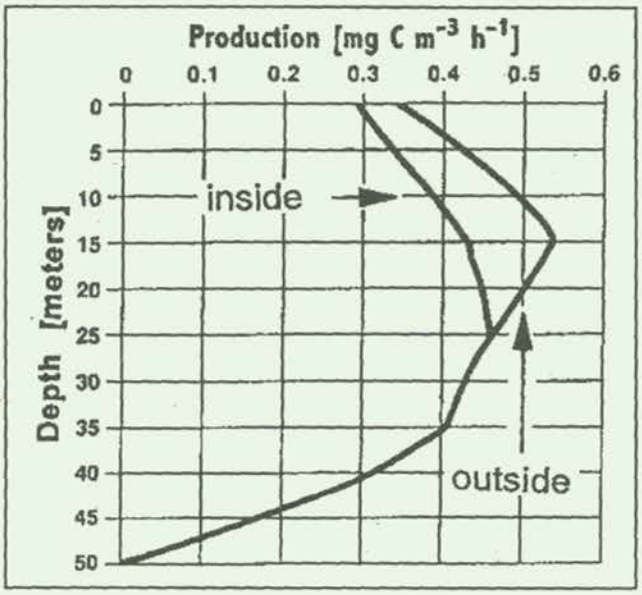

Fig. 5.2. Average values for in situ phytoplankton productivity versus depth (m) within the marginal ice zone of the Bellinghausen Sea in austral spring of 1990 in which reduced productivity inside ozone hole is compared with productivity outside hole. Integrated over depth in the water column, reductions in productivity ranged from 6 to 12%. On an annual basis, this range corresponds to an estimated annual productivity loss of 7 to 14 teragrams which is 2 to 4% of production in the Antarctic marginal ice zone and about 0.1% of global phytoplankton production [*Smith et al., 1992*].

A large fraction of the sea surface is covered by an organic microlayer that may have significant effects on air-sea gas exchange. The sea surface microlayer is fully exposed to solar UV radiation and thus may be particularly susceptible to effects of enhanced UV radiation [*Duce and Liss, 1995*].

As in the case of terrestrial ecosystems, few data are available on the effects of UV radiation on aquatic biota involved in the nitrogen cycle. Changes in species composition noted above are likely to affect nitrogen cycling, and suppression of assimilatory nitrate reduction by phytoplankton has been demonstrated *[UNEP, 1991]*. The effects of UV-B on decomposition processes that are discussed below also are likely to perturb aquatic nitrogen cycling. Moreover, solar UV-B radiation is mainly responsible for the photodegradation of nitrate in water [*Zafiriou and True, 1979; Zepp et al., 1987*]; among other species, hydroxyl radicals are produced in this photoreaction. Nitrite is also degraded by solar UV radiation to form nitric oxide (NO), hydroxyl radicals, and other products, but this reaction is mainly induced by UV-A radiation [*Zafiriou and Bonneau, 1987*]. Effects of UV-B on marine nitrogen cycling could affect sea-to-air exchange of N_2O and NO. However, the role of the ocean as a source of atmospheric N_2O is poorly defined [*IPCC, 1992; Butcher et al., 1992*].

Decomposition

Enhanced UV radiation may affect the decomposition of POC and DOC through its effects on bacterial activity and through photodegradation of DOC. Freshwater and marine bacteria from both freshwaters and the sea are impacted by changes in solar UV radiation [*for review see Karentz et al. ,1994*] and action spectra indicate that UV-B radiation is mainly involved [*Calkins and Barcelo, 1982*]. This has been confirmed by field studies which indicate that current levels of solar UV radiation reduce bacterioplankton growth in the upper ocean [*Herndl et al., 1993*]. This effect may retard the decomposition of labile organic matter in the upper ocean. Effects on other biogeochemical cycles are discussed below.

That aquatic DOM is photoreactive has been established by numerous studies [*Kouassi et al., 1990, 1992; Frimmel and Bauer, 1987; Kieber et al., 1990; Francko, 1990; Mopper et al., 1991; Valentine and Zepp, 1993; Miller and Zepp, 1994*]. Evidence for such photoreactivity derives in part from observed changes in the electronic absorption spectrum of the organic matter as well as in the fluorescence intensity and spectrum. The sunlight-induced decrease in absorbance is not accompanied by a corresponding change in dissolved organic carbon content (DOC), although conversion to various UV-transparent products does occur (see below). These spectral changes involve greater bleaching of the ultraviolet part of DOM spectra than the visible part [*Kouassi et al., 1992; Miller and Zepp, 1994*]. Thus, photodegradation of DOM may result in deeper penetration of solar UV (compared to visible) radiation into the sea and freshwaters.

The photoinduced fading of DOM is accompanied by the formation of a variety of organic and inorganic compounds. The photoproducts of the biologically refractory DOM in natural waters are DIC [*Miller and Zepp, 1994*]; low molecular weight compounds that are biologically labile, *e.g.*, formaldehyde, acetaldehyde, and the alpha-keto acid, glyoxylate [*Kieber et al., 1989*]; the trace gases, CO and COS; and other unidentified species. Photoproduction rates of these compounds are greatest near the surface of inland and coastal waters and least for open ocean waters. Francko [*1990*] has reviewed the rather sparse literature on effects of solar radiation on the bioavailability of DOM. DIC is the major product from the photodegradation of DOM derived from a coastal estuary and two rivers, including DOM in the Mississippi River plume, Gulf of Mexico [*Miller and Zepp, 1994*]. The formation rate of DIC is at least an order of magnitude greater than that of other photoproducts. Mopper et al. [*1991*] have argued that photodegradation may limit the lifetime of biologically refractory DOM in the ocean.

UV-B radiation was mainly responsible for the photodegradation of DOM in Biscayne Bay (Miami), Florida, other coastal waters and the open sea [*Kieber et al., 1990; Mopper et al., 1991*]. and also induces the photoproduction of COS in near coastal seawater [*Zepp and Andreae, 1994*] (Figure 5.3). Although solar UV radiation is predominantly responsible for DOM photodegradation, the action spectra vary from one region to another and action tails well into the UV-A region in some cases [*Valentine and Zepp, 1993; Zepp and Andreae, 1994]* (Figure 5.3).

Photochemical reactions of DOM in the surface ocean produce dissolved gases that are supersaturated with respect to an equilibrium state with observed atmospheric concentrations. This imbalance, or 'dis-equilbria', drives the flux of these trace gases to the atmosphere from the ocean. In order to predict quantitatively the effects of decreases in stratospheric ozone and enhanced UV-B radiation on the photoproduction of these gases, action spectra are required. The air-sea exchange of gases also is affected by changes in wind speed caused by climate change. Wind speed affects sea-to-air transfer coefficients as well as vertical mixing in the upper ocean. To provide a framework for estimation of the flux and distribution of CO and COS in the upper ocean, Najjar et al. [*1994*] have described a model that takes into account photoproduction, turbulent mixing and chemical and biotic sinks for CO and COS in the upper ocean.

DOM photoreactions are believed to be the main source of CO in seawater; its loss has been ascribed primarily to microbial metabolism. As a result of these two processes, CO emissions from the sea follow a diurnal pattern with maximum near surface ocean concentrations greatly exceeding saturation during daylight.

Although the sea is thought to be a net source of CO, great uncertainty exists regarding the strength of this source. Estimates range from 10 Tg/y up to 200 Tg/y [*Erickson, 1989; IPCC, 1992*]. Photodegradation of DOM in wetlands and near coastal waters may be an important regional source of CO [*Valentine and Zepp, 1993*]. Action spectra and quantum yields for CO photoproduction were found to be similar for water obtained from several wetland and near coastal sites in North America. For wavelengths > 300 nm, the greatest action for CO production was in the UV-B region, but the spectra tailed out well into the UV-A region.

Interrelationships among biogeochemical processes in the ocean and atmosphere can sometimes lead to feedbacks. Such a feedback relationship involving marine CO and tropospheric ozone illustrates a possible feedback between ozone depletion and air-sea exchange of trace gases [*Erickson, 1989*].

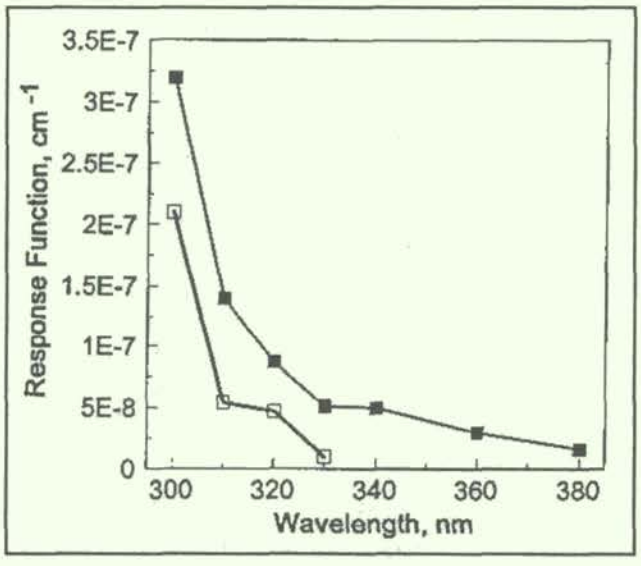

Fig. 5.3. Comparison of action spectra for the photoproduction of COS in seawater obtained from coastal regions of the North Sea (□) and Gulf of Mexico (■). North Sea water was obtained near Bremerhaven, Germany (54°N, 8°E) and Gulf of Mexico water near Turkey Point, Florida (30°N, 84.5°W). Samples used in the action spectra studies were studied within 12 hours of the time of collection [*Zepp and Andreae, 1994*].

Sulfur Cycle

Increased UV-B can influence the sulfur cycle (Figure 5.4) via impacts on both aquatic and terrestrial ecosystems. Changes in the sea-to-air transfer of DMS and COS may influence the radiative balance of the atmosphere. As noted in a previous section, the growth and productivity of oceanic phytoplankton as well bacterioplankton growth may be affected by a variety of stressors including increased UV-B. Production of dimethylsulfonium propionate (DMSP), the precursor compound of DMS, by phytoplankton such as coccolithophorids provides the primary source (up to 90%) of sulfur for cloud condensation nuclei in the remote marine atmosphere. On a global scale, marine emissions of DMS account for about 15% of the total atmospheric sulfur input [*Bates et al., 1992*]. Because the main sources of DMS in seawater are particular species of phytoplankton, any alteration in the fecundity and species distribution of phytoplankton communities could have a direct effect on the surface ocean DMS concentration and subsequently the sea-to-air flux of DMS. In addition to its effects on phytoplankton, UV-B radiation may affect the loss of DMS through microbial [*Kiene and Bates, 1990*] and photooxidative degradation. UV-B induced changes in these various upper oceanic processes that affect DMS may result in changes in net sea-to-air flux.

Field studies have indicated that a variety of processes affect the atmospheric concentrations of COS [*Andreae and Ferek, 1992*]. These studies show that COS is formed primarily by photochemical processes in the upper layers of the ocean. Zepp and Andreae [*1994*] have found that the photochemical formation of COS from dissolved organosulfur compounds in sea water can be photosensitized by DOM. Because rates of photosensitized reactions are generally much more rapid in coastal waters than in the open sea [*Kieber et al., 1990; Zafiriou and Dister, 1991*], these results help to explain why concentrations of COS have been observed to be highest in coastal regions [*Andreae and Ferek, 1992*]. Global estimates of COS production recently have been derived using Coastal Zone Color Scanner satellite data and general circulation models [*Erickson and Eaton, 1993*]. Wavelength studies of COS formation in coastal seawater samples have confirmed that COS is predominantly formed by the action of middle UV radiation (280-340 nm), but that action spectra for the North Sea and Gulf of Mexico differed significantly beyond 320 nm [*Zepp and Andreae, 1994*] (Figure 5.3).

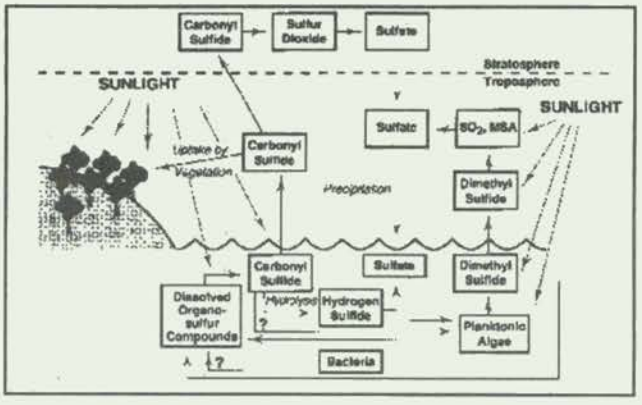

Fig. 5.4. Biogeochemical processes affecting the global sulfur cycle [*adapted from SCOPE, 1993*]

Oxygen Cycle

The previously-discussed effects of UV-B radiation on photosynthesis and microbial decomposition also can affect the oxygen cycle in both aquatic and terrestrial ecosystems. Photooxidation of marine and freshwater DOM leads to consumption of oxygen as it is combined with the DOM carbon. DOM photooxidation also is accompanied by reduction of oxygen to form superoxide [*Zafiriou and Dister, 1991*], which dismutes (*i.e.*, disproportionates) to form hydrogen peroxide. Other reactive oxygen species are produced on absorption of UV radiation by freshwater and marine chromophores [*see Waite et al., 1988 and Blough and Zepp, 1994, for reviews*]. Hydrogen peroxide, through interactions with marine biota and chemical constituents, is oxidized back to oxygen or reduced to water. Action spectra for the photoproduction of hydrogen peroxide in sea water and freshwaters indicate that solar UV radiation is most effective [*Moore et al., 1993*]. Action is most pronounced in the UV-B region, although UV-A radiation also is involved. A model that describes the upper ocean distribution of hydrogen peroxide has been developed [*Sikorski and Zika, 1993*].

Metals Cycles

Field and laboratory studies over the last 5 years have indicated that solar UV radiation enhances the reductive dissolution of iron and manganese oxides/hydroxides in oxygenated natural waters [*Faust, 1994; Sulzberger, 1994; Waite et al., 1994*]. Reductive dissolution converts the thermodynamically stable, but biologically unavailable, oxides of these trace metals into more bioavailable forms, and thus may help control marine productivity in parts of the ocean that are limited by iron or manganese. The action spectra for iron photodissolution processes have not been determined and likely are variable. Light enhances the dissolution of an amorphous manganese oxide in seawater and this process helps account for the

surface maxima in dissolved manganese (Mn[II]) observed in the ocean [*Sunda and Huntsman, 1990*]. UV-B radiation inhibits the microbial oxidation of soluble Mn[II] to low-solubility Mn[IV] oxides [*Sunda and Huntsman, 1990*]. In most of these cases, the presence of aquatic DOM was shown to be essential for the occurrence of photodissolution. That naturally occurring organic compounds are capable of inducing or assisting the photodissolution of iron and manganese oxides has been confirmed in a number of laboratory studies using organic acids that are present in fresh and marine waters, e.g. humic, fulvic and hydroxycarboxylic acids [*Waite et al., 1994*].

CFC Substitutes

Considerable research on the development of suitable CFC substitutes has taken place during the past few years. This research has included intense studies of the atmospheric fate and impact of HFC and HCFC substitutes for CFCs [*see AFEAS, 1994 and Wallington et al., 1994 for reviews*]. In addition to evaluations of the ozone depletion potentials of these substitutes, studies have included initial evaluations of potential impacts of deposition of selected atmospheric degradation products of HCFCs and HFCs. TFA, the major atmospheric degradation product of HCFC-123, HCFC-124, and HCFC-134a was selected for study, because it is resistant to abiotic degradation, including atmospheric decomposition, and likely to become globally distributed. Measurements of TFA in the present environment are sparse. During late 1993 and early 1994, TFA was detected in the atmosphere near Tuebingen, Germany and on spruce needles in Sweden. It is most likely that the source of this TFA was atmospheric degradation of the anesthetic, halothane. Models indicate that most of the TFA formed from HCFCs and HFCs should be deposited in the ocean, where it will be diluted to very low concentrations. Up to 30% may be deposited on land. Recent field studies have shown that TFA, a hydrophilic substance, is not likely to accumulate in most soils or biota, although accumulation in acidic organic soils may be possible. Evidence is now emerging that TFA may be degradable by microorganisms [*Visscher et al., 1994*] and that, even at high concentrations, it appears not to significantly inhibit the metabolism of acetate. Additional research is currently underway to better elucidate the biospheric fate and impacts of TFA and potential effects of TFA on biogeochemical cycles.

Conclusions

Potential effects of enhanced UV-B radiation on terrestrial and aquatic carbon, nitrogen, sulfur, oxygen, and metal cycles have been identified. These effects and companion effects on biogeochemical cycles in the atmosphere may result in feedbacks that either reinforce or attenuate the buildup of greenhouse gases

and aerosols in the atmosphere. Radiation amplification factors shown in Chapter 1 for some of the aquatic photochemical processes discussed in this section indicate that they are approximately as sensitive to changes in the stratospheric ozone layer as the effects on health, plants, and tropospheric photolysis.

Increasing UV-B radiation has the potential to change the quantities and chemical species of carbon that are exchanged between the atmosphere and terrestrial biosphere and also the carbon that is stored in soils and aquatic systems. The effects of UV-B on carbon storage and carbon fluxes on land are complex, varying between ecosystems, species and even crop cultivars. In some systems, UV-B can, for example, increase carbon storage in soils, whereas in others it can enhance the degradation of lignin in soil organic matter and the photoproduction of chemically-important gases such as carbon monoxide.. Responses of plants to UV-B have been shown to increase over time; impacts on natural ecosystems may be subtle but may lead to species shifts in the long term. Consequently, there is a need for research on the impacts of UV-B radiation on biogeochemical cycling to develop a new focus, in addition to investigations to determine short term physiological responses. This focus should address long-term productivity responses under natural conditions.

Laboratory and field experiments in aquatic ecosystems have shown that enhanced UV-B has a variety of effects on biogeochemical cycles. For example, photosynthesis has been suppressed by ozone depletion and enhanced UV-B radiation over the Antarctic. Moreover, recent studies indicate that photodegradation of DOM in the upper ocean has multiple effects on biogeochemical cycles, ranging from changes in the penetration of UV-B into the sea to enhanced formation of DIC and CO. Sulfur cycling in marine systems also might be affected by changes in UV-B radiation with resulting effects on the sea to air fluxes of COS and DMS. Metal cycles and bioavailability, especially those of the trace nutrients, iron and manganese, are sensitive to UV changes as well. Models designed to simulate these effects and their interactions with changing climatic conditions are just beginning to be developed.

The results discussed here suggest that changing UV-B radiation may affect global biogeochemical cycles and related feedback interactions. It should be emphasized that evaluations of regional and global scale effects require the development of appropriate models and observational approaches. Earth system models that incorporate solar UV-B radiation as a forcing variable are required in order to integrate, evaluate and predict ecosystem effects and related feedbacks on a global scale.

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CHAPTER 6

EFFECTS OF INCREASED SOLAR ULTRAVIOLET RADIATION ON TROPOSPHERIC COMPOSITION AND AIR QUALITY

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Summary

Reductions of stratospheric ozone and the concomitant increases of UV-B radiation penetrating to the lower atmosphere result in higher photodissociation rates of key trace gases that control the chemical reactivity of the troposphere. This can increase both production and destruction of tropospheric ozone (O_3) and related oxidants such as hydrogen peroxide (H_2O_2), which are known to have adverse effects on human health, terrestrial plants, and outdoor materials. Changes in the atmospheric concentrations of the hydroxyl radical (OH) may change the atmospheric lifetimes of climatically important gases such as methane (CH_4 and the CFC substitutes.

Trends in the photodissociation rate coefficient of tropospheric O_3, of about +0.32±0.04 percent per year in the northern hemisphere and +0.40±0.05 percent per year in the southern hemisphere, have been estimated from satellite measurements of the ozone column between 1979 and 1992. The corresponding model-calculated changes in tropospheric chemical composition are non-linear and sensitive to the prevailing levels of nitrogen oxides (NO_x). In polluted regions (high NO_x), tropospheric O_3 is expected to increase, reaching potentially harmfully concentrations earlier in the day, and leading to more frequent exceedance of oxidant standards for air quality in urban areas where O_3 levels are routinely near such air quality thresholds. In more pristine regions (lower NO_x), O_3 increases can be lower or even negative. Other oxidants, such as H_2O_2 and OH, are projected to increase for both polluted and pristine regions. Changes to H_2O_2 concentrations may have some impact on the geographical distribution of acid precipitation. Rural regions may become more urban-like and the percentage of areas with remote tropospheric conditions may decline.

Increases in OH concentrations cause a nearly proportionate decrease in the steady state tropospheric concentrations of CH_4 and CFC substitutes such as the HCFCs and HFCs. Thus, the measured reductions in the ozone column (TOMS, 1979-92) are likely to have moderated CH_4 increases over the past decade, and may account for about 1/3 of the slowing of the global CH_4 trends.

Increased tropospheric reactivity could also lead to changes in the production of particulates such as cloud condensation nuclei, from the oxidation and subsequent nucleation of sulfur of both anthropogenic and natural origin (e.g., carbonyl sulfide and dimethylsulfide). While these processes are still not fully understood, they exemplify the possibility of complex feedbacks between stratospheric ozone reductions, tropospheric chemistry, and climate change.

Introduction

Ultraviolet-B radiation (UV-B, 280-315 nm) is one of the key environmental factors controlling the chemistry of the lower atmosphere (the troposphere). UV-B is sufficiently energetic to break the bonds of gases such as ozone (O_3), nitrogen dioxide (NO_2), formaldehyde (HCHO), hydrogen peroxide (H_2O_2) and nitric acid (HNO_3), producing highly reactive atomic and molecular radical species (O, H, OH, HO_2, etc.). These photo-fragments effectively drive the tropospheric oxidation cycles, and thus determine the lifetimes and abundance of many other atmospheric chemical species.

UV-B enhancements (resulting from stratospheric O_3 reductions, see Chapter 1) are expected to affect tropospheric oxidant concentrations on many geographical scales. Tropospheric O_3 is a major constituent of the photochemical smog encountered in many polluted urban environments, and is known to have adverse effects on human health *[Lippmann, 1991]* and outdoor materials *[Andrady, 1993]*. On broader suburban and rural scales, oxidants including O_3 and H_2O_2 cause damage to vegetation and play a role in the acidification of rain *[Penkett et al., 1979; Moller, 1989; NAPAP, 1991]*. Global-scale changes in tropospheric O_3 are of concern both because O_3 is a major greenhouse gas, and because it is the chemical precursor of the OH radical, the principal cleaning (oxidizing) agent of the global troposphere. Changes in OH concentrations affect directly the rate of removal of many other atmospheric gases involved in climate and ozone chemistry, including methane (CH_4) and the hydrogen-containing CFC substitutes (e.g., HFCs, HCFCs) *[WMO, 1994]*.

Photodissociation Rate Response to Increased UV-B

The rates of some chemical reactions in the troposphere depend directly on the amount of available UV-B *[Leighton, 1961]*. The reaction rate coefficient, or J value, is given by the expression

$$J = \int F(\lambda)\ \sigma(\lambda)\ \phi(\lambda)\ d\lambda$$

where λ is the wavelength (nm), $F(\lambda)$ is the spectral actinic flux (quanta cm^{-2} s^{-1} nm^{-1}), $\sigma(\lambda)$ is the molecular absorption cross section

($cm^2 molec^{-1}$), and $\phi(\lambda)$ is the photodissociation quantum yield (molec $quanta^{-1}$).

The spectral actinic flux in the UV-B region is a strong function of the ozone column. The most sensitive J values for key reactions are listed in Table 1 of Chapter 1. Comparable sensitivities have been calculated by Madronich and Granier *[1994]* and Fuglestvedt et al. *[1994]*, though for different locations and times. Madronich and Granier *[1994]* calculated the trends in J_1, the O_3 photodissociation rate coefficient, associated with the 1979-1992 TOMS O_3 column data record. Figure 1 shows that the global J_1 has increased by about 0.36±0.04 percent per year, with slightly higher values in the southern hemisphere (0.40±0.05 percent per year) than in the northern hemisphere (0.32± 0.05 percent per year).

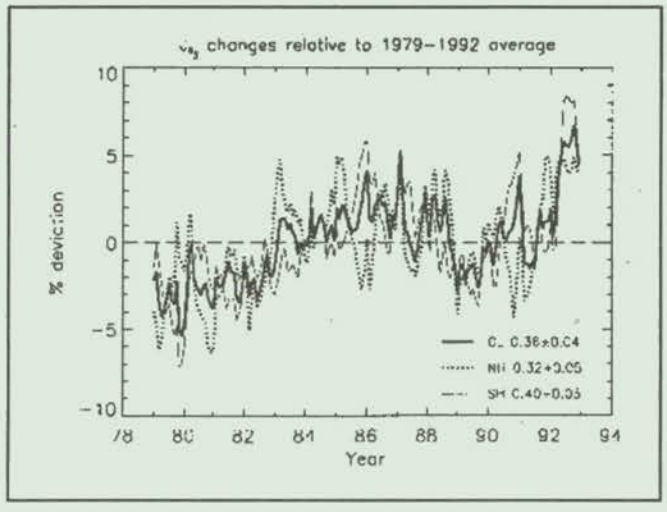

Fig. 6.1. Changes in mid-tropospheric rate coefficients for the photodissociation reaction $O_3 + hn \rightarrow O(^1D) + O_2$, computed using ozone column measurements from the Nimbus 7 satellite (TOMS, version 6 data). Values are given as monthly deviations from the corresponding 1979-1992 averages. Thick solid curve is the area-weighted global average, thin solid line and dotted line are respectively the southern hemisphere and northern hemisphere area-weighted averages. Values next to legend are linear trends, and their corresponding uncertainties, expressed as percent per year relative to the 1979 intercept. From Madronich and Granier [1994].

Changes in Tropospheric Chemical Composition

Changes in O_3, H_2O_2 and HO_x

Translating changes in J values to changes in atmospheric chemical composition is not straightforward because tropospheric chemistry

is highly non-linear. Of special interest are the concentrations of important oxidants such as O_3, H_2O_2, and OH, which react with various gases in the troposphere. In particular, the OH radical is the most important cleansing agent of the troposphere.

The photochemical production of tropospheric O_3 is due almost exclusively to the photodissociation of NO_2,

$$NO_2 + h\nu \ (\lambda < 420 \text{ nm}) \rightarrow NO + O(^3P)$$

followed rapidly by recombination of the atom with molecular oxygen,

$$O(^3P) + O_2 \rightarrow O_3 \ .$$

Ozone loss occurs when its photodissociation,

$$O_3 + h\nu \ (\lambda < 320 \text{ nm}) \rightarrow O(^1D) + O_2$$

is followed by reaction of $O(^1D)$, usually with water vapor:

$$O(^1D) + H_2O \rightarrow OH + OH$$

These last two reaction are also the main source of tropospheric OH radicals *[Levy, 1971]*. Additional loss of O_3 may occur through the catalytic cycle

$$OH + O_3 \rightarrow HO_2 + O2$$

$$HO_2 + O_3 \rightarrow OH + 2O_2$$

as well as other reactions. The net ozone production/destruction depends sensitively on the amounts and partitioning of the NO_x (= NO + NO_2) and HO_x (= OH + HO_2) species, which are in turn determined by complex sequences of reactions involving carbon monoxide (CO) and hydrocarbons, as well as other tropospheric compounds. Detailed discussions of these reaction sequences are beyond the scope here (but see for example *[Finlayson-Pitts and Pitts, 1986]*), although some of the non-linearities that they induce may already be evident from the well-known reactions

$$OH + CO + O_2 \rightarrow HO_2 + CO2$$

$$HO_2 + NO \rightarrow OH + NO2$$

$$O_3 + NO \rightarrow O_2 + NO_2$$

The HO_x species are ultimately removed by termination reactions, leading to the formation of oxidants such as hydrogen peroxide, e.g.

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \ .$$

Consideration of the above reactions under scenarios of enhanced UV-B radiation shows that both increased production and increased destruction of tropospheric O_3 are possible. The sign and magnitude of the net effect are complex functions of the concentrations of

various compounds (especially O_3, H_2O, NO_x, CO, and hydrocarbons), and may well be different for different chemical regimes (e.g., polluted vs. pristine).

Estimates of the tropospheric response to UV changes are still a matter of active research and the results appear to be sensitive to model formulation. Liu and Trainer *[1988]* used a simple zero-dimensional chemistry model to derive the changes in O_3 and OH as a function of prescribed NO_x concentrations. They found that a 20 percent loss of stratospheric ozone at northern mid-latitudes could reduce tropospheric O_3 by 10-35 percent for NO_x levels between 0.01 to 0.10 ppbv (parts per billion by volume), while O_3 increases substantially when NO_x levels are higher than 0.1-0.2 ppbv (e.g., in many rural and most urban regions). Different results were obtained by Thompson et al., *[1991]* using a one-dimensional model for different chemical regimes, with decreases in tropospheric O_3 concentrations for all regions considered, including relatively polluted areas.

Modeling studies also show that OH concentrations respond to changes in J_1 in a complex way. For a one percent increase in J_1, the OH concentration increased by about 0.9 percent at low NO_x and by 0.3 percent at high NO_x *[Liu and Trainer, 1988]*; by 0.3 percent for marine low latitudes and 0.7 percent for urban mid-latitude regions *[Thompson et al. 1991]*; and by 0.5-1.0 percent when averaged globally and annually based on a recent three-dimensional model *[Fuglestvedt et al., 1994]*.

H_2O_2 levels are projected to increase globally *[Thompson et al., 1989, 1991; Fuglestvedt et al., 1994]*. For scenarios with higher NO_x, significantly larger H_2O_2 (and HO_2) levels were calculated for rural and continental conditions, while for the remote regions only a slight increase was obtained.

Thus, it may be concluded from current models that enhanced UV will increase the OH, HO_2 and H_2O_2 concentrations, but the exact amount of the increase remains unclear, with results apparently being sensitive to model formulation. Model-calculated changes in tropospheric O_3 appear to be very sensitive to the NO_x levels of specific regions. Some O_3 is also transported downward from the stratosphere, so that decreases of stratospheric O_3 could result in lower O_3 input from the stratosphere to the troposphere, but quantitative assessments of this effect have not been made. Measurements by Schnell et al. *[1991]* show that Antarctic surface O_3 decreased by 17 percent over 1976-89 during spring and summer, and were attributed to increased UV-B levels associated with the O_3 hole, rather than reduced downward transport from the stratosphere.

Many environmental concerns related to urban and regional air quality are likely to be affected by increased oxidant concentrations. Urban and surrounding areas routinely experience high NO_x and volatile organic carbon concentrations due to anthropogenic emissions, which leads to very reactive chemistry and

generates high levels of ozone and other oxidants through the photo- chemical smog formation process. Some of these oxidants, such as formaldehyde, HCHO, can produce odd-hydrogen radicals upon absorption of UV-B *[Finlayson-Pitts and Pitts, 1986]*, providing additional chemical channels that could contribute to increased urban reactivity with future increases in UV-B. Increased UV-B radiation could produce even higher levels of urban ozone, as well as potentially harmful concentrations of ozone earlier in the day, and nearer to emission sources and population centers *[Gery et al., 1987; Whitten and Gery, 1986]*. It was suggested by Gery et al. *[1987]* that, if UV levels are increased, significantly more stringent regulation of volatile organic emissions will be required in urban locations to maintain photochemical oxidants below air quality standards. De Leeuw and Van Rheineck Leyssius *[1991]* have similarly estimated that, given constant emissions, air quality violations will be much more frequent in European urban areas if UV levels increase.

Because increased UV-B would make the lower troposphere more reactive, some rural regions may become more urban-like and the percentage of areas with remote tropospheric conditions may decline; this will change the global distribution of polluted areas *[Gery, 1993]*. On the global scale, the increased tropospheric reactivity caused by UV-B radiation could lead to increases in global aerosol production, providing additional condensation nuclei to the lower stratosphere where heterogeneous ozone destruction processes could become more important in non-polar regions *[Gery, 1993]*.

H_2O_2 is the most important oxidant of sulfur(IV) in the aqueous phase when the pH is less than about 4.5 *[Penkett et al., 1979]* and has attracted increasing attention over the past decade, because it was identified as one of the dominant trace species in polar ice *[Neftel et al., 1984]* and its concentrations have increased by 50 percent over the past 200 years, with most of the increase occurring in the past 20 years *[Sigg et al., 1991]*. Potential changes to H_2O_2 concentrations would be interesting with respect to the formation of acidic precipitation. The predicted substantial increase in H_2O_2 concentrations over large geographical areas caused by increased UV-B levels in troposphere *[Gery et al., 1987; Fuglestvedt et al., 1994]* may have some impact on the geographical distribution of acid precipitation. However, no quantitative estimates of these effects are yet available.

Changes in CH_4 Lifetime

UV-related increases in tropospheric OH may affect the concentration of other important gases. Methane is removed from the atmosphere primarily via the reaction

$$OH + CH_4 \rightarrow CH_3 + H_2O$$

with a lifetime of about 10 years. Pre-industrial atmospheric CH_4 concentrations were near 600 ppbv, but increased emissions (most likely due to human activities) have brought the current value near 1,800 ppbv. Recent measurements of the rate of CH_4 increases show that the trend has slowed in the past decade from about 14 ppbv per year to about 9 ppbv per year. It has been proposed that the slowing of the CH_4 trend may be partly due to the increased OH resulting from tropospheric UV increases *[Madronich and Granier, 1992, 1994; Fuglestvedt et al. , 1994]*. Increase in OH concentrations will decrease the steady state CH_4 concentration by nearly the same proportion. The time-dependent response of CH_4 depends on the detailed scenario for OH increase. Madronich and Grainer *[1992, 1994]* used the 1979-92 O_3 column measurements (Nimbus 7 TOMS), to calculate the global increase of J_1 (see Figure 6.1) and assumed a corresponding linear OH increases at a rate of 0.36 percent per year beginning in 1979. In this scenario, in 1993 the CH_4 is reduced by about 35 ppbv from the value it would have achieved without the OH increases, which may be compared with a measured atmospheric increase of about 150 ppbv over the same time *[Khalil et al., 1993; Steele et al., 1992]*. Three-dimensional model results obtained by Fuglestvedt et al. *[1994]* are roughly comparable, suggesting that about 1/3 of the slowing is due to the increased UV levels.

Effects of Changes in Emissions from Natural Ecosystems

As mentioned in previous chapters, both natural terrestrial and aquatic ecosystems are likely to be affected by UV radiation changes. For example, increased penetration of UV radiation into the oceans is expected to affect both the viability of living organisms, and the photochemical processing of non-living organic and inorganic matter. Thus, changes may be expected in the ocean-to-atmosphere emissions of various gases including carbon monoxide (CO), carbonyl sulfide (COS), dimethyl sulfide (DMS), and other carbon and sulfur compounds *[Najjar et al., 1994]*. Some of these species are believed to be the primary source of natural sulfate aerosols, which have roles in the destruction of ozone, climate change, and acidification of precipitation. For example, aerosols formed by DMS oxidation are believed to influence the ability of marine clouds to reflect incoming solar radiation, and may thus influence climate *[Charlson et al., 1987]*. Another example is COS, which is believed to be a major source of sulfur atoms to the stratosphere and of the resulting natural stratospheric sulfate aerosol layer. Current theories of stratospheric O_3 chemistry suggest that aerosols may play a role in the destruction of O_3, so that UV-induced increases in emissions of, e.g., COS, may constitute a yet unquantified positive feedback on stratospheric O_3 depletion.

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CHAPTER 7

EFFECTS OF INCREASED SOLAR ULTRAVIOLET RADIATION ON MATERIALS

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Summary

Synthetic polymers, naturally-occurring biopolymers, as well as some other materials of commercial interest are adversely affected by solar UV radiation. Applications of these materials, particularly plastics, in situations which demand routine exposure to sunlight is only possible through the use of light-stabilizers and/or surface treatments to protect them from sunlight. Any increase in solar UV content due to partial ozone depletion will therefore accelerate the photodegradation rates of these materials, limiting their service lifetimes outdoors.

The nature and the extent of such damage due to increased UV radiation in sunlight is quantified in action spectra. In spite of the several action spectra for polymers, reported in the research literature, the information is often inadequate to make reliable estimates of the increased damage. The specific formulation of the polymer material, the damage criterion employed, and even the manner in which data is interpreted, can often influence the results. However, it is clear from the available data that the shorter wavelength UV-B processes are mainly responsible for photodamage ranging from discoloration to loss of mechanical integrity in polymers exposed to solar radiation. The molecular level interpretation of these changes remain unclear in many instances.

The use of higher levels of conventional light stabilizers in polymer formulations will likely be employed to mitigate the effects of increased UV levels in sunlight. However, such an approach assumes that a) these stabilizers continue to be effective under spectrally- altered sunlight conditions; b) they are themselves photostable on exposure to UV-rich sunlight; and c) they can be sufficiently effective at low enough concentrations to economically serve the purpose. Experimental data bearing on these issues is sparse. On-going research, particularly those relating to extreme-environment exposure of polymers, is expected to shed more light on these unresolved questions. Substitution of the affected

materials by more photostable varieties of plastics and other materials also remains an attractive possibility. Both these approaches will add to the cost of plastic products in target applications. With plastics rapidly displacing conventional materials in numerous applications, this is an important consideration particularly in the developing world.

Introduction

Most synthetic polymers as well as naturally - occurring biopolymers are readily affected by solar ultraviolet (UV) radiation. The deleterious effects of UV-B on polymers (plastics and rubber) are well known, and in applications which demand routine exposure to solar radiation, photo-stabilizers are commonly used in polymer products to ensure adequate lifetimes. Wood and other biopolymeric materials are similarly affected; surface coating of wood is employed to control the light-induced damage. Applications of particular interest are building products which account for nearly a third of the plastics production in the US as well as in Western Europe. The consistent trend towards increased use of plastics in buildings at the expense of more traditional materials of construction such as metal, glass, mortar, and wood, is a global one and is particularly strong in developing countries with a high demand for low-cost housing. In addition to use in building, polymeric materials are used in numerous other applications where they are routinely exposed to solar radiation (Table 7.1).

The outdoor service lifetimes of plastics building materials, even under present exposure conditions, are determined by their susceptibility to UV-B radiation in terrestrial sunlight. Therefore, a partial depletion of the stratospheric ozone layer, and the resulting increase in UV-B content in sunlight reaching the earth's surface, will have a definite impact on the use of materials in outdoor applications. As both synthetic polymers and biomaterials will undergo light-induced chemical changes, consequent deterioration in useful properties might be expected at significantly faster rates under such conditions. These changes might be mitigated at least in part, however, by the use of higher levels of conventional stabilizers in polymer formulations, by the use of new high-efficiency stabilizer systems, and by the substitution of better UV-resistant types of polymers for outdoor applications of interest. The effectiveness of some of these strategies have not been demonstrated for exposure conditions involving spectrally-altered, UV-B rich sunlight. Increased cost associated with each approach, and their effectiveness, may alter the economics of the use of plastics and rubber in building construction.

Table 7.1. Materials Routinely Exposed to Solar UV-B Radiation.

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1. Building Materials: Plastics - Pipes, water storage tanks, window/door frames, siding, gutters, roofing, glazing, exterior fascia, cable coverings, and conduits. Wood used in buildings.
2. Outdoor Furniture and Surfaces: Stadium seats, park benches, beach furniture and artificial turf.
3. Transportation Applications: Composites, other polymers, and wood, used in Aircrafts, Automobiles, and Marine Vessels. Automotive and aircraft tires.
4. Agricultural Applications: Greenhouse coverings, mulch films, and irrigation hoses.
5. Coatings and Paints: Coatings for protection of outdoor surfaces, outdoor artwork, dyes, highway pavement markings, and road signs.
6. Textile Products: Fabrics used outdoors (e.g. sails), geomembranes, netting and commercial fishing gear.
7. Biopolymers: Wool, human hair, Chitin/Chitosan*.
8. Packaging: Heavy-duty sacs.
9. Miscellaneous: Resins for restoration of outdoor statues, leather products, solar panel materials, paper or paperboard products used outdoors.

* Shell of crabs and shrimp is composed of Chitin, the second most abundant biopolymer. Chitosans occur in the cell wall of fungi.

Severity of the impact of increased UV-B levels on the outdoor lifetimes of materials depend on both the geographic location of exposure and the susceptibility of the particular material to UV-B radiation. While the higher latitudes will experience the high levels of ozone depletion, the high ambient temperatures in the near-equator regions will tend to severely magnify the effect of even a very marginal increase in solar UV-B in these regions. The effects of a uniquely harsh combination of high levels of solar UV-B from spectrally altered sunlight, and the high temperatures leading to severe heat build-up in materials exposed outdoors, on the lifetime of building products at these latitudes is not well understood.

The cost advantage offered by durable plastic building products have made them popular in developing countries including those in near-equator regions. Wood and natural materials have long been the conventional building materials for dwellings in these regions. With the lifetimes of both plastics and wood affected by UV-B increase, a partial ozone depletion will have very significant socio-economic impacts on these populations.

To make a realistic assessment of the impact of a partial ozone-layer depletion on materials, several key types of data are needed. These are, a) the spectral sensitivity of plastics and biomaterials of interest, b) dose -response data to estimate the increased damage to be anticipated as a result of the UV-B increment in terrestrial sunlight, and c) data on the effectiveness of conventional and new types of light stabilizers in specific polymers, under exposure to spectrally-altered sunlight. Only a fraction of the needed data is currently available, and a reliable quantitative assessment is therefore difficult at the present time. However, spectral sensitivity data on several relevant polymers, data on high-UV desert exposures of polymers, and some preliminary information on stabilizer effectiveness, have been reported in recent years. The availability of such data continues to increase the reliability of the assessment process.

UV-Induced Damage to Polymers

The chemistry of UV-induced damage to polymers is not completely understood. The basic chemical processes that occur in key polymers exposed to solar UV-B radiation, however, have been broadly identified.

Discoloration of materials due to formation of colored chemical species from photoreactions is a primary consequence of exposure of polymers to UV radiation. While mechanical properties also suffer on continued exposure, the rate of discoloration often determines the service life of the product. In the case of poly(vinyl chloride), (PVC), typical formulations used in the building applications (for instance in siding, and in window frames), the predominant change caused by UV-B is the discoloration resulting from photo-dehydrochlorination of the polymer [*Andrady et. al. ,1989, Andrady et. al. ,1990*]. The yellowing obtained is uneven and gradually increases with prolonged exposure. Adequate stabilization with an opacifier (rutile titania) controls the rate of discoloration in white profiles used in siding, window frames and pipes [*Titow, 1984*]. Polycarbonates used in glazing also undergoes yellowing [*Andrady et. al., 1992*], but due to a combination of photo-Fries rearrangement (shown below) and oxidative reactions [*Factor and Chu, 1980*] . In this reaction the bisphenol A units photoisomerize into phenyl salicylate units and possibly to dihydroxybenzophenone units. The use of UV absorbers in the formulation is necessary to control rate of yellowing *[Davis and Sims, 1983]*.

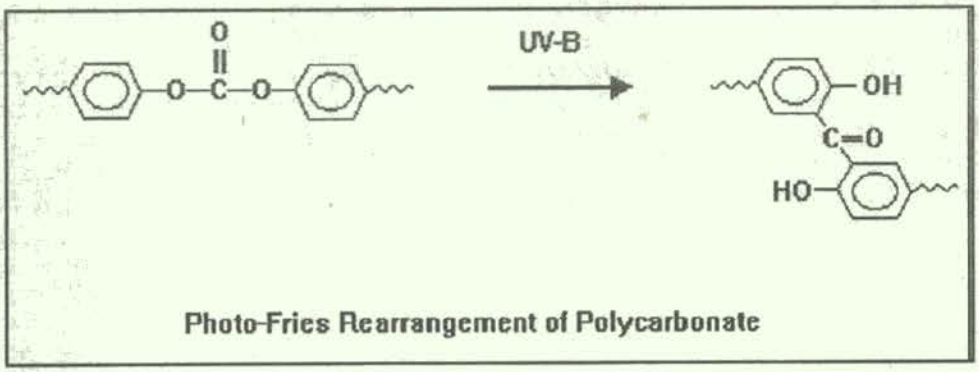

Photo-Fries Rearrangement of Polycarbonate

Wood and paper also undergo yellowing discoloration on exposure to solar UV-B [*Andrady et.al., 1991; Forsskahl et.al., 1993, Heitner, 1993*]. when the lignin component in wood undergoes photodegradation. In a study involving 75 varieties of commercially important wood, 65 percent were found to discolor due to UV light [*Sanderman et.al., 1962*]. On exposure to UV radiation, the fractions of both holocellulose and lignin reduce and that of extractives increase, but the percent reduction in lignin is relatively higher than that of cellulose [*Hon, 1993*]. Cellulose in wood has been shown to undergo a free radical mediated degradation on exposure to wavelengths < 340 nm. Electron spin resonance spectroscopic data suggest scission of the C_5 - C_6 bond in glucose units in the molecule during irradiation [*Hon, 1981*].

Wool readily undergoes light induced yellowing due to solar UV-B radiation. The amino acid residues, particularly tryptophan, histidine and cystine, degrade extensively on irradiation. Some free radical mediated main-chain scission of wool molecules also accompany photoyellowing [*Launer, 1965*]. Role of UV-B radiation in generating free-radicals in human hair has also been reported [*Jahan et.al. 1987*]. Presence of free-radicals often leads to degradation in polymer materials.

Both photo-initiated thermooxidative processes and photodegradation reactions may lead to chain-scission in polymers exposed to solar radiation. These are often free-radical processes and may also involve concurrent cross linking. As the desirable mechanical properties of polymers are a consequence of their long chain-like molecular structure, chain scission leads to deterioration of these properties. This in turn impacts their outdoor service lives. Polyethylene films exposed to solar UV-B radiation readily loose their extensibility and strength [*Hamid et. al. 1988*], as well as their average molecular weight [*Andrady et. al., 1993*]. While the change in UV-induced loss in elongation was shown to generally correlate with the development of carbonyl functionalities, it is preferable to use both measures when predictions of weatherability of polyethylene is attempted [*Tidjani et.al., 1993*]. In polyethylene, photoinitiation is thought to

originate from polymer-oxygen complexes while in polypropylene the initiation is via photolysis of tertiery hydroperoxide groups [*Gugumus, 1994*]. Solar UV-B is also known to degrade polystyrene foam [*Andrady et. al., 1991*], a popular packaging and material. These changes in bulk mechanical properties reflect changes in macromolecular chain scission (and/or cross linking) resulting from photodegradation. Changes in viscosity or gel permeation characteristics of polymers have been used [*Torikai et.al., 1993a ; Andrady et. al., 1993*] to establish molecular level changes during photodegradation.

It has been suggested that unless the ozone losses exceed an arbitrary value of 15 percent in summer months, the increased deleterious effects on polymers might be minimal [*Prickett, 1994*]. These conclusions based on biologically effective UV doses and the geographic variations of terrestrial UV currently observed, do not take into account the synergistic effects of the temperature in polymer photodegradation. In near-equator regions (for instance, in Dhahran, Saudi Arabia) where the ambient air temperatures can be as high as 50 C, even a very small increase in UV-B levels can translate into significant increases in the rate of degradation. A more reliable assessment must be based on activation spectra of relevant polymer formulations.

Spectral Sensitivity

The spectral sensitivity of polymers is determined from exposure experiments using monochromatic radiation, or from exposures to filtered xenon sources (whose spectral irradiance distribution is designed to closely approximate terrestrial sunlight at unit air mass) and a series of cut-on filters. Early experimental data is of limited value because of incomplete descriptions of the polymer formulations and processing techniques used in sample preparation, and because mercury vapor lamps were used as sources in these studies. Such lamps emit short wavelength UV radiation not typically found in terrestrial sunlight.

Table 7.2 summarizes the available data on spectral sensitivity of polymeric materials. Data on UV-A sensitive materials are not included because ozone depletion is expected to mainly affect the UV-B region of the solar spectrum. Data generated using a borosilicate-filtered xenon source, with cut-on filters to separate the effect of different spectral regions allow the identification of spectral regions most effective in bringing about the damage of interest. Such activation spectra will be source-specific, and those reported in the Table are specific for filtered - xenon source spectrum and the indicated damage criterion only. Spectral sensitivity can also be studied in experiments where materials are exposed to monochromatic radiation. Using either experimental approach it is possible to estimate the damage obtained per available photon, and plot as a function of wavelength of exposure, to obtain an action spectrum. Information from the two approaches

should agree in instances where there is no significant synergism or mutual cancellation of effects obtained at different wavelengths. In the case of PVC, the yellowing discoloration brought about by the UV-B region of the solar spectrum is offset to some extent by the photobleaching of chromophores afforded by the 500nm - 600 nm band of visible light [*Andrady et. al., 1989*]. In spite of the high quantum efficiency of photobleaching reaction [*Decker et. al., 1988*] relative to that of yellowing, this apparantly plays only a minor role in the overall photodegradation process, and the monochromatic wavelength sensitivity data was consistent with activation spectra for yellowing under white light [*Andrady et.al., 1989a*]. Figure 7.1 illustrates the action spectra of common polymer formulations for yellowing.

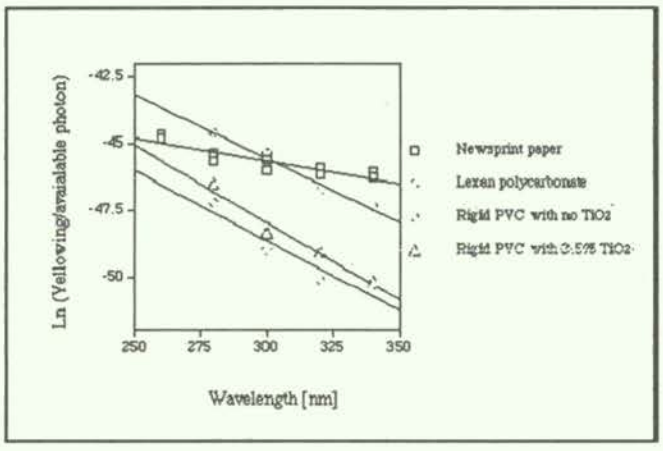

Fig. 7.1. Spectral sensitivity of selected polymeric materials.

Scission (and sometimes cross linking) of macromolecular chains making up the polymer, is a common consequence of photodegradation. These changes result in a drastic reductions in the mechanical integrity of the polymer and therefore influence their useful lifetimes outdoors. Recently the action spectra for chain scission in several polymers including polystyrene [*Torikai et.al., 1993b*], polyethylene [*Andrady et. al. 1994*], and polycarbonate [*Torikai et. al., 1993a*] have been reported. Activation spectra based on tensile properties of materials are of particular interest as the mechanical integrity of plastics is frequently measured in terms of tensile properties. Figure 7.2 shows relevant data for {ethylene - carbon monoxide (~1 %) } copolymer film exposed to white light from a xenon source [*Andrady et. al. 1994*]; a sharp transition from almost no effect to drastic deterioration is obtained around 330 nm. The standard error associated with elongation at break measurements is generally large, and the scatter in Figure 7.2 is not unusual. A more fundamental measure of chain-scission is the change in solution viscosity, resulting from a change in average molecular weight. Recently viscosity data on polycarbonate [*Torikai*

et. al., 1993a], and polystyrene [*Torikai et.al., 1993b*] were reported, with either 300 nm or 280 nm - 300 nm being identified as the wavelengths most effective in causing chain scission. A quantum yield of 0 - 1 x 10^{-3} scission events per photon was reported for polycarbonate.

Table 7.2. Reported Spectral Sensitivity Data on Materials

POLYMER FORMULATION	DAMAGE CRITERION	MAXIMUM EFFECT*	SOURCE
Polyehtylene [PE]			
LLDPE Base Polymer LLDPE + Flame retardant	Optical Density (UV/Vis)	260*	Torikai. (1993c)
HDPE + Flame retardant	Optical Density (UV/Vis)	300	
LDPE Base Polymer	Discoloration	310	Hirt et.al (1967)
Poly(vinyl chloride) [PVC]			
Base Polymer film	Discoloration (Y.I.)	320	Hirt (1967)
Rigid PVC + titania	Discoloration (Y.I.)	310-325	Andrady (1989)
Base polymer film	Spectroscopy (FTIR)	355-385	Martin (1971)
Polypropylene [PP]			
Base Polymer Film	Spectroscopy (FTIR)	260-280	Torikai (1993b)
PP + Flame retardant	Chain Scission (GPC)	260-280	
PP molded pieces	Extensibility (Tensile)	315-330	Andrady (1994)
Polystyrene [PS]			
Base Polymer	Optical Density (UV/Vis)	260-320	Torikai (1993b)
PS + Flame retardant (I)	Optical Density (UV/Vis)	280	
PS + Flame retardant (II)	Optical Density (UV/Vis)	310	
Base Polymer	Chain Scission (GPC)	280	
PS + Flame retardant (I)	Chain Scission (GPC)	300	
PS + Flame retardant (II)	Chain Scission (GPC)	300	
PS (photodegradable)	Discoloration	320-345	Andrady (1994)
Polycarbonate [PC]			
Base Polymer	Chain Scission (Visc.)	280-320	Torikai (1993a)
PC extruded sheet	Discoloration (Y.I.)	280	Andrady (1994)
PC + photostabilizer	Discoloration (Y.I.)	310-340	Andrady (1994)

Poly(methyl metha-crylate) [PMMA}

Base Polymer	Chain Scission (Visc.)	300	Mitsuoka (1993)
Copolymers and Blends			
ECO copolymer (1% CO)	Optical Density (UV/Vis)	280-340	Aoki (1992)
	Extensibility (Tensile)	<320	Andrady (1994)
PC/PMMA Blend	Chain Scission (Visc.)	<280	Osawa (1991)
Biopolymers			
Wood Pulp (mechanical)	Discoloration (Y.I.)	334-354	Andrady (1991)
Wood Pulp (refiner pulp)	Brightness (UV/Vis)	450-500	Forsskahl (1993)
Wool	Discoloration (Y.I.)	290-311	Launer (1965)
	Discoloration (Y.I.)	280*	Lennox (1971)

NOTES.

1. Column 1 abbreviations. LLDPE - Linear Low Density Polyethylene, HDPE - High Density Polyethylene, LDPE - Low Density Polyethylene, PMMA - Poly(methyl methacrylate), ECO - copolymer of ethylene and carbon monoxide.
2. Column 2 abbreviations. UV/Vis. : UV - Visible Spectroscopy, Y.I.: Yellowness Index, FTIR: Fourier Transform Infra-red Spectroscopy, GPC: Gel Permeation Chromatography.
3. Column 3. Wavelength interval in the white light (filtered xenon - source) spectrum at which maximum damage was obtained. Single wavelengths refer to data from monochromatic exposure experiments, and indicate the wavelength at which maximum damage was obtained. A '*' indicates that this was also the shortest wavelength used in the experiment.

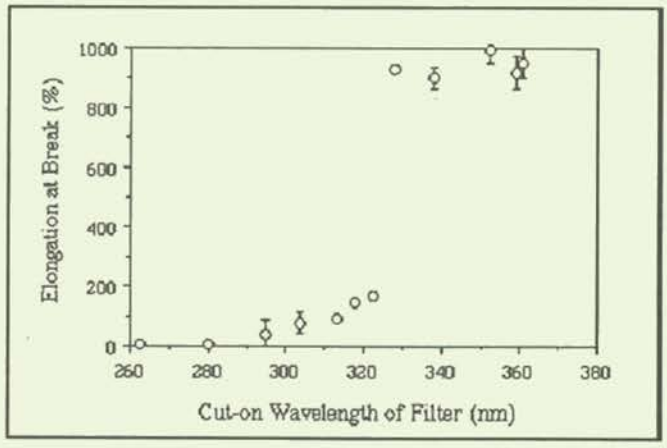

Fig. 7.2. Elongation at break for (ethylene -carbon monoxide) copolymer films exposed behind cut-on filters to a white light source (Borosilicate-filtered Xenon source).

Activation spectra for yellowing of biopolymeric materials such as wood pulp [*Andrady et.al. 1991*] and wool [*Lennox et.al. 1971*] have also been reported. With wool and paper made from mechanical pulps, premature yellowing takes place on exposure to solar UV-B light. Figure 7.3 shows the activation spectrum for yellowing of newsprint paper made from pinewood (*Pinus taeda*) exposed to white light from a xenon source.

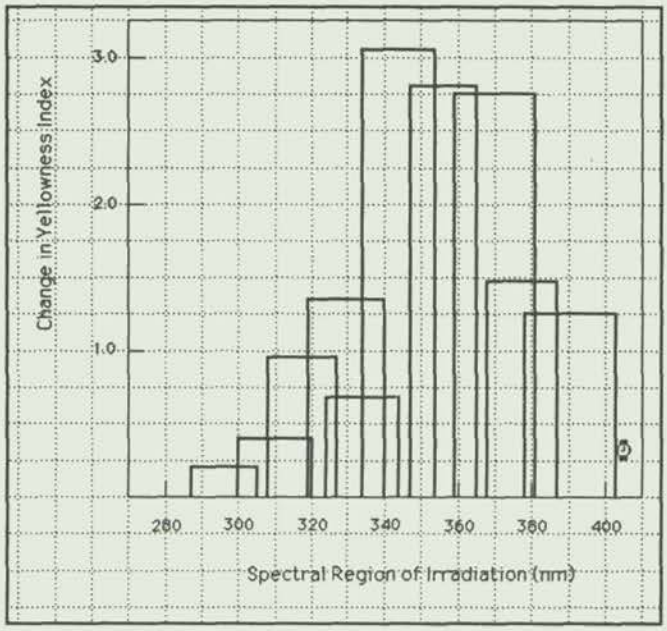

Fig. 7.3. Activation spectrum for yellowing of newsprint paper exposed to a white light source (Borosilicate-filtered Xenon source).

Increased rates of UV-B induced degradation of polymers may also affect post-consumer plastic waste management technologies such as recycling and photodegradable polymers. Depending on the geographic location, plastics in the litter stream will undergo higher extents of photodegradation prior to collection for recycling. The significance of this incremental exposure on recyclate quality is not clear at this time.

Responses to increased Solar UV Radiation

In principal, there are two basic approaches to maintaining current service lives of selected materials in spite of a moderate increase in UV levels in sunlight. One is to substitute materials; more photoresistant, albeit more expensive, polymers or other materials might be used for those applications that demand routine exposure to sunlight. For instance, the PVC formulations used in exterior profile (for instance in window frames) might be replaced with better weather-resistant copolymers such as (acrylonitrile - butadiene - styrene), or with PVC - capped with films or layers of selected polymers with superior weatherability [*Moore, 1994*]. Alternatively, an effort might be made to use conventional or novel light - stabilizers to address the problem. Polymers such as PVC are inherently photolabile, and their outdoor use is possible only due to the effectiveness of light- and heat-stabilizer technology, with impressive classes of photostabilizers such as hindered amine

systems (HALS) being recently developed [*Al-Malaika et.al. 1983*]. It is likely and certainly not unreasonable to expect the polymer industry worldwide to explore the full capability of stabilizers to address the problem of increased solar UV-B component. The cost of UV stabilizer systems is a very significant component of the cost of plastic formulations used in outdoor applications; with polyethylene greenhouse film formulations, as much as 30 percent of the compound cost might be ascribed to the photostabilizer. Increasing levels of stabilizer will therefore have a definite impact on the economics of plastics use in outdoor applications.

The basic question then would be whether increasing levels of conventional photostabilizers in common polymer formulations will result in a concomitant increase in the service life of materials exposed to spectrally - altered, UV-rich sunlight? Early investigations of the issue in CIAP (Climatic Impact Assessment Program) assumed that such an approach will be successful and even calculated (based on Beer - Lambert Law) factor increases in stabilizer needed to offset a given increase in total UV radiation levels [*Shultz et.al., 1975*]. These calculations, however, were not based on experimental data pertaining to specific stabilizer / polymer combinations. Some data is also available from industry sources and in technical literature on the effectiveness of higher levels of photostabilizer in typical formulations in increasing the service life of polymers. However, this data pertains almost exclusively to photodamage to materials from sunlight with present-day levels of UV-B. The effect of increasing levels of a common type of photostabilizer in polyethylene film is shown in Figure 7.4 to illustrate the efficiency of the additive in maintaining service life, and to show that the protective action can be a non-linear function at high levels of the additive. This data is on Chimasorb 944 LD stabilized LDPE films exposed for a three year period under desert conditions in Dhahran, Saudi Arabia [*Hamid et.al. 1994*]. The high ambient temperatures in desert locations will further exacerbate the problem of maintaining reasonable lifetimes for plastic products exposed to sunlight with increased UV-B component. In an empirical study on LDPE weathering under desert conditions Hamid et.al. [*Hamid et.al. 1991*] found the elongation at break to be a sensitive indicator of the extent of weathering. The study found total UV-B as well as total sunlight to correlate particularly well with changes in properties of the polymer on exposure. Another relevant study was carried out by Bauer et.al. [*Bauer et.al. 1990, 1992*] on photo-degradation of organic coatings photostabilized by HALS compounds. A "Harsh" exposure involving high-intensity short-wave UV radiation, and an "Ambient" exposure with simulated solar radiation were used to rank a series of HALS. The ranking of the effectiveness of different stabilizers was very different under the two exposure conditions. Some commercial HALS compounds are known to be photolyzed on exposure to short wavelength UV radiation [*Al-Malaika et.al., 1983 ; Chen et.al., 1988*].

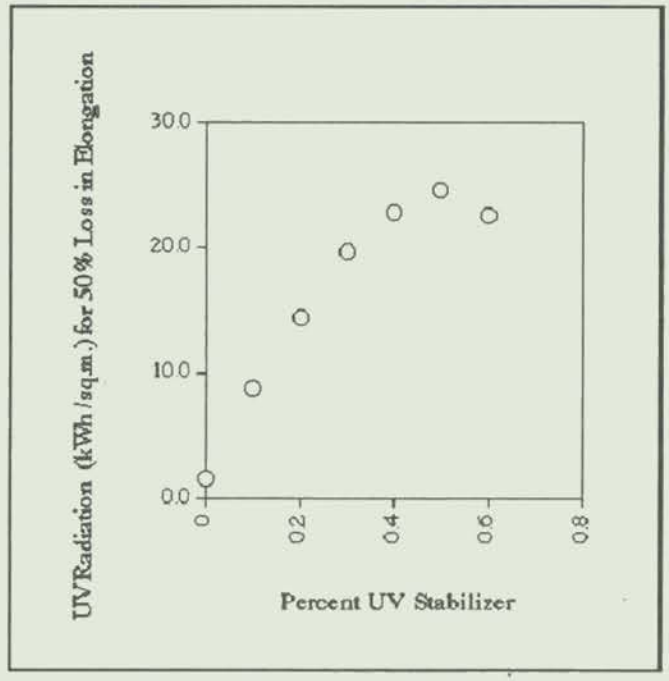

Fig. 7.4. Solar UV radiation needed to reduce the elongation at break by 50 percent, of LDPE films containing different levels of UV stabilizer.

Hitherto, there was little need to address the question of spectrally-altered sunlight and its effect on weathering of materials. The efficiency and effectiveness of conventional stabilizers under spectrally-altered sunlight has not been studied and therefore remains essentially unknown.

Increase in levels of photostabilizers may offset the increased rate of photodegradation caused by higher solar UV levels resulting from a partial ozone depletion. However, the effect of higher stabilizer levels on other useful properties of the material must also be considered; at least in the case of rigid PVC profile formulations increased titania levels can lead to several negative consequences [*Mastro, 1983*]. An attractive alternative is the use of improved grades, specially coated grades, of rutile to obtain higher levels of protection at low levels of additive [*Day, 1990*]. The relative importance of different approaches to mitigation, including the use of alternate materials of superior UV resistance, will invariably be determined by the costs associated with each strategy. Insufficiant data is available to estimate these costs and therefore the impact on building materials industry at this time.

In the case of biomaterials, the mitigation of the effects of higher UV levels in sunlight is considerably more difficult. While wood surfaces can be treated either with coatings or other

stabilizers, the same is generally not true of paper made of mechanical pulps. Light - induced yellowing and the related loss in brightness is a key factor limiting the use of mechanical pulps [*Hemmingson et.al., 1989*]. With materials such as wool, chitins, natural fibers used in netting and cordage, the impact of damage due to increased solar UV levels has not been established with any degree of certainty. While UV-induced degradation reactions in these materials are known, the extent to which such changes interfere with the performance of these materials, or affect the economic value of these materials (specially with wool or paper) has not been comprehensively addressed.

Conclusions

Both naturally occurring biopolymer materials as well as synthetic polymers undergo degradation reactions on exposure to solar UV-B radiation. With synthetic polymers, it is the effective photostabilization that ensures adequate lifetimes for products used outdoors even under present exposure conditions. Any increase in the UV-B content of terrestrial sunlight must therefore reduce the service life of products based on these materials.

Some relevant action spectra for typical formulations of common polymers are available. In spite of many recent pertinent contributions in the literature, a complete understanding of the wavelength sensitivity of key formulations used in building applications has not been achieved. To be useful in models assessing damage, the action spectra have to address relevant formulations of more common polymers, and pertain to those properties (often mechanical properties) of interest to end-users. In the case of biomaterials routinely exposed to sunlight, even less data is available; action spectra are known only for a few of these.

With synthetic polymers there is a likelihood that either increasing the levels of conventional stabilizers, or the use of novel stabilizers, will alleviate some of the deleterious effects of increased UV-B in sunlight. However, insufficient data on weathering studies based on spectrally altered white light, precludes confirmation of the efficacy of this strategy. Intensity - dependence of the key light stabilizers for polymers, under different and relevant light - temperature domains has not yet been reported. Therefore the economic feasibility of this primary industry response to stratospheric ozone depletion, cannot be realistically assessed at this time.

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APPENDIX C

LIST OF ABBREVIATIONS

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AF	Amplification Factor
AIDS	acquired immunodeficiency disease syndrome
BAF	Biological Amplification Factor
BCC	basal cell carcinoma
CFC	chlorofluorocarbon
CM	cutaneous melanoma
CO	carbon monoxide. A chemically-reactive trace gas that is believed to play an important role in controlling the oxidizing capacity of the free troposphere.
COS	carbonyl sulfide. The most concentrated sulfur containing gas in the troposphere. COS is believed to be a source of background sulfate aerosols in the stratosphere.
CO_2	carbon dioxide
CZCS	coastal zone color scanner
DIC	Dissolved inorganic carbon. Total concentration of dissolved inorganic carbon in water, expressed in units of grams carbon per liter
DMS	dimethyl sulfide. The major volatile sulfur compound of biogenic origin emitted from the ocean into the atmosphere. DMS reacts in the troposphere to produce sulfate aerosols.
DNA	deoxyribonucleic acid
DOC	Dissolved organic carbon. Total concentration of dissolved organic substances in water, expressed in units of grams carbon per liter
DOM	Dissolved organic matter. Total concentration of dissolved organic substances in water, usually expressed in units of grams carbon per liter
DU	Dobson Unit (2.69×10^{19} molecules cm^{-2})
EC_{50}	concentration resulting in 50% of specified effect
g DW	Grams per dry weight
Gt	Gigaton. 10^9 tons (10^{15} grams)
HCFC	Hydrochlorofluorocarbon. The class of industrially produced compounds containing carbon, hydrogen, chlorine and fluorine. Can be used as chlorofluorocarbon substitutes.
HFC	Hydrofluorocarbon. The class of industrially produced compounds containing carbon, hydrogen and fluorine. Can be used as chlorofluorocarbon substitutes
HIV	human immunodeficiency virus
HSV	herpes simplex virus
ISLSCP	International Satellite Land Surface Climatology Project
IL-1, 10	Interleukin -1, 10
MeBr	methyl bromide
NLOM	Non living organic matter in the environment, e.g. litter, detritus
NMHC	Non methane hydrocarbons. Volatile hydrocarbons emitted from terrestrial plants and marine phytoplankton that participate in various tropospheric chemical reactions
NMSC	non-melanoma skin cancer
NO	Nitric oxide. A highly reactive trace nitrogen species that participates in a variety of chemical reactions in the troposphere
NO_x	Nitrogen oxides. Reactive nitrogen-containing species, nitric oxide and nitrogen dioxide, that play an important role in tropospheric chemistry
N_2O	Nitrous oxide. An important greenhouse gas that also participates in stratospheric reactions that deplete ozone
PAM	pulse amplitude modulation
PAR	Photosynthetically active radiation. Generally defined as electromagnetic radiation in the 400 to 700 nm range
POC	Particulate organic carbon. Total concentration of particulate organic substances in water, expressed in units of grams carbon per liter
RAF	Radiative Amplification Factor
SBUV	Solar Backscatter Ultraviolet (instrument)
SCC	squamous cell carcinoma

SCUP	skin cancer utrecht - Philadelphia
SOM	Soil organic matter
SP	xeroderma pigmentosum
TFA	Trifluoroacetic acid. A tropospheric oxidation product of certain HFCs and HCFCs
Tg	Teragram. 10^{12} grams
Th 1, 2	T-helper 1, 2 lymphocyte
TNF	Tumor necrosis factor - alpha
TOMS	Total Ozone Mapping Spectrometer
UCA	urocanic acid
UNEP	United Nations Environment Programme
USEPA	United States Environmental Protection Agency
UV	ultraviolet
UV-A	Ultraviolet-A radiation. Electromagnetic radiation of wavelengths in the 315 to 400 nm range
UV-B	Ultraviolet-B radiation. Electromagnetic radiation of wavelengths in the 280 to 315 nm range
WHO	World Health Organization
WMO	World Meteorological Organization