UNITED NATIONS
ENVIRONMENT PROGRAMME

ENVIRONMENTAL EFFECTS OF OZONE DEPLETION: 1991 UPDATE

Panel Report Pursuant to Article 6 of the Montreal Protocol
on Substances that Deplete the Ozone Layer
Under the Auspices of the
United Nations Environment Programme (UNEP)

November 1991

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INTRODUCTION

ENVIRONMENTAL EFFECTS OF OZONE DEPLETION

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 every four years.

The latest assessments were made in 1989. For the reconsideration of the agreements in the Montreal Protocol in 1992, UNEP decided that the 1989 assessments would be updated, rather than making completely new ones. The present report is such an update of the 1989 Environmental Effects Panel Report, and focuses on developments since 1989. Information covered in the previous report that is still up-to-date is not repeated. For this reason, the chapters of this update include the summary of the corresponding chapter in the 1989 Report.

The occasion calls for an evaluation of how research on effects of increased UV-B radiation has proceeded during the past years. We cannot conceal that progress is disappointing. Many of the "Research Needs" formulated in previous reports have to be listed again. The scientific community has followed some of the recommendations, but by no means all. Urgent problems are still waiting to be addressed.

The underlying cause has been signalled over many years by the UNEP Coordinating Committee on the Ozone Layer. Funding for research on the consequences of increased UV-B radiation is disproportionately low, typically less than 1 percent of what is made available for atmospheric research in relation to ozone depletion. This comment is still valid. There is improvement of funding in some countries, but this is counterbalanced by a decrease in other countries. Several research groups, having contributed important information for previous assessments, have even ceased to exist. Effects research is necessary to provide policy makers with relevant information, so that they may evaluate response strategies to future challenges. The possibility to do this in a timely fashion may well depend on the funding situation.

Increased UV-B radiation will have many effects on man, animals, plants, and materials. For several potentially important effects, our Panel could do no more than express its concern; more knowledge is needed to come to firm conclusions. The deleterious effects that we recognize are serious enough to plea for action by the nations of the world to protect the ozone layer.

J.C. van der Leun
M. Tevini

EXECUTIVE SUMMARY

ENVIRONMENTAL EFFECTS OF OZONE DEPLETION

SOLAR INTERACTIONS

- Significant global scale decreases in total ozone have occurred over the past ten years.
- All other factors being constant, there is no scientific doubt that decreases in total ozone will increase UV-B radiation at ground level.
- Tropospheric ozone and aerosols may have masked the consequences of stratospheric ozone depletion for UV-B in some industrialized regions.
- It is likely that in areas remote from anthropogenic emissions, the UV-B changes due to stratospheric ozone depletion would be only partially compensated by tropospheric ozone and aerosol increases.
- There are no reliable estimates of the direction or magnitude of effects of any cloud cover trends on UV-B.
- Efforts to improve local and regional air quality may bring to light the increases in UV-B associated with the depletion of stratospheric ozone.

HUMAN HEALTH

- The induction of immunosuppression by UV-B has now been demonstrated in humans, not only those of light pigmentation, but also deeply pigmented individuals.

  This places all of the world's populations at risk of the potential adverse impacts of UV-B on the immune system, including possible increases in the incidence or severity of infectious disease.
- An increased number of adverse ocular effects have been associated with exposure to UV. These include age-related nearsightedness, deformation of the lens capsule, and nuclear cataract (a form of cataract which previous information excluded from consideration). These effects appear to be independent of pigmentation. Estimates of risk would increase slightly if one were to include nuclear cataract among the forms of cataract increasing with ozone depletion. It is now predicted that, all other things being equal, a sustained 10% decrease in ozone will be associated with between 1.6 and 1.75 million additional cases of cataract per year world-wide.
- Recent information on the relationship of non-melanoma skin cancer to UV exposures confirms previous findings and has allowed refinement of the carcinogenic action spectrum. Incorporation of this new information into the risk estimation process has led to slightly lower predictions. It is now predicted that a sustained 10% decrease in ozone will be associated with a 26% increase in non-melanoma skin cancer. All other things remaining constant, this would mean an increase in excess of 300,000 cases per year world-wide.

TERRESTRIAL PLANTS

- Continued research on plant responses to UV-B radiation underscores the concern for agriculture, forestry, and natural ecosystems as the ozone layer is depleted.
- Growth and photosynthesis of certain plants (e.g., seedlings of rye, maize, and sunflower) can be inhibited even under ambient levels of UV-B radiation.
- Certain environmental factors, both biotic (e.g., plant diseases and competition with other plants) and abiotic (e.g., carbon dioxide, temperature, heavy metals, and water availability), can interact with the effect of UV-B radiation in plants. This makes it difficult to make quantitative predictions.
- Although most research to date has been with plants from temperate regions, data also show that certain tropical species may be adversely affected by enhanced UV-B radiation.

AQUATIC ECOSYSTEMS

- Marine phytoplankton produces at least as much biomass as all terrestrial ecosystems combined.
- Recent results show that the aquatic ecosystem is already under UV-B stress and there is concern that an increase in UV-B radiation will cause detrimental effects.
- One consequence of losses in phytoplankton is reduced biomass production which is propagated throughout the whole food web. This may result in losses of biomass for human consumption.
- The marine phytoplankton is a major sink for atmospheric carbon dioxide. Any reduction of the populations would decrease the uptake of carbon dioxide and so augment the greenhouse effect. Also, phytoplankton production of DMS (dimethylsulphate), which acts as a precursor of cloud nucleation, would be reduced, hence potentially affecting global climate.
- A UV-B induced decrease in microorganisms fixing atmospheric nitrogen would require significant substitution by artificial fertilizers, e.g., in rice production.

TROPOSPHERIC AIR QUALITY

- Chemical reactivity in the troposphere is expected to increase in response to increases in UV-B.
- Tropospheric ozone concentrations could rise in moderate to heavily polluted areas, but should decrease in unpolluted regions (with low oxides of nitrogen levels), as recently confirmed by measurements in the Antarctic.
- Other potentially harmful substances (hydrogen peroxide, acids, and aerosols) are expected to increase in all regions of the troposphere due to the enhanced chemical reactivity.
- These changes could exacerbate problems of human health and welfare, increase damage to the biosphere, and might make current air quality goals more difficult and expensive to attain.

MATERIALS DAMAGE

- UV-B radiation is particularly effective in light-induced degradation of wood and plastic products, leading to discoloration and loss of strength. Increased UV-B content in sunlight will cause more rapid degradation, resulting in increased costs of using higher levels of conventional light stabilizers, possible design of new stabilizers, and faster replacement of the affected products.
- Available research data are inadequate to reliably estimate the damage from higher UV-B levels to materials. Very limited relevant data are available for important classes of materials such as wood, plastic coatings, plastics used outdoors, and rubber. Data pertaining to performance of plastics in near-equator regions of the world, with the harshest exposure environments, are particularly needed.
- Some on-going work relating to exposure of plastics under desert conditions is likely to contribute some of the needed data within the next few years. This may lead to improved assessment of damage to plastics resulting from partial ozone depletion, at that time.

KEY AREAS OF UNCERTAINTY

The key areas of uncertainty are the following:

- Quantification of the primary effects on food production and quality, on forestry, and on natural ecosystems.
- Clarification and quantification of influences on human health, especially the immune system, and occurrences of melanomas and cataracts.
- Effects on biota of the enhanced UV radiation during the Antarctic springtime ozone depletion.

CHAPTER 1

CHANGES IN BIOLOGICALLY ACTIVE ULTRAVIOLET RADIATION REACHING THE EARTH'S SURFACE

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1991 REPORT SUMMARY

Significant global scale decreases in total ozone have occurred over the years 1979-1989. All other factors being constant, there is no scientific doubt that such decreases in total ozone will increase ultraviolet-B (UV-B) radiation (280-315 nm) at ground level. Calculations based on the measured ozone trends indicate increases in UV-B over large areas of earth. In the northern hemisphere, the annual DNA-damage weighted dose (one estimate of biologically active UV radiation) is estimated to have increased by 5% per decade at 30°N and about 10% per decade in the polar region. In the southern hemisphere, the trends are +5% per decade at 30°S, +15% per decade at 55°S, and +40% per decade at 85°S. In the equatorial region (30°S to 30°N) no statistically significant trends are found. In addition, large UV-B increases have been directly measured during spring and early summer in the Antarctic.

UV-B penetration to the surface of the earth is also affected by tropospheric ozone, aerosols, and clouds. Increases in tropospheric ozone and aerosols since the pre-industrial era may have decreased UV-B levels in industrialized regions by amounts comparable to the increases estimated from stratospheric ozone change over the period 1979 to 1989. It is likely that, in areas remote from anthropogenic sources of aerosols and other precursors of tropospheric ozone, the calculated UV-B changes due to stratospheric ozone decreases would be only partially compensated by the possible effect of clouds. There are no reliable estimates of the direction or magnitude of the effect of any cloud cover trends on UV-B.

1989 REPORT SUMMARY

With the depletion of the ozone layer, the atmosphere becomes more transparent to solar ultraviolet radiation. Only a certain type of ultraviolet radiation is affected, that in a wavelength range of 280 to 315 nm, which is called UV-B radiation. Both the intensity and quality (wavelength composition) of the UV-B are affected by changes in ozone; the intensity increases and the wavelength composition is shifted to proportionately more radiation at shorter wavelengths. These changes must be evaluated with respect to biological responses and other phenomena affected by increased UV-B because these effects are usually very dependent on the quality of the UV-B. This is done by computing changes in "effective UV-B."

Concern about ozone reduction revolves around ozone in the stratosphere where most of the total atmospheric ozone resides (ca. 90+%). Ozone in the troposphere may be increasing, at least in local urban areas. For filtering sunlight, it is the total ozone column that is important. Thus, the net change of ozone in the upper and lower atmosphere is of consequence. In addition to ozone, effective UV-B is affected by the position of the sun in the sky (solar elevation angle) and cloud cover. Even without changes in the ozone layer, there are strong seasonal and latitudinal differences in effective UV-B. Under cloudless skies, the UV-B is much more intense in the summer months than during other seasons, and, at any time of the year, it is much stronger at lower than higher latitudes.

Apart from the Antarctic ozone hole, there have already been general reductions in stratospheric ozone. Using ozone layer thickness data from satellite observations, computations show that effective UV-B on clear days should have increased by as much as 10% at temperate latitudes during the cooler months of the year. The absolute increments of effective UV-B at tropical and temperate latitudes during the warmer months are calculated to be at least as great as the increased UV-B associated with the Antarctic ozone hole.

Predictions of increased UV-B associated with computed ozone reductions over the century period from 1960 to 2060 are shown for two scenarios of CFC release rates. The first is for CFC release as permitted by the Montreal Protocol agreements. The second scenario involves a more stringent control whereby CFC release is reduced to 5% of the levels of the first scenario by the year 2000 and held constant thereafter. The second scenario results in increased effective UV-B levels that are less than half the values computed for the first scenario.

INTRODUCTION

Reductions in stratospheric ozone due to anthropogenic influences may allow the penetration of more UV-B radiation (280-315 nm wavelength) to the lower atmosphere and the surface of earth. UV-B radiation affects many chemical and biological processes. Its potential increases are of considerable concern, as UV-B has adverse effects on living tissue. Since the publication of the 1989 United Nations Environmental Programme report on the effects of stratospheric ozone depletion *[UNEP, 1989]*, new information has become available on the changes in the composition of the atmosphere and the interpretation of the new data. There have also been some significant revisions of previously reported measurements.

The modification of UV-B by known changes in stratospheric ozone is, in principle, well understood, because the ozone absorption spectrum has been measured with sufficient accuracy *[DeMore et al., 1990]*. Geometric parameters, such as variations in the earth-sun distance and the angle of incidence of solar radiation at the top of the atmosphere (a function of time of day, year, and latitude) are easily calculated. The theory behind the absorption and scattering of radiation is well established, and atmospheric transmission is easily computed for idealized conditions (horizontally homogeneous gas phase atmosphere of known composition). The dependence of surface UV-B on these simple parameters was reviewed in the earlier UNEP Report *[UNEP, 1989; see also Dahlback et al., 1989; Frederick et al., 1989; Moan et al., 1989]*. *Figure 1.1* shows the resulting latitudinal and seasonal distribution of surface UV-B radiation weighted by the DNA action spectrum.

Other environmental factors known to affect the UV-B levels include surface reflections, clouds, aerosols, and various tropospheric pollutants. These factors tend to be highly variable in both space and time, and may account for some of the conflicting trends in the few available long-term observational records of UV-B radiation. The potential effects of these environmental factors were acknowledged in the earlier report *[UNEP, 1989]*, but no quantitative estimates were made at that time.

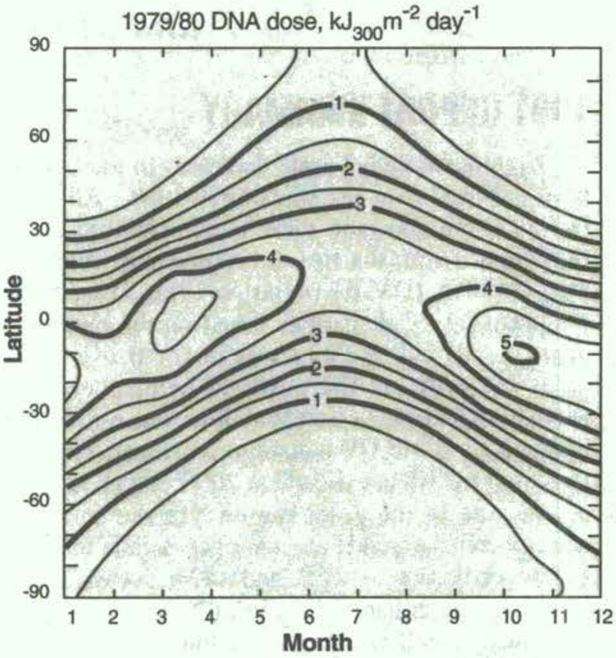

Figure 1.1 Daily effective UV-B dose, illustrated for DNA damage *[Setlow, 1974]*, computed for cloudless skies using TOMS ozone column data for the years 1979 and 1980.

This update to the 1989 UNEP Report addresses the changes in UV radiation resulting from new total ozone measurements, as well as from possible long-term changes in tropospheric ozone, aerosols, and clouds. Of particular interest are the possible trends in tropospheric pollutants, to the extent that these may partially offset or supplement the UV-B increases due to stratospheric ozone reduction. Most of the UV-B estimates are made on the basis of the spectral dependence of DNA damage proposed by Setlow *[1974]*. Therefore, we have also included, for comparison, a compilation of the sensitivity to ozone changes for several other biological and chemical photo-processes.

RECENT MEASUREMENTS OF UV RADIATION TRENDS

At the present time, there are insufficient direct measurements of UV-B at the earth's surface available for constructing a global climatology, or to estimate long-term trends on extended geographic scales. Problems in obtaining reliable climatology measurements and trends include (1) the ambiguities in constructing a detector which fairly represents the sensitivity of different biological and chemical targets (with different wavelength dependencies, and sensitivity to different orientations), (2) the difficulties of maintaining accurate field instrument calibrations over a period of many years, (3) the practical limitations in the deployment of a global monitoring network, especially with the potential for bias from locally polluted areas, and (4) the absence of a baseline, long-term, historical UV record.

The most comprehensive UV data are from the Robertson-Berger (R-B) meter network of 25 United States stations and 11 non-U.S. stations, with varying lengths of operation *[Cotton, 1990]*. In the United States, the R-B meter measurements of integrated, annual UV radiation decreased from 1974 to 1985, between 0.5% and 1.1% per year *[Scotto et al., 1988]*. Aside from possible problems in the long-term calibration of the R-B meters, this result was seen as somewhat surprising in view of stratospheric ozone depletion. Grant *[1988]* suggested that local pollution may have accounted for the decrease, since the R-B meters operated mostly in urban and near-urban sites. In the Soviet Union, Garadzha and Nezval *[1987]* found a 12% decrease in the R-B meter measurements of UV radiation in Moscow between 1968 and 1983, with a concurrent 15% increase in turbidity, and a 13% increase in cloudiness. R-B meter data obtained at a station in the Swiss Alps (3.6 km above sea level) showed increases of 0.7±0.2% per year between 1981 and 1989 *[Blumthaler and Ambach, 1990]*.

Detailed spectral irradiance measurements are being made at a few locations *[Stamnes et al., 1988; Henriksen et al., 1989a, 1989b; Bittar and McKenzie, 1990; Henriksen et al., 1990; Stamnes et al., 1990; Lubin et al., 1991]*, but the geographical coverage and time span of these measurements are too small to extract statistically significant UV distribution and trend information. However, the spectral measurements provide useful platforms for the validation of radiative transfer models that are used to calculate UV radiation under a variety of conditions. For example, measurements at the McMurdo and Palmer stations in Antarctica clearly demonstrated the enhancement of UV radiation under the springtime ozone holes of 1988, 1989, and 1990 *[Stamnes et al., 1990; Lubin et al., 1991]*. Furthermore, increased UV levels were detected in Melbourne in December 1987, concurrent with the reduced ozone levels thought to be associated with the break-up of the polar vortex in the late spring *[Roy et al., 1990]*.

There is also direct observational evidence for global-scale change in the relative intensity of different wavelengths inside the UV-B range. This information is available from the Dobson ozone measuring instruments, and is essentially the raw data from which ozone columns and their long-term trends are derived *[Bojkov et al., 1990]*.

OZONE-RELATED CHANGES

Since October 1978, measurements of the vertical ozone column over the globe have been made from the Total Ozone Mapping Spectrometer (TOMS) aboard the Nimbus 7 satellite. The TOMS monitors solar radiation reflected from the atmosphere at four UV wavelengths, and the amount of ozone present is calculated from the ratio of the radiation measured at different wavelengths. Due to difficulties in correcting for the progressive deterioration of optical components, the TOMS ozone trends derived previously *[WMO, 1988; WMO, 1989; UNEP, 1989]* have been recently re-examined. Herman et al. *[1991]* have developed a new correction procedure based on an internally self-consistent calibration with different wavelength pairs. The revised TOMS ozone column data (version 6) are now in agreement with standard measurements (overpass comparisons with the ground-based Dobson standard instrument No. 83).

The revised TOMS data have been analyzed statistically by Stolarski et al. *[1991]* for the 11.6 year period between November 1978 and May 1990. The integrated ozone column between latitudes 65°S to 65°N was found to have decreased by 3%, at a rate of change of -0.26±0.14% per year, after eliminating the effects of the 11 year solar cycle (1.5% variation in ozone over the cycle) and the quasi-biennial oscillation (1% variation in ozone over the cycle). Statistically significant (two standard deviations, or 2σ) negative ozone trends were found southward of 30°S at all times of the year, between 30°N-60°N in the winter and spring, and between 50°N-60°N in the summer. The strongest declines were observed in the Antarctic spring (-2.0% to -3.0% per year), and at latitudes 40°N-50°N in the late winter (-0.8% per year). The decreases in the southern mid- and high- latitudes seem to be explained by the heterogeneous chemistry in the polar vortex, and the subsequent break up of the vortex and mixing of ozone-poor air to lower latitudes.

Dobson measurements in the northern hemisphere *[Bojkov et al., 1990]* show weaker trends than the TOMS data. Because of the different geographical coverage and time records (1970-1986 for Dobson data and 1978-Present for TOMS data), a direct comparison between these two data sets is not possible, especially in view of the increasing anthropogenic gas trends and the associated non-linearities of the atmospheric chemistry. The relative importance of recent trends has been demonstrated by Frederick et al. *[1991]*, who showed that in the latitude band of 40°N-52°N, UV-B trends that were estimated from Dobson measurements are significantly greater over the years 1970-1988, than during the 1957-1988 data record.

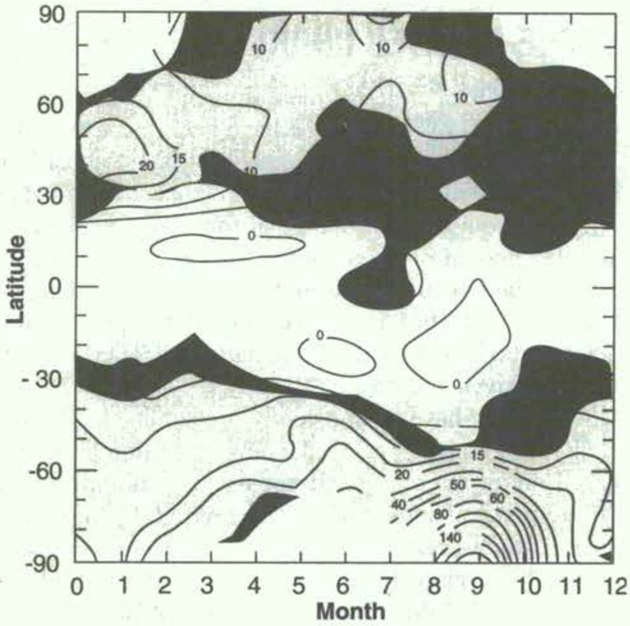

Figure 1.2 Trend in daily effective UV-B dose for DNA damage *[Setlow, 1974]* for cloudless skies, computed using TOMS data over the 11 year period 1979-1989, and expressed as percent per decade. White areas indicate regions of no light (polar winter) and regions where the trends are within 1σ of zero (no trend); orange areas are within 2σ; green areas differ from zero by more than 2σ *[Madronich, 1991]*.

The revised TOMS data have recently been analyzed to estimate the trends in biologically active UV radiation *[Madronich, 1991]*. Daily UV doses were averaged for each month between January 1979 and December 1989, for 10° latitude increments. A linear fitting of the average daily doses for each month produced a seasonally and latitudinally dependent trend. *Figure 1.2* shows the trends in surface UV radiation weighted with the generalized DNA damage spectrum of Setlow *[1974]*. These values, calculated for cloudless, aerosol-free conditions, show statistically significant (2σ) increases of 5% to 20% per decade for daily doses of UV radiation in the 30°N-60°N band during late winter and early spring, 5% to 10% increases in summer poleward of 60°N, and 5% or greater increases poleward of 30°S from spring to late fall. The strong enhancement of UV-B radiation under "ozone hole" conditions in the Antarctic spring is apparent. No statistically significant trends are seen in the tropics. However, it should be noted that in the tropics, the UV-B radiation levels are normally higher than elsewhere, so that even small fractional changes may result in substantial increases in total UV-B doses.

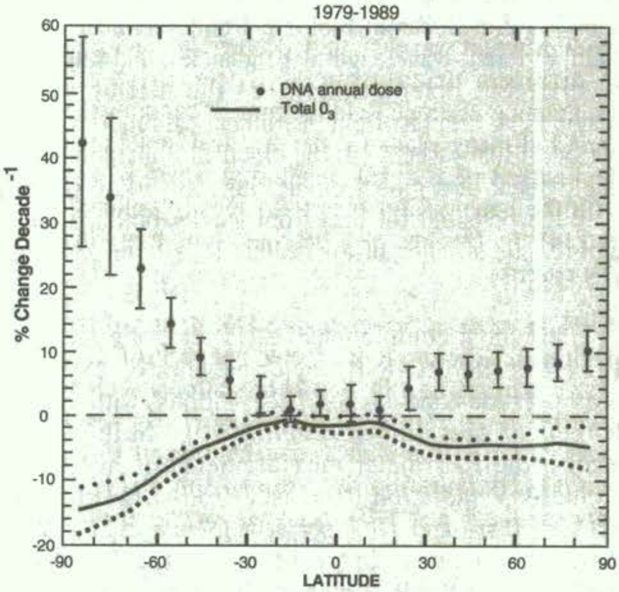

Figure 1.3 Trend in the annually integrated effective UV-B dose for DNA damage *[Setlow, 1974]* for cloudless skies, computed using TOMS data over the 11 year period 1979-1989, and expressed as percent per year. Also shown are the ozone column trends (solid lines) and 1σ uncertainties (dotted lines). Zero trend is shown by dashed line *[Madronich, 1991]*.

Cumulative yearly UV-B doses are a function of not only the annually averaged ozone column, but also of its seasonal variation of both ozone and radiation. Since the most severe ozone depletions seem to occur in the late winter and spring *[Stolarski et al., 1991]*, when unperturbed radiation levels are expected to be relatively low, it is of some interest to examine how the seasonality affects trends in cumulative annual UV-B doses. *Figure 1.3* shows that statistically significant (2σ) trends are present in both hemispheres poleward of 30°, and increase towards the pole. In the northern hemisphere, values range between 5% per decade to 11% per decade, while in the southern hemisphere values increase rapidly with latitude, from 10% per decade at 45°S to about 40% per decade at 85°S. Again, no trend is observed in the tropics.

Tropospheric ozone accounts for about one tenth of the total ozone column *[WMO, 1989]*, but is highly variable in both time and space, making it difficult to accurately establish its current global distributions and trends. Tropospheric ozone sources include intrusions of stratospheric air into the troposphere, and tropospheric photochemical production from nitrogen oxides, carbon monoxide, and hydrocarbons, all of which have significant natural and anthropogenic sources. High amounts of ozone have been observed in several urban areas, and on a regional scale in industrialized countries where chemical precursor concentrations are highest *[Finlayson-Pitts and Pitts, 1986; Logan, 1989]*. A particularly large positive trend in tropospheric ozone was reported recently by Staehelin and Schmid *[1991]*. Their analysis of 20 years (1969-1988) of ozone balloon soundings over Payerne, Switzerland showed significant increases in tropospheric ozone concentrations of approximately 1.4% per year at 900 mbar, 1.6% per year at 800 mbar, and 1.0% per year in the upper troposphere. The largest increments occurred in the last seven years of the data record.

In areas remote from industrial activity, tropospheric ozone concentrations are substantially lower. Typically high concentrations and increasing trends are found in the northern hemisphere, with slightly negative trends in the southern hemisphere. For example, measurements through the 1970s and 1980s by Oltmans et al. *[1989]* indicate increases in surface ozone of (0.79±0.44)% per year at Barrow, Alaska and (0.78±0.42)% per year at Mauna Loa, Hawaii, but decreases at Samoa of (0.26±0.65)% per year and at the South Pole of (0.46±0.37)% per year. It is still unclear whether the trends in remote measurements reflect increased photochemical production in the troposphere or fluctuations in transport from the stratosphere or other latitudes.

The trends in tropospheric ozone add to the uncertainty of the TOMS total ozone column data, since the TOMS does not fully detect tropospheric ozone *[Klenk et al., 1982]*. It is unclear how much of the tropospheric trend is convolved in the total ozone trends derived from TOMS data. Stolarski et al. *[1991]* used an assumed 50% efficiency for tropospheric ozone detection to estimate that the tropospheric trend detected by Staehelin and Schmid *[1991]* is small compared to the trend in total ozone (about 1/10 of the total ozone column trend in winter at 45°N, and about 1/20 in summer).

Tropospheric ozone can contribute to the UV-B optical depth of the atmosphere by absorbing radiation transmitted through the stratosphere. The computation of the effect of tropospheric ozone is complicated by the fact that 50% to 100% of the UV-B radiation reaching the lower troposphere is diffuse, due to scattering by air molecules (Rayleigh scattering). Brühl and Crutzen *[1989]* have pointed out that this scattering changes the average photon pathlength through tropospheric ozone. The pathlengths for diffuse light are generally longer than those for the direct solar beam if the solar zenith angles are less than 60°. Thus, for geographical regions and seasons having prevailing zenith angles less than 60°, tropospheric ozone absorbs UV radiation more effectively than stratospheric ozone, on a molecule by molecule basis. This effect is reversed at the large prevailing zenith angles typical of polar regions and mid-latitude winters. *Figure 1.4* illustrates the sensitivity of DNA daily dose rates to tropospheric ozone, assuming a constant ozone mixing ratio in the troposphere between 0 and 10 km, for 40°N. The difference between the summer and winter curves is due largely to the seasonal change in prevailing zenith angles. Penkett *[1989]* has suggested that, based on the observed tropospheric ozone increases, on the negative R-B meter trends of Scotto et al. *[1988]*, and on the modeling by Brühl and Crutzen *[1989]*, UV levels may actually be decreasing in the northern hemisphere.

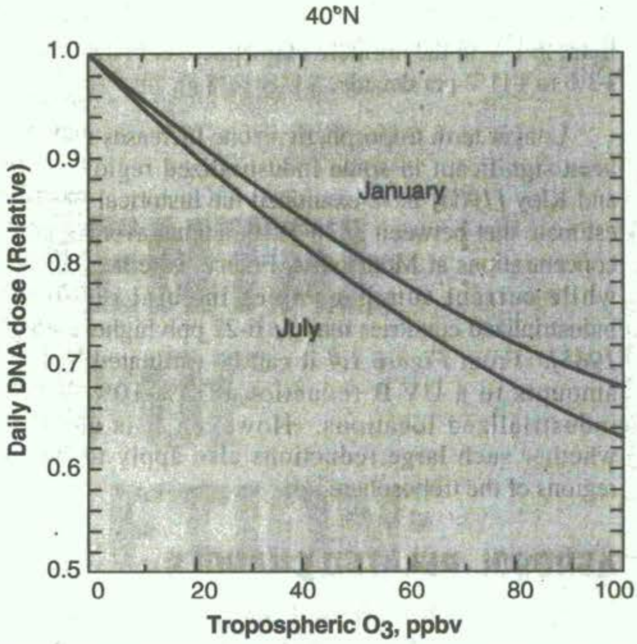

Figure 1.4 Effect of troposheric ozone on daily UV-B dose for DNA damage *[Setlow, 1974]* by tropospheric ozone, calculated assuming a constant ozone mixing ratio from sea level to 10 km.

Figure 1.4 may also be used for obtaining an approximate estimate of the effects of tropospheric ozone changes on DNA-weighted UV-B radiation. For example, Staehelin and Schmid *[1991]* reported that ozone concentrations at 800 mbar have increased from around 34 ppb in 1969 to approximately 46 ppb in 1989. From *Figure 1.4*, the corresponding change in UV-B radiation is about -4% over this 20 year period, or -2% per decade. This value is significantly smaller than the +5% to +11% per decade increase derived from the TOMS data (see *Figure 1.3*), which already contains some of the tropospheric ozone trend, albeit with reduced sensitivity. Thus we estimate that the combined trend in UV in the northern hemisphere is in the range of +3% to +11% per decade.

Longer term tropospheric ozone increases may have been significant in some industrialized regions. Volz and Kley *[1988]* have examined the historical record to estimate that between 1876-1910, annual average ozone concentrations at Montsouris, France were near 10 ppb, while current summer values in rural regions of industrialized countries may be 6-22 ppb higher *[Logan, 1985]*. From *Figure 1.4* it can be estimated that this amounts to a UV-B reduction of 3%-10% at such industrialized locations. However, it is unknown whether such large reductions also apply to remote regions of the troposphere.

AEROSOL-RELATED CHANGES

The tropospheric aerosol content of the atmosphere has been identified as a major factor in determining the amount of radiation reaching urban and suburban areas *[UNEP, 1989]*, and has been invoked qualitatively to explain negative trends in UV radiation at some urban locations *[Garadzha and Nezval, 1987; Grant, 1988]*. A recent study by Liu et al. *[1991]* suggests that aerosols may have caused substantial reductions of UV radiation on a much larger geographical scale in industrialized countries. Estimates of the mean annual average visual range, measured horizontally at 550 nm, show a decrease from about 95±45 km in pre-industrial times (background), to 15-25 km in the mid-1970s, for rural regions of the eastern United States and western Europe. Most of this aerosol consists of sulfate particles produced by atmospheric photo-oxidation of anthropogenic SO_2 emissions. SO_2 emissions in the United States have generally increased from the beginning of this century through the 1950s and 1960s. In more recent times, they have remained relatively steady or have declined in some regions, while continuing to increase in others *[NRC, 1986]*.

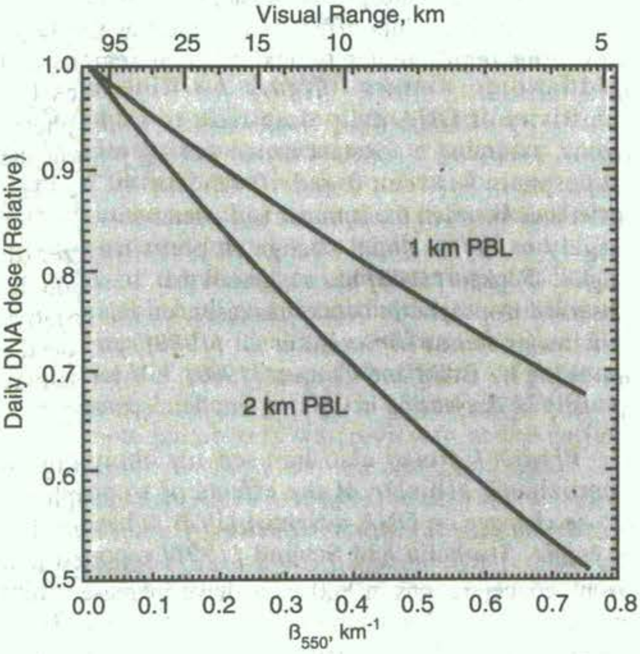

Figure 1.5 Ratio of daily DNA dose with aerosols to DNA dose in aerosol-free atmosphere (Rayleigh visual range of 386 km), for different aerosol loadings. The lower scale gives the ground-level total extinction coefficient at 550 nm, which is related to the visual range (V.R.) by the expression $\beta_{550} = 3.912/\text{V.R.}$ Results for two different planetary boundary layer heights (PBL) are shown *[Liu et al., 1991]*.

The relation between aerosol extinction, visual range, and DNA daily dose is illustrated in *Figure 1.5*, for mid-summer, 40°N conditions *[Liu et al., 1991]*. DNA dose reductions of about 6% to 18% from background radiation may have occurred due to aerosol scattering and absorption. The changes are comparable to, or larger than, the UV enhancements estimated from the TOMS ozone column measurements and the tropospheric ozone changes. This may partially explain the observed declines in UV measured with the R-B meters *[Scotto et al., 1988; Garadzha and Nezval, 1987]*.

As with tropospheric ozone, the temporal and geographical distribution of tropospheric aerosols is highly variable, and the global climatology and trend analyses are uncertain *[Kent et al., 1991]*. Future trends in atmospheric aerosol loading need to be monitored carefully. Because of concern about the environmental impacts of acidic precipitation, there may be significant reductions of sulfur emissions in some regions, particularly those from coal combustion. Some of this "pollution shield" *[Grant, 1988]* will be removed, and the effects of stratospheric ozone depletion may become more evident in large-scale regions of industrialized countries.

Stratospheric aerosols may also change the amount of UV radiation reaching the surface of the earth. Michelangeli et al. *[1991]* recently studied the radiative effects of stratospheric aerosols following the 1982 eruption of El Chichón. Using an optical depth of 0.25 (measured by DeLuisi et al. *[1983]* over Mauna Loa in the plume of this eruption), surface UV changes of +45% at 290 nm, +3% at 295 nm, -5% at 300 nm, -11% at 310 nm, -7% at 315 nm, and -6% at 320 nm were calculated. The increases at short wavelengths appear to result from photon pathlength changes in highly absorbing layers of stratospheric ozone. However, the absolute radiation reaching the surface at those wavelengths is exceedingly small. We have applied these changes to the calculation of the DNA-damage weighted dose rate under similar conditions, and find a net decrease of about -8%. This attests to the dominance of the ~310 nm peak response of the spectral dose rate. Volcanic aerosols tend to be distributed through the stratosphere and then decay with a time constant of between 0.5 and 1.5 years, so that the associated optical depths become much smaller *[Yue et al., 1991]*. However, heterogeneous chemistry on the sulfate particles may impact the stratospheric ozone, particularly in the presence of chlorine. This remains a current subject of study *[Hoffman and Solomon, 1989; Brasseur et al., 1990]*, especially in view of the 1991 eruption of Mt. Pinatubo.

CLOUD-RELATED CHANGES

The effect clouds have on surface UV radiation is clearly significant. However, because cloud cover and type are highly variable, extensive averaging is required to assess their effect on UV climatology and trends. A comprehensive assessment is largely lacking at the present time, although some progress has been made in describing both temporally and spatially averaged contributions of clouds to surface UV.

The average attenuation by a complete cloud cover may range, depending on the type of cloud and the solar zenith angle, between 56% *[Buttner, 1938]* and 90% *[Josefsson, 1986]*. Parameterizations of transmission in relation to cloud type have been proposed *[Haurwitz, 1948; Jones et al., 1981]*. Ilyas *[1987]* examined the dependence of measured UV-A radiation on visually estimated fractional cloud coverage at Penang, Malaysia and found an approximately linear reduction of UV with increasing cloud amount, down to 46% of the clear sky values during complete cloud cover. Frederick and Snell *[1990]* analyzed 1974 R-B meter readings from four United States stations, and found annual mean reductions of 27% at Mauna Loa, Hawaii, 22% at El Paso, Texas, 38% at Philadelphia, Pennsylvania, and 33% at Bismarck, North Dakota. In another study, Frederick and Lubin *[1988]* estimated the reduction of UV-B due to clouds based on measurements from the solar backscattered ultraviolet (SBUV) instrument aboard the Nimbus 7 satellite for July 1979. Their results suggest that the average UV reduction (relative to cloudless skies) was around 30% at 60°S and 60°N, approximately 10% at 20°S and 20°N, and near 20% at the Equator. All of these empirically-derived reductions may be dependent on the particular locations and seasons, and should be applied with some caution.

There are even greater uncertainties about how cloud distributions and optical properties will change in response to global change. Different global climate models show significantly different cloud-climate couplings *[Cess et al., 1989]*. Cloud optical properties may be altered through changes in condensation nuclei production by sulfates derived from natural sources, such as dimethyl sulfide from the ocean, and anthropogenic sources, such as SO_2 from coal combustion *[Charlson et al., 1987]*. A first attempt to study the effect of cloud climate change on UV radiation was reported by Madronich *[1990]*. Taking results from two climate models, and using a 2°K sea surface temperature increase as a surrogate for climate change *[Cess et al., 1989]*, UV-B radiation for July was calculated to increase by 5%-10% in the regions between 45°S and 45°N, and decrease poleward of these latitudes. More recently, Bachelet et al. *[1991]* examined the predictions of three different climate models for a doubled CO_2 scenario, and used the Ilyas *[1987]* parameterization to estimate the effect of clouds on UV-B in rice-growing regions of South East Asia. Again, both the sign and the magnitude of the cloud changes (and therefore the UV-B changes) were model-dependent. Because of the high uncertainties in predicting future cloud changes, these results should not be regarded as predictive, but rather as indicative of the fact that substantial changes in cloud cover may affect UV radiation to an extent comparable to moderate changes in stratospheric ozone, tropospheric ozone, and aerosol loadings. Clearly more work is needed to establish the UV consequences of the current cloud climatology and trends.

RADIATION AMPLIFICATION FACTORS

The results presented so far have been expressed in terms of the generalized DNA damage spectrum of Setlow *[1974]*. Various biological and chemical processes have different responses to the ultraviolet spectrum (action spectra), and therefore to ozone depletion. To avoid showing analogs of *Figures 1.1* through *1.5* for each of the many processes of interests, we present in *Table 1.1* a comparison of the Radiation Amplification Factors (RAFs) for some of these processes. The RAFs are defined as the change (fractional differential) in the effective daily dose relative to the change (fractional, negative differential) in the total ozone column. For example, a 1% ozone reduction will cause an increase in fibroblast killing (second entry of *Table 1.1*) of 0.3% in January and 0.6% in July.

It should be noted that RAFs provide an indication of how the composite radiation at different wavelengths changes as filtering by ozone is altered. Thus, they are useful for assessing relative changes in potentially effective UV-B radiation. They do not, however, incorporate the absolute sensitivity of biological processes, which also depend on other factors including repair mechanisms and other environmental stresses.

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

Effect	RAF		Reference
	January	July	
DNA Related			
Mutagenicity and Fibroblast killing	[1.7] 2.2	[2.7] 2.0	Zölzer and Kiefer, 1984; Peak et 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.
Generalized DNA damage	1.9	1.9	Setlow, 1974
HIV-1 activation	[0.1] 4.4	[0.1] 3.3	Stein et al., 1989.
Plant Effects			
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.
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^+-stimualated ATPase inactiv.	[0.3] 2.1	[0.3] 1.6	Imbrie and Murphy, 1982.
Skin			
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.
Melanogensis	1.7	1.6	Parrish et al., 1982.
Erythema	1.7	1.7	Parrish et al., 1982.
Erythema reference	1.1	1.1	McKinlay and Diffey, 1987.
Skin cancer in SKH-1 hairless mice (Utrecht)	1.4	1.3	de Gruijl, 1991.
Eyes			
Damage to cornea	1.2	1.1	Pitts et al., 1977.
Damage to lens (cataract)	0.8	0.7	Pitts et al., 1977.
Movement			
Inhibition of motility in *Euglena gracilis*	1.9	1.5	Häder and Worrest, 1991.
Materials damage			
Yellowness induction in poly vinyl chloride	0.2	0.2	Andrady et al., 1989.
Yellowness induction in polycarbonate	0.4	0.4	Andrady et al., 1991.
Other			
Immune suppression	[0.4] 1.0	[0.4] 0.8	DeFabo and Noonan, 1983.
Tropospheric rate coefficient for $O_3 + h\nu \rightarrow O_2 + O(^1D)$	1.8	1.6	Madronich (in press), 1991.
Robertson-Berger meter	0.8	0.7	Urbach et al., 1974.

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.

For the RAF computations, the spectral irradiance at the surface was calculated for 30°N conditions, using the 11.6 year average of the 1978-1990 TOMS ozone data, cloud-free and aerosol-free skies, 5% surface albedo, sea level, and a delta-Eddington radiative transfer scheme at 1 nm intervals over 280-400 nm. The daily dose was computed by the convolution of the spectral irradiance with the different process-specific action spectra, followed by an integration at 15 minute increments over the day. To obtain the RAFs, the calculation was repeated with 1% increments to ozone concentrations, applied equally at all altitudes. Additional details of the calculation are given in WMO *[1989]* where it was also shown that the RAFs are insensitive to many environmental conditions such as clouds, surface albedo, and aerosols, as long as these are maintained constant during the change in the total ozone column. Slightly different RAF values would be obtained if the total ozone column were increased by additions of stratospheric ozone or, alternatively, only the tropospheric ozone *[Brühl and Crutzen, 1989]*. Also, because of the non-linear nature of atmospheric transmission, the RAFs may be different for much larger changes in the ozone column.

Table 1.1 shows a large range of RAF values, from about 0.1 to about 4. While the RAFs for some processes appear reasonably established, there are significant uncertainties for others. An outstanding problem is the determination of action spectra in the long wavelength region (UV-A), since even relatively small "tails" can reduce the RAFs significantly. In compiling *Table 1.1*, exponential tail extrapolations were carried out in most cases, and those processes for which such extrapolation produced significant RAF decreases are shown in brackets. Also, in some cases, conflicting spectral information exists. For example, experiments on the duckweed *Wolfiella hyalina [Wan and Björn, 1991]* lend support to the conclusion that the generalized plant action spectrum of Caldwell et al. *[1986]* is a reasonable approximation for the spectral dependence of the ultraviolet inhibition of biomass production by seed plants. On the other hand, limited data by Mitchell *[1990]*, Holm-Hansen *[1990]*, and Smith and Baker *[1982]* suggest that the action spectrum for UV inhibition of growth or photosynthetic carbon assimilation by phytoplankton is less steep, approaching the one determined by several groups for photosynthetic electron transport. Clearly, further work is needed to obtain accurate and representative action spectra.

It is important to note that RAF for R-B meters is substantially smaller than the RAFs for most of the biological and chemical processes of interest. This complicates the interpretation of some of the trends observed with R-B meters (see above). For example, if the increasing trend of +0.7% per year observed by Blumthaler and Ambach *[1990]* is due to depletion of overhead ozone, the corresponding trends in biological effects may be amplified by the ratio of RAF values, e.g., +1.1% per year for erythema *[McKinlay and Diffey, 1987]*, +1.9% per year for DNA damage *[Setlow, 1974]*, and +1.6% per year for melanogenesis *[Parrish et al., 1982]*. If, however, the trends in R-B meter observations result from changes in tropospheric aerosols and cloud cover, which are only weakly dependent on wavelength, no significant RAF amplification is expected. This may be the case for the negative trends reported by Scotto et al. *[1988]* and Garadzha and Nezval *[1987]*.

CONCLUSION

There is now compelling evidence that significant changes in the global-scale ozone distributions have been occurring over the past ten years. The most recent total ozone measurements (TOMS version 6) imply increases of annual DNA-damage weighted UV-B over large geographical areas of the earth. In the northern hemisphere the trends range from +5% per decade at 30°N to about +11% per decade in the polar region, while in the southern hemisphere the trends are +5% per decade at 30°S, +10% per decade at 55°S, and +40% per decade at 85°S. In the equatorial region (30°S to 30°N), trends are not statistically significant.

All other factors being constant, there is no scientific doubt that the calculated UV increases would be observed at the surface. However, other factors also affect the transmission through the atmosphere. In polluted urban and regional areas of industrialized countries, tropospheric ozone and sulfate aerosols have been generally increasing, although their variability is large and trends are difficult to estimate. Analysis of recent studies indicates that at most about 2% per decade decrease in UV-B can be expected from tropospheric ozone trends. However, large cumulative increases in tropospheric ozone and sulfate aerosols may have occurred over the last 100 years, and may have reduced the UV-B between 3% and 10% for ozone, and between 6% and 18% for sulfate aerosols in some locations. Tropospheric ozone and sulfate aerosols are believed to result primarily from human activities, and tend to be largest near industrialized and densely populated areas. Efforts to improve the air quality in these areas are likely to reduce their concentrations, and may bring to light the increases in UV-B associated with the depletion of stratospheric ozone. Furthermore, there is some concern about the fact that most of the UV monitoring is being carried out in industrialized regions of the northern hemisphere, where current UV reductions may be largest. In less industrialized regions, the atmosphere may be more transparent, but monitoring of the UV radiation is inadequate.

Tropospheric pollutants are likely to be much less important on the average global scale, and particularly in regions far from direct emissions sources. In these regions, it is expected that the depletion of stratospheric ozone will have its full impact on the UV-B radiation reaching the ground or the ocean surface. Due to the unfortunate absence of a suitable global UV-B monitoring network, no direct observational evidence is available, except in Antarctica, Australia, and New Zealand where the large springtime ozone hole and its break-up have stimulated great scientific interest. Here, measured and calculated UV-B increases are in reasonable agreement.

Future changes in cloud cover might affect the average intensity of UV-B radiation reaching the surface, by amounts comparable to that from moderate ozone and aerosol changes. At present, there are no reliable estimates of the sign or magnitude of current cloud cover trends, nor does it appear possible to make reliable predictions of the sign or magnitude of cloud cover changes which may result from anthropogenically driven climate change.

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1991 REPORT SUMMARY

In the past two years, there have been relatively few additions to the scientific literature regarding UV radiation and human health. However, for the most part, the new material confirms the information presented in the 1989 UNEP Report. The possible forms of ocular damage associated with UV radiation have been increased to include age-related near-sightedness, damage to the anterior lens capsule, and nuclear cataract. In the 1989 Report, nuclear cataract was specifically excluded. New data suggest that it should now be included as an effect of UV exposure.

New studies on the immunologic impacts of UV radiation continue to support the theory that UV radiation may exacerbate infectious diseases. Such concerns are not limited to fair-skinned populations but are also observed in deeply pigmented individuals, where pigment may be constitutive or acquired.

Exposure to sunlight has now been associated with another cancer: that of the salivary gland. These findings suggest the possibility of a systemic effect of UV-B in humans, since the salivary gland is rarely, if ever, exposed.

Estimates of increases in skin cancer incidence have been lowered slightly, due to a new action spectrum and associated changes in the biological amplification factor (BAF) and radiation amplification factor (RAF). These new values are probably not significantly different from the original estimates. However, on the basis of this information, it is estimated that a sustained 10% reduction in ozone would result in a 26% increase in non-melanoma skin cancer (NMSC) world-wide. Using very conservative assumptions (detailed in the text), it can be estimated that such an increase would be equivalent to more than 300,000 additional cases of NMSC and 4,500 cases of melanoma. This may be an extremely conservative estimate, possibly off by a factor of two or more.

1989 REPORT SUMMARY

The increases in ultraviolet-B (UV-B) radiation that will result from depletion of stratospheric ozone are likely to result in a variety of impacts on human health. These range from an increased incidence of cataracts and skin cancer to possible increases in the incidence or severity of certain infectious diseases.

Exposure to ultraviolet radiation has been associated with damage to the cornea, lens, and retina of the eye. The principal corneal damage linked to UV exposures is photokeratitis, which appears to be related to acute UV-B exposures. The principal lenticular damage is cataract. The relationship between UV-B exposure and two forms of cataract — corticular and posterior subcapsular — appears to be related to cumulative exposure. Both life time cumulative exposure and annual average exposure are directly related to risk. It has been estimated that a 1% decrease in stratospheric ozone will be accompanied by a 0.6% to 0.8% increase in cataract. Retinal damage is rare but can occur particularly in those individuals whose lens have been removed in cataract operations.

Ultraviolet radiation is known to affect the immunological defenses of the skin, the first barrier of the body to foreign agents. In tumor systems and with defined antigens, it is clear that UV radiation compromises the ability of the host to immunologically respond either locally (after low doses) or systemically (after higher doses). Preliminary experiments of infectious diseases using animal models have indicated that UV-B can also adversely affect the ability of animals to respond to or contain various infectious agents. Although there are as yet no epidemiologic data to suggest that such effects occur in human populations, nevertheless, animal data suggest that an increase in the severity

of certain infections may occur as UV-B fluxes increase due to ozone depletion. In areas of the world where such infections already pose a significant challenge to the public health care delivery systems, the added insult may be significant.

The relationship between UV-B exposure and two forms of non-melanoma skin cancer, basal cell and squamous cell carcinoma, appears to be one of increased risk with increased total lifetime doses to the target cell. Phenotypic characteristics such as skin color can modify the amount of ambient UV that gets transmitted to the target cell, so that fair-skinned individuals are more susceptible than dark-skinned individuals receiving the same amount of ambient exposure. The relationship between UV-B exposure and melanoma skin cancer is probably more complex; it is certainly less well understood. Some data suggest that intermittent severe exposure, i.e., sunburns, are important. Other studies suggest that early exposures (before the ages of 10-14) are of more concern than those acquired later in life. Using dose-response relationships derived from animal experiments and human epidemiologic studies, it is estimated that a 1% decrease in stratospheric ozone will result in a 3% increase in non-melanoma skin cancer, and a lower but still significant increase in melanoma.

NEW INFORMATION AND RECENT DEVELOPMENTS

The chapter on human health in the 1989 Report is still an adequate review of existing knowledge. However, there are a few new developments that should be mentioned.

OCULAR DAMAGE

Recent literature indicates the possibility of two additional cases where the ocular system was affected by exposure to sunlight (and presumably UV-B), presbyopia, and deformations of the anterior lens capsule. Presbyopia is the loss of the ability of the eye to accommodate changes in focal length. This is thought to result from the aging of the crystalline lens, and it commonly requires the use of reading glasses for viewing near-by objects. In a recent study by Stevens and Bergmanson *[1989]*, an association was found between the early onset of presbyopia and living in areas of high sunlight (and high temperatures). A study of vision problems in a human population in Somalia found that deformations of the anterior lens capsule in the central pupillary area show a strong association with climactic keratopathy, and by inference, reflected UV-B. The deformations found in this case interfere severely with vision *[Johnson et al., 1989]*.

Several recent case-control studies *[Collman, et al., 1988; Mohan et al., 1989]* have, for the most part, confirmed the relationship, discussed in the 1989 Report, between sunlight exposure and cortical and posterior subcapsular cataract. In contrast to the lack of association between sunlight exposure and nuclear cataract stated in the previous report *[Taylor et al., 1988]*, Mohan et al. *[1989]* found an association between sunlight and all forms of cataract, including nuclear and mixed.

It was also noted in the 1989 Report that a mechanism for the relationship of cataract to solar exposure was not well understood. In recent literature there are indications that the development of cataract may be related to the loss of the orderly arrangement of densely packed lens crystallin which is required to maintain lens transparency *[Andley and Clark, 1989; Taylor, 1989]*. Another study indicated that UV irradiation increases fragmentation in the ß-crystallin *[Andley and Clark, 1989]*, which in turn results in an increase of insoluble protein within lens fibers contributing to the formation of opacities *[Stevens and Bergmanson, 1989]*. In addition, the relationship between ocular melanoma and sunlight exposure has been confirmed by Seddon et al. *[1990]*.

INFLUENCE OF UV-B ON INFECTIOUS DISEASES

As indicated in the 1989 Report, one concern regarding increases in human exposure to UV-B radiation is the possibility of an increase in infectious diseases. With the exception of data showing an exacerbation of herpes infections *[Spruance, 1985; Perna et al., 1987]*, there was little or no information on this issue from human studies. Also, there has been little additional information that could assist in making sound predictions of the consequences of ozone depletion for infectious diseases. Several new reports have appeared which enlarge the list of viruses that may be activated by UV irradiation *in vitro*. In addition to the herpes simplex virus, these include HIV-1, the human immunodeficiency virus *[Zmudzka and Beer, 1990]*, and a variety of papilloma viruses, the human forms of which have been associated with a variety of hyperplastic, dysplastic, and malignant lesions of the squamous epithelium *[Schmitt et al., 1989; Tilbrook et al., 1989; Jensen et al., 1991]*. It should be noted that in the case of both herpes infections and HIV, the UV-induced activation has been demonstrated both *in vitro* and *in vivo*. However, the *in vivo* activation of HIV was demonstrated in a transgenic mouse system bearing only a portion of the HIV-1 genome, the long terminal repeat. Nevertheless, it is becoming clear that activation of HIV-1 by UV radiation is a cause for concern. It should also be stressed that the activation of viruses by UV is unlikely to result in an increased rate of infection. It would result in the increased severity of the disease, or a more rapid course of infection.

There is a growing body of literature indicating that the impacts of UV-B on the immune system first demonstrated in mice may also occur in humans. This information is presented in detail below, and contributes to the theory that increases in ambient UV associated with stratospheric ozone depletion could exacerbate the course of infectious diseases.

UV-INDUCED IMMUNOSUPPRESSION IN HUMANS

In the 1989 Report, in addition to the effect of UV-B on herpes infections in humans, the impacts of UV-B on the human immune system were demonstrated by Baadsgaard et al. *[1987]* and Scheibner et al. *[1987]* as having an effect on antigen presenting cells. Recent work by Cooper et al. *[1991]* confirms these impacts and shows that UV-B can suppress sensitization to certain substances in humans. Unlike early studies which showed impacts at very low doses, immunosuppression was observed by Cooper et al. *[1991]* with UV doses that induced a sunburn. Moreover, these authors found that individuals who received a sunburning dose of UV over most of the body could still have mounted an immunological reaction if they were sensitized in an unirradiated area of skin (the immunosuppressive effect could only be demonstrated locally rather than systemically). The suppression of the sensitization correlated well with skin's local depletion of Langerhans (antigen presenting) cells at the UV irradiated site.

Another study, directed at investigating immunosuppression associated with non-melanoma skin cancer (NMSC), has documented immunosuppression in both cancer patients and healthy individuals following deliberate exposure to UV-B. Yoshikawa et al. *[1990]* reported a difference in susceptibility to UV-B-induced immunosuppression between a population of healthy volunteers, and a population of NMSC patients. A small area of skin on the buttock of each individual was repeatedly exposed to UV radiation, leading to a pronounced sunburn. After the last exposure, a substance (DNCB) was applied to the sunburned area. Without the UV-B exposure, this procedure would normally sensitize the individual to the substance. A second contact with DNCB, the so-called challenge, at a different area of skin, would lead to a severe, inflammatory reaction at the second site of contact. This reaction is immunologically mediated. The results of this study showed that only 1 out of the 12 skin cancer patients reacted to the challenge, whereas there was a reaction from 22 of the 34 healthy volunteers. Thus, the development of non-melanoma skin cancer is associated with immunosuppression in these individuals. It remains to be seen whether the difference between patients and controls observed by these authors is due to a predisposing flaw in the immune system, or to the development of cancer. A subsequent study by this group *[Vermeer et al., 1991]* also demonstrated that the proportion of normal individuals in the United States population sensitive to the immunosuppressive effects of UV radiation is independent of skin pigmentation. This confirms the earlier finding of Scheibner et al. *[1987]* showing the effects on Langerhans cells in individuals of both Celtic and Aboriginal heritage. It clearly indicates that the population at risk for UV-induced immunosuppression is not limited to light-skinned individuals, but includes deeply pigmented individuals as well.

CANCER

In the 1989 Report, the only data presented regarding cancer dealt with tumors of the eye and skin, focusing closely on melanoma and non-melanoma skin cancer (basal cell carcinoma-BCC and squamous cell carcinoma-SCC) in humans. However, two recent reports indicate that other cancers may be associated with exposure to UV-B. Reports by Spitz et al. *[1988, 1990]* suggest that in addition to lip cancer (normally included in the category of non-melanoma skin cancer), salivary gland cancers may be related to UV radiation exposure. The evidence is somewhat circumstantial and is derived from co-associations between these tumors and melanomas observed in an epidemiologic study designed to examine the relationship between melanoma, lip cancer, and salivary cancer. The study found a significantly increased risk for subsequent lip cancer among men with an initial salivary gland cancer (RR = 8.7), a significantly increased risk for melanoma among women with an initial salivary gland cancer (RR = 7.1), and a significant association between an initial lip cancer and risk of subsequent salivary gland cancer among men (RR = 12.7).

Non-Melanoma Skin Cancer

Although we are able to quantitatively estimate the potential long-term consequences from increased UV-B for skin cancer and cataract, our best estimates are for NMSC, particularly SCC. Because both human and animal studies are in agreement regarding a dose-response relationship, it is possible to develop an action spectrum for carcinogenesis in an animal model.

Carcinogenic UV Doses

For a proper assessment of the carcinogenic risk posed by an increased UV load, biologically meaningful UV radiation measurements are needed. It has long been known that UV-B radiation (wavelengths between 280 nm and 315 nm) is the most carcinogenic part of the solar UV spectrum reaching the earth's surface *[Roffo, 1934]*. This was established in animal experiments, and it is not possible to extract such information for humans from epidemiological data. Therefore, further animal data are needed for a proper definition of a carcinogenic UV dose.

A carcinogenic UV dose has been assumed to be approximately equal to effective UV doses for other biologically detrimental effects, such as sunburn or mutations in cells. This was based on a crude similarity in wavelength dependence of the effects, or an assumed mechanism of UV carcinogenesis (mutations leading to malignant cell proliferation). As was pointed out in the 1989 Report, more experimental information has become available on UV carcinogenesis in the Skh:HR1 albino hairless mouse. The available data contain the required spectral information on UV carcinogenesis, albeit in a very implicit way. None of the currently used definitions of a carcinogenic UV dose yield a statistically adequate description of these data *[de Gruijl and van der Leun, 1991]*. An updated and adequate definition has been produced by using a mathematical technique to derive an action spectrum that can be used as a set of weights to reflect the carcinogenic efficiencies at the UV wavelengths. This newly derived action spectrum, UTR5, is depicted in *Figure 2.1*. The other curves depict older approximations of the carcinogenic action spectrum.

UTR5 is a genuine carcinogenic action spectrum, as it has been derived from experimental data on UV carcinogenesis. Its applicability to humans may be debatable, but at the moment it probably gives the best estimate of a carcinogenic UV dose.

Increases in Skin Cancer

The new carcinogenic action spectrum slightly alters the risk assessment of ozone depletion. With a new radiation amplification factor (RAF) of 1.4, a 1% decrease in ozone will result in an increase of the annual carcinogenic dose by about 1.4% (for 0° to 60° latitude).

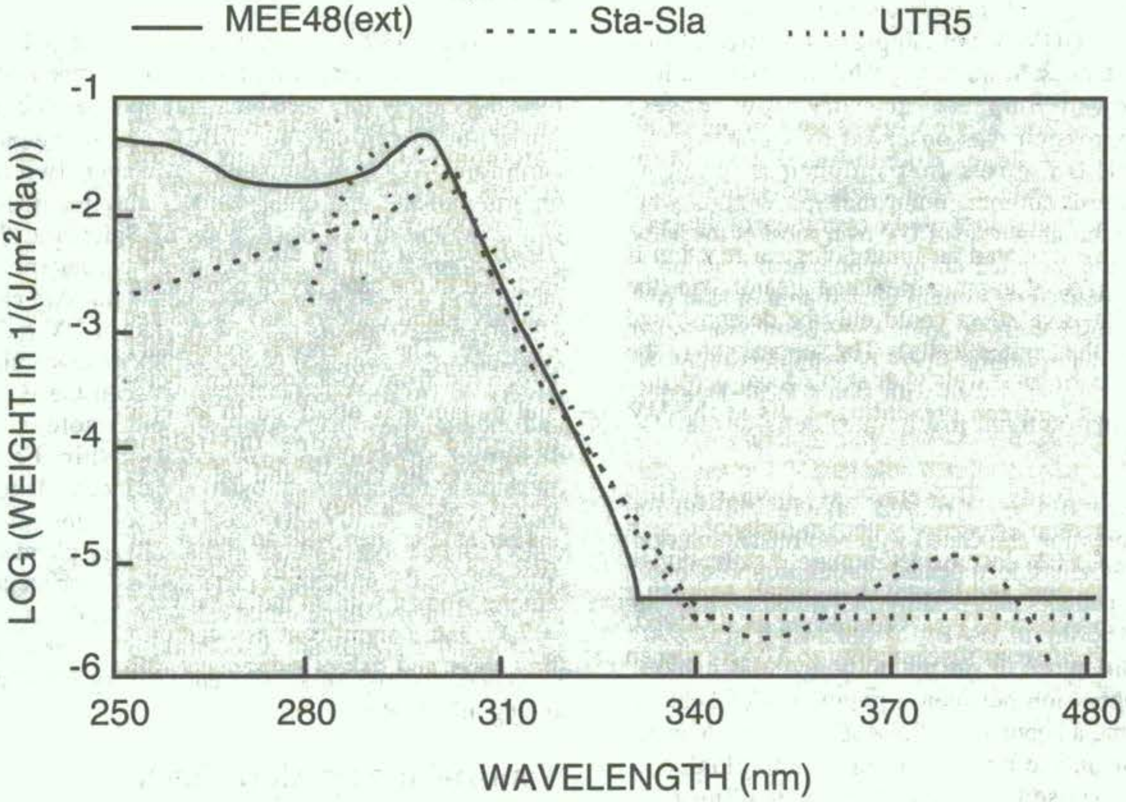

Figure 2.1 Wavelength Dependency of Carcinogen in Hairless Mice (the Weights are the inverted daily doses reguired to induce tumors in 50% of the mice in 300 days).

With the earlier action spectra, the RAF was approximately 1.6%.

With the new action spectrum, the new biological amplification factor (BAF) is 1.4 for BCC and 2.5 for SCC. The calculated incidences of BCC and SCC will eventually increase by 1.4 ± 0.4% and 2.5 ± 0.7%, respectively, for every 1% increase in the annual carcinogenic dose *[de Gruijl and van der Leun, 1991]*. The earlier estimates were 1.7% and 2.9%, respectively, for a 1% increase in dosage. These numbers are derived from epidemiologic data of the fair-skinned population in the United States *[Scotto et al., 1981]*.

Taking the new RAF and BAF values, a 1% depletion of ozone will eventually increase the BCC incidence by 2.0 ± 0.5%, and the SCC incidence by 3.5 ± 1.0%. This is somewhat lower than the 2.7% and 4.6% presented earlier. These values are in relatively close agreement with the work of Moan *[1991]* who estimated a 1.6% to 2.3% increase in SCC and BCC in the Norwegian population for a 1% depletion of ozone.

Taking BCC and SCC together in a ratio of 4:1, a 1% ozone depletion will result in a 2.3 ± 0.4% increase in the incidence of skin cancer, excluding melanomas (these cancers are usually referred to as non-melanoma skin cancers). With 500,000 new cases of a year in the United States, a 2.3% increase amounts to 11,500 additional cases per year.

A precise estimate of the increase in NMSC cases or deaths world-wide would be difficult to develop. A very conservative estimate can be made using the following assumptions: 1) ozone depletion stays constant at 10% for two to four decades; 2) the population sensitive to UV radiation stays constant at 500 million (about 10% of the world population today); and 3) the incidence of NMSC is 232/100,000 (i.e., that observed in the United States in 1977) *[Scotto et al., 1981]*, and melanoma skin cancer (9/100,000) observed in the United States, is equivalent to that of the sensitive population worldwide *[Scotto et al., 1991]*. On the basis of these assumptions, it is estimated that after three to four decades, a 10% decrease in ozone would be expected to result in 300,000 additional non-melanoma and 4,500 melanoma skin cancers worldwide. It must be emphasized that this is a very conservative estimate, particularly for non-melanoma skin cancer for which there is little current information. There is new information from the northwestern United States indicating an incidence rate of squamous cell carcinoma (SCC) as high as 106/100,000 in 1986. If the 1:4 SCC to basal cell carcinoma (BCC) ratio observed in earlier studies is maintained, the current U.S. incidence rate could be 400/100,000 rather than the 200/100,000 used in the calculation above. It is likely that the other assumptions are equally conservative.

There are several caveats which must be made with regard to estimates such as those provided above. First, the estimated increases pertain to stationary situations (the new levels of incidence will eventually be reached after the change in ozone, if everything else remains the same). Second, the above estimates are probably most appropriate for SCC. While a similar approach can be used for BCC, these tumors are not normally induced in hairless mice by UV. Third, the slope of the dose-response relationship derived from human epidemiologic data differs for SCC and BCC. Last, a recent study in Maryland watermen found that SCC but not BCC showed a strong relationship to cumulative sun exposure. One possible explanation for this observation is that the dose-response relationship for BCC in humans can become saturated. There is either a portion of the population that is not sensitive, or there is a dose above which additional cases are induced in a non-linear fashion *[Strickland et al., 1990; Vitasa et al., 1990]*. No similar observation has been made in Australian populations, where one would expect similarly high exposures to occur in a much larger population. Conceivably, the observation of such saturations could be specific to the genetic make-up of the particular population under study. Were the dose-response relationship for BCC to demonstrate such a saturation, the increase in risk due to ozone depletion is likely to be different from those given above. Similar caveats need to be noted also for melanoma as well as the additional caveat that it differs with regard to the human dose measures.

Improved data are leading the way to increase the accuracy of predictions. In this process, the sensitivities of the carcinogenic dose and non-melanoma skin cancer incidence to changes in ozone have become smaller than initially estimated. However, the updated predictions confirm the earlier recognition that an increase in non-melanoma skin cancer will be greater than a comparable decrease of ozone in the atmosphere.

Melanoma Skin Cancer

Although there has been little progress in understanding the etiology of melanomas in humans since the 1989 Report, there are a few points worth mentioning in regard to the involvement of UV radiation.

Animal Experiments

Dr. Kripke and her co-workers at the M.D. Anderson Cancer Center in Houston, Texas, have made, and continue to make, extensive studies of the possible role of UV radiation in the formation of melanomas in mice *[Donawho and Kripke, 1991]*. Their experiments are based on earlier ones by Berkelhammer et al. *[1982]*, who induced melanomas in mice with chemicals.

Romerdahl et al. *[1989]* found that if UV radiation was substituted for one of the chemicals in the original experiment, the melanomas still occurred, albeit later and in much lower numbers. However, when UV irradiation was added to the chemical exposure, the melanomas occurred sooner. It was demonstrated that the acceleration of the appearance of melanomas by UV irradiation was due to a local effect at the site where the melanoma developed *[Romerdahl et al., 1989]*, possibly being an immunologically mediated effect.

From these experiments, it appears that UV radiation can play various roles in the etiology of melanomas. This could explain the seemingly ambiguous information from the epidemiology on UV radiation as a risk factor for melanomas *[de Gruijl, 1989]*. It also indicates that UV radiation can be an important co-factor in the genesis of melanomas. The nature of this effect and its possible relevance for melanomas in humans need to be studied further.

Findings in Humans

Scotto et al. *[1991]* have recently analyzed trends in skin melanoma death rates by cohort for fair skinned males and females in the United States between 1950 and 1984. These authors observed upward trends for older men and women (over 40) and downward trends for the younger cohorts. Assuming that lifestyles remain the same and ultraviolet radiation levels remain constant, these authors project that the 2% to 3% increase in death rates per annum observed since 1950 will discontinue. The curve will eventually bend downward by the second decade of the 21st century. This information is critical in assessing the risks of stratospheric ozone depletion, and would be needed to incorporate the cohort data and age-specific trend analyses into the baseline data. Similar information is also critical to estimate the potential increases in non-melanoma skin cancer. Unfortunately, most countries are not collecting sufficient data on NMSC to be able to conduct such trend and cohort analysis.

Other information contributes to a better understanding of the possible mechanism involved in the induction of melanoma by UV radiation. A study of possible mutations in ras-oncogenies in human melanomas showed that melanomas occurring in sun-exposed skin areas exhibit a high frequency (7 out of 10) of point mutations in the N-ras gene *[Van't Veer et al., 1989]*. These mutations occurred at a location where two neighboring thymines are situated on a complementary strand of the DNA. Neighboring thymine are potential sites of UV damage (the thymine can be "welded" together to form a dimer). Thus, UV radiation is implicated in this particular mutation of the N-ras oncogene, and may be implicated in the etiology of melanomas (of the non-lentigo malignant types) in areas of skin regularly exposed to sunlight.

LINKAGES

Animal Health

The consequences of increased UV-B irradiation on the health of animals was only briefly touched upon in the 1989 Report. Data obtained from experimental animals were used to give an insight into the impacts of UV radiation on human health. Most of the exposures used in experimental animal studies differ greatly from what would occur in the natural environment (the use of hairless or shaved animals, and very high doses of UV-B). Both wild and domestic animals have dense fur coats protecting their skins against UV radiation. Yet, there are indications that sunlight causes cancers in domestic animals that are similar to those observed in humans. These are limited to eye tissue or sparsely haired, light-colored skinned animals. Skin tumors have been almost exclusively SCC and have been observed in cows, goats, sheep *[Emmett, 1973]*, cats *[Dorn et al., 1971]* and dogs *[Madewell et al., 1981]*. Eye tumors are also SCC, and they have been observed in horses, dogs, cats, sheep, swine, and particularly in cattle *[Hargis, 1981]*. The 1989 Report discussed in some detail skin tumors induced in experimental animals with UV radiation. However, eye tumors have also been induced in guinea pigs and hamsters *[Freeman and Knox, 1964]*, and rats and mice *[Roffo, 1934, 1939]*. While pigmentation appears to protect cattle (white-faced Herefords were more susceptible than black Angus) *[Anderson, 1963]*, in experiments with hamsters and rats, the eyes in pigmented animals were more susceptible than the eyes of albinos *[Freeman and Knox, 1964]*.

Toxicity of CFC Substitutes

The Montreal Protocol requires the phase out of fully halogenated chlorofluorocarbons. Most of these will be replaced with new chemicals, which have not yet been released into the environment. A secondary effect of the human response to stratospheric ozone depletion will be the exposure of human and environmental populations to a new class of chemicals and their degradation products. Clearly, the toxicity of these chemicals to the ozone layer, and the human and environmental populations, needs to be characterized. The U.S. Environmental Protection Agency has recently reviewed the toxicity information available for two classes of these replacement chemicals: aqueous and terpene cleaning chemicals, and hydrofluorcarbon (HFC) and hydrochlorofluorocarbons (HCFC) *[U.S. EPA, 1990a, 1990b]*. *Table 2.1* lists the aqueous and terpene cleaners which were reviewed.

The preliminary information presented in the report on cleaners *[U.S. EPA, 1990a]* indicated that in general "...the aqueous and terpene cleaners can be used in a manner that is safe to workers, the general population and the environment given appropriate technological changes and exposure control practices." *Table 2.2* lists the hydrofluorocarbons and hydrochlorofluorocarbons for which the review was performed.

The report on HFCs and HCFCs also concluded that these chemicals could be used in a manner consistent with safety for humans and environmental populations *[U.S. EPA 1990b]*. However, both reports cautioned that these were interim assessments based on limited data and a variety of assumptions. As more data are accumulated, it is conceivable that these conclusions may change. For instance, preliminary information on HCFC-123 suggests that it has induced an increase in non-malignant tumors. This has resulted in manufacturers lowering their allowable exposure limits from 100 ppm to 10 ppm while maintaining that the compound can be used safely, given the above constraints *[Weise, 1991]*.

Table 2.1 Potential CFC Substitutes Cleaners

Name	CAS Number
Aqueous Cleaners	
Ammonium hydroxide	1336-21-6
Potassium hydroxide	1310-58-3
Sodium hydroxide	1310-73-2
Diethylene glycol monobutyl ether	112-34-5
Dodecanedioic acid	693-23-2
Ethylenediaminetetraacetic acid	60-00-4
Tetrasodium salt	64-02-8
Monoethanolamine	141-43-5
Diethanolamine	111-42-2
Triethanolamine	102-71-6
Borax	1303-96-4
Sodium carbonate	497-19-8
Sodium gluconate	527-07-1
Sodium silicate	1344-09-8
Sodium metasilicate	6834-92-0
Sodium tripolyphosphate	7758-29-4
Trisodium phosphate	7601-54-9
Tetrasodium pyrophosphate	7722-88-5
Sodium xylene sulfonate	7320-34-5
Sodium xylene sulfonate	1300-72-7
Terpene Cleaners	
d-limonene	5989-27-5
anethole	480-23-8
alpha-pinene	7785-70-8
beta-pinene	18172-67-3
alpha-terpinene	99-86-5
beta-terpinene	99-85-4
terpinoline	586-62-9
dipentene	138-86-3

Table 2.2 Potential CFC Substitutes
HCFCs & HFCs

Name	Commerical Name	CAS Number
HFC		
Pentafluoroethane	HFC-125	354-33-6
Tetrafluoroethane	HFC-134a	811-97-2
Difluoroethane	HFC-152a	75-37-6
HCFC		
Chlorodifluoromethane	HCFC-22	75-45-6
Dichloro-trifluoroethane	HCFC-123	306-83-2
Chloro-tetrafluoroethane	HCFC-124	2837-89-0
Dichloro-fluoroethane	HCFC-141b	1717-00-6
Chloro-difluoroethane	HCFC-142c	75-68-3

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CHAPTER 3

TERRESTRIAL PLANTS

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1991 REPORT SUMMARY

The potential importance of current solar UV-B levels, even in the absence of further ozone reduction, has been demonstrated experimentally by reducing present day levels of solar UV-B radiation reaching the plants under investigation. It has been shown that plant growth, and in some cases photosynthesis, can be altered in seedlings. Whether this holds true for mature plants is not yet known, but these results indicate the potential importance of solar UV-B radiation even without ozone reduction.

Continued research on plant responses to UV-B radiation underscores the concern for agriculture, forestry, and natural ecosystems as the ozone layer is depleted. Yet, quantitative predictions are complicated by several factors, such as carbon dioxide concentration and temperature. These are relevant to global climatic change, and have been shown to influence the manner in which plants respond to increased UV-B radiation. For example, the stimulating effect of carbon dioxide enhancement may be altered by UV-B and may involve more than one photosynthetic process. Therefore, carbon dioxide may not fully compensate for negative UV-B effects. Temperature has also been shown to influence UV-B effects on growth and physiological processes in some of the species investigated. Other abiotic factors, such as heavy metals, may also modify UV-B influences on plants.

Recent measurements of the penetration of UV-B radiation into plant tissues have confirmed that internal changes in anatomical features and pigmentation vary among plant species. These changes result in alterations in plant response to UV-B radiation. Increased UV-B has also been shown to alter the biotic relationships of higher plants as demonstrated by the changes in plant disease susceptibility and the balance of competition between plant species.

More has been learned about the mechanisms of UV-B action. Both long-term UV-B irradiation of whole plants and short-term irradiation of chloroplasts may induce the synthesis of certain polypeptides in photosynthetic membranes that could play a role in mitigating UV-B damage. The influence of UV-B on growth appears to be mediated by phytohormones, either through photodestruction or enzymatic reactions. Whether other morphological responses to UV-B are also mediated by phytohormones remains to be demonstrated. Repair of DNA damage by photoreactivation has been clearly demonstrated in several plant systems. However, the limits of this photoreactivation capacity have not yet been determined.

Field and greenhouse studies have shown that growth and photosynthesis are negatively affected by enhanced UV-B radiation in some tree species such as the loblolly pine. Although little data are available for tropical species, preliminary greenhouse studies indicate that growth, photosynthesis, and yield decreased in some rice cultivars. Care should be taken in assessing and generalizing the results from particular plant species and cultivars to other species, since there appears to be a great range of UV-B responses among plants.

1989 REPORT SUMMARY

Much of the research on the potential impacts of an increase in solar UV-B radiation has centered on the effects on plant growth and physiology under artificial UV-B irradiation supplied to plants in growth chambers or greenhouses. However, these artificial sources do not precisely match the solar spectrum. Due to the wavelength dependency of photobiological processes, weighting functions have been developed based on action spectra for specific responses to assess the biological effectiveness of the irradiation sources and of predicted ozone depletion. Recent experiments also have utilized

ozone to filter natural solar radiation and simulate an environment of reduced UV-B for comparative purposes.

Overall, the effectiveness of UV-B varies both among species and among cultivars of a given species. Of those plants which have been tested, a large proportion exhibit reduced plant growth (plant height, dry weight, leaf area, etc.), photosynthetic activity, and flowering. Competitive interactions also may be altered indirectly by differential growth responses. Photosynthetic activity may be reduced by direct effects on the photosynthetic process or metabolic pathways, or indirectly through effects on photosynthetic pigments or stomatal function. The dose response of these changes has yet to be clearly demonstrated in most cases. Plants sensitive to UV-B may also respond by accumulating UV-absorbing compounds in their outer tissue layers, which presumably protect sensitive targets from UV damage. The key enzymes in biosynthetic pathways of these compounds have been shown to be specifically induced by UV-B irradiation via gene activation.

Few studies have documented the effects of UV-B on total plant yield under field conditions. One notable exception is a six-year field study with soybean demonstrating harvestable yield reductions under a simulated 25% ozone depletion. These effects are further modified by prevailing microclimatic conditions. Plants tend to be less sensitive to UV-B radiation under drought or mineral deficiency, while sensitivity increases under low levels of visible light. Further studies are needed to understand the mechanisms of UV-B effects and the interactions with present stresses and future projected changes in the environment.

INTRODUCTION

Since the last UNEP Report in 1989, there have been international UV-B effects workshops held in the United States, Australia, India, Malaysia, and other countries illustrating the international attention this environmental perturbation has received within the scientific community. In the last few years, new technology and instrumentation have become available to more accurately measure UV-B radiation and its penetration into plants. Systems have been developed to better simulate ozone depletion scenarios and to measure plant responses. Since the last assessment, several dozen reports on the effects of UV-B radiation on plants have appeared. This report gives some of the highlights of this new information.

NEW INFORMATION AND RECENT DEVELOPMENTS

Irradiation Systems

Two approaches have been used to study the effects of increased levels of UV-B radiation in the field. Most of this work has utilized fluorescent sunlamps to artificially supplement ambient levels of solar UV-B radiation. The other approach is to use natural solar UV-B radiation in regions of high ambient UV-B radiation. An ozone cuvette is positioned over plant growth chambers. Plants grown beneath these ozone cuvettes receive less than the ambient levels of UV-B and can be used to simulate ambient levels at higher latitudes or lower elevations. Both of these approaches will be briefly described below.

UV-Modulation System

Generally speaking, artificial UV-B radiation has been supplied by filtered sunlamps as a square wave. These systems have utilized timers to control the irradiation period which turn on at specific times, producing a constant lamp output until switched off. One problem associated with a constant lamp output is that the ratio between natural and artificial UV radiation varies hourly, diurnally, and seasonally. Therefore unrealistic levels of UV-B are provided in the mornings, afternoons, and on cloudy days. Since ambient levels of UV-B are low during these times, the artificial UV from the lamps would remain unrealistically high. To provide a more realistic simulation of the increase in UV-B radiation resulting from stratospheric ozone depletion, Caldwell et al. *[1983]* designed a modulation system to monitor ambient UV-B and provide a constant ratio of UV-B supplementation above the ambient signal. This system modulates lamp output in accordance with actual changes in the solar UV-B radiation reaching the ground.

Recently, another modulation system has been developed *[Yu et al., 1991]* utilizing a true condition closed-loop feedback control system. This continuously monitors natural solar UV-B fluences and provides a constant, proportional UV-B supplement underneath lamp banks. In this system, the same type of sensor is used for both control and feedback, resulting in the best spectral match with respect to temperature and solar angle. The control detector monitors solar UV-B radiation and provides a control signal, corresponding to the level of radiation. This signal then controls the output of a lamp bank, which is measured along with ambient levels of UV-B at the plant surface (true condition monitoring) by dual detectors to minimize shading effects. A signal processing unit in the controller then compares this signal with the control signal and automatically adjusts the lamp output through feedback to a power adjuster in the controller. This maintains a predetermined UV-B supplement as natural solar UV-B fluence changes. The primary advantages of this new modulation system are that it supplies a uniform irradiance field, is nearly maintenance free, has a higher efficiency and dynamic range, and can be computer operated and controlled. A field study is presently being conducted in the United States to compare plant responses between plants grown under the modulated system and those grown under a square wave irradiation system *[Teramura, 1991]*.

Ozone Cuvette Technique

The ozone filter technique used to attenuate solar UV-B radiation was described in the 1989 UNEP Report. It utilizes two identical growth chambers covered with a UV transmitting filter. Ambient UV-B radiation is attenuated in one growth chamber by passing ozone through the cuvette on top. Plants beneath this cuvette receive less than ambient levels of UV-B radiation, which then simulate natural levels of UV-B found at more northern latitudes or at lower elevations. The second growth chamber utilizes ambient air in the cuvette on top, therefore plants beneath it receive only ambient levels of UV-B radiation. In addition to UV-B radiation, these growth chambers can also be used to simultaneously study temperature and CO_2 effects on plants. The advantage of this technique is that it is adaptable for simulating natural solar UV-B radiation at many latitudes and altitudes.

UV Penetration Into The Leaf

It has been found that UV-B radiation has a direct effect on photosynthesis, while at the same time, reductions in photosynthesis often accompany changes in leaf pigmentation, anatomy, and leaf thickness. After exposure to enhanced UV-B radiation, the internal light regime of leaves is altered *[Bornman and Vogelmann, 1991]*. In a recent study, *Brassica campestris* (origin: northern latitudes) and *B. carinata* (origin: southern latitudes, Ethiopia) were subjected to 6.3 kJ m^{-2} day^{-1} of UV-B radiation with a background visible photon flux density of 1,800 μmol m^{-2} s^{-1} *[Bornman and Vogelmann, 1991]*. *Brassica campestris*, more sensitive to UV radiation, responded by increasing leaf thickness by 45% as well as increasing UV-B screening pigments by 21% relative to controls. Chlorophyll content (per leaf area) and photosynthesis, measured as chlorophyll fluorescence, decreased. Concomitant with these changes, scattered light within the leaves of UV-treated plants increased. Since the distribution of photosynthetically active radiation was altered at different depths within leaves after UV radiation, these changes can also be expected to have an indirect effect on photosynthetic capacity.

In another study, a group of 22 diverse plant species including herbaceous and woody dicotyledons, grasses, and conifers, was shown to have widely varying UV-B penetration *[Day et al., 1991]*. For instance, epidermal transmittance of the herbaceous dicotyledons ranged from 18% to 41% with penetration up to 140 mm, while conifer needles excluded a large percentage of the incident UV-B radiation. Penetration of UV-B radiation into leaves of the woody dicotyledons and grasses was in between that of the herbaceous dicotyledons and conifers.

UV-Protection

Epidermal Pigments

UV-B radiation induces flavonoid production *[Wellmann, 1971]*, and may regulate the synthesis of UV protective flavonoids *[Braun and Tevini, 1991]*. In a study using two important crops (rye and oat), UV-fluence and wavelength dependent accumulation of isovitexin derivatives in the epidermal layer of rye seedlings prevented damage to chloroplast functions. In contrast, photosynthetic function was low without the accumulation of screening pigments *[Tevini et al., 1991a]*. Because the epidermal layer of oat seedlings already accumulates large amounts of UV-absorbing pigments during early development, the photosynthetic apparatus is better protected than rye seedlings against damaging UV-B radiation *[Braun, 1991]*. This inherently higher flavonoid production occurs even in the absence of UV-B irradiation, and therefore appears to be constitutive in nature. Another example of UV-B induction of flavonoids was demonstrated in two species of columbines, *Aquilegia caerulea*, growing in alpine environments, and *Aquilegia canadensis*, which grows at lower elevations *[Larson et al., 1990]*. In both species, flavonoid content increased upon UV-B irradiation, even though the alpine species accumulated higher amounts in the UV-B-free controls when compared to *A. canadensis* after UV-B irradiation. This demonstrates that plants which are already genetically adapted to higher UV-B radiation environments can further increase their adaptation capacity.

Photorepair

A second important protective mechanism in plants is photoreactivation. The UV-induced production of DNA pyrimidine dimers can be repaired by DNA photolyase. This enzyme was shown to increase with

UV-B irradiation in *Arabidopsis [Pang and Hays, 1991]* but also by visible light via phytochrome in bean seedlings *[Langer and Wellmann, 1990]*. This inducibility means that *de novo* synthesis of DNA photolyase itself is a target for UV damage. Thus, the repair capacity of the cell may be reduced in the presence of increasing UV-B radiation, which is anticipated from stratospheric ozone depletion *[Wellmann, 1991]*.

Growth

Growth Chamber Studies

The growth of many plant species is reduced by enhanced levels of UV-B radiation, as shown in the 1989 UNEP Report. The ozone filter technique was used to simulate a relative solar UV-B enhancement of 20% by providing 54.4 kJ m^{-2} day^{-1} (unweighted) or 5.1 kJ m^{-2} day^{-1} of biologically effective radiation ($UV\text{-}B_{BE}$) through one cuvette and 45.3 kJ m^{-2} day^{-1} (unweighted) or 3.6 kJ m^{-2} day^{-1} $UV\text{-}B_{BE}$ through the other cuvette *[Tevini et al., 1991b]*. These were average values measured from May 1990 to August 1990 and are equivalent to an ozone depletion of approximately 10%. In this study, plant height, leaf area, and the dry weight of sunflower, corn, and rye seedlings were significantly reduced. However, oat seedlings remained almost unaffected *[Tevini et al., 1991b]*. The reduction of hypocotyl growth of sunflower seedlings under artificial UV-B irradiation is associated with a UV-dependent destruction of the growth regulator indole-3-acetic acid (IAA) and the formation of growth inhibiting IAA photoproducts. The inhibition of elongation in UV-irradiated sunflower seedlings might also be due to the action of peroxidases working as IAA-oxidase, causing a decrease in cell wall extensibility of the hypocotyl epidermis *[Ros, 1990]*.

Greenhouse Studies

Only recently has there been any information on the effects of UV-B radiation on tropical plants. Rice is among the most important tropical crop plants in the world. Sixteen rice *(Oryza sativa* L.) cultivars from several different geographical regions were grown for 12 weeks in greenhouses with supplemental levels of UV-B radiation, which simulated a 20% ozone depletion over the Equator (15.7 kJ m^{-2} day^{-1} $UV\text{-}B_{BE}$). Alterations in biomass, morphology, and maximum photosynthesis were determined *[Teramura et al., 1991]*. Approximately one-third of all cultivars tested showed a statistically significant decrease in total biomass with increased UV-B radiation. For these sensitive cultivars, leaf area and tiller number were also significantly reduced. Photosynthetic capacity, as determined by oxygen evolution, declined for some cultivars, but only a weak relationship existed between changes in photosynthesis and biomass with increasing UV-B radiation. In one of the rice cultivars tested, total biomass significantly increased by 20% when grown under enhanced levels of UV-B radiation. Therefore, despite the fact that the effects of UV-B radiation are generally damaging, in some cases, it has been reported to have a stimulating effect. Such positive growth effects are presently not easily explainable. Results from this experiment indicate that 1) a number of rice cultivars are sensitive to potential increases in UV-B radiation; and 2) the diversity exhibited by rice in response to increased levels of UV-B suggests that selective breeding might be successfully used to develop UV-B tolerant rice cultivars. Other preliminary screening studies on rice seedlings also corroborate these observations *[Coronel et al., 1990]*.

Field studies

Since the last UNEP Report, Sinclair et al. *[1990]* published results of a field study conducted in 1981 on six soybean cultivars grown under a simulated 16% ozone depletion. The results of this study showed that UV-B radiation had little effect on dry weight production, or on final seed yield. In a six year field study on a UV-sensitive soybean, Teramura et al. *[1990a]* showed a statistically significant 19%-25% reduction in seed yield in five of the six years when grown under a simulated 25% ozone depletion scenario (13.6 kJ m^{-2} day^{-1} $UV\text{-}B_{BE}$). Significant yield reductions were observed only in one of the six years when grown under a simulated 16% ozone depletion scenario. It is presently unclear whether these different results were due to inherent cultivar differences in UV-B responsiveness (only one of the eight cultivars used in the two studies were common to both), differences in UV-B dose applied (16% vs. 25% ozone depletion), or due to problems associated with single year field studies.

Only three field studies have evaluated the influence of increasing UV-B radiation on the physiology, growth, or development of tree species. Two of these were single season studies. In the only multi-season study conducted to date *[Sullivan and Teramura, 1991]*, loblolly pine *(Pinus taeda* L.) seed, obtained from seven contrasting geographical locations, was grown under natural and supplemental levels of UV-B radiation. Irradiation treatments were continued for the remaining three seasons on plants from four of the seven seed sources, and for only one year for three seed sources. The supplemental irradiances simulated those that would be anticipated with stratospheric ozone reductions of 16% and 25% (11.5 and 13.6 kJ m^{-2} $UV\text{-}B_{BE}$) over Beltsville, Maryland (39°N), USA.

The effects of UV-B radiation on plant growth during the first year varied among the seed sources. The growth of plants from two of the seven seed sources showed statistically significant reductions following a single irradiation season. After three years of supplemental irradiation, plant biomass was significantly reduced in three of the four seed sources (to 20%) at the lower simulated ozone depletion. The reductions in biomass were generally due to concurrent decreases in both above- and below-ground biomass. In some cases, reductions in biomass were also observed in the absence of corresponding reductions in photosynthesis. This may have been due to decreased allocation of biomass into needle tissue and/or direct effects of UV-B radiation on needle growth. These results suggest that the effects of UV-B radiation may accumulate in trees, and that increased UV-B radiation could significantly reduce the growth of loblolly pine over its lifetime. However, they also point to a need for multiple season research in any analysis of potential consequences of ozone depletion on the long-term growth of trees.

Morphological Responses and Competitive Balance

Enhanced UV-B radiation can cause changes in the growth form of plants without necessarily decreasing plant production. Such changes include reduced leaf length, increased branching, and increased number of leaves *[Barnes et al., 1990]*. These changes seem to be rather general among different crop and weed species. Both graminoid and broad-leaf species respond in this fashion, with graminoids generally more responsive. Although these growth form changes do not lead to changes in the production of monocultures, in mixed species stands these alterations can lead to a change in the balance of competition for light.

Earlier multi-year field studies had shown that the balance of competition between wheat and wild oat (a common weed) began to favor wheat when mixtures of these species were subjected to increased UV-B irradiation *[Barnes et al., 1988]*. In a recent study involving canopy light microclimate assessments and a detailed canopy radiation interception model, it was shown that the shift in growth form of the two species was sufficient to quantitatively explain the change in the competitive balance *[Ryel et al., 1990]*. Thus, in many cases where plants are not necessarily depressed in overall growth by increased UV-B radiation, changes in growth form can have ecologically meaningful consequences. The direction of competitive balance changes are not easily predicted at present. However, altered competitive balance also has important implications for mixed-crop agriculture and species composition of nonagricultural ecosystems.

Photosynthesis

In a three year field study with loblolly pine trees *[Sullivan and Teramura, 1991]*, supplemental levels of UV-B radiation simulated a 16% and 25% ozone depletion (11.5 and 13.6 kJ m^{-2} UV-B_{BE}). Photosynthetic capacity was generally reduced by increasing UV-B fluences. However, the absolute reductions varied from 0 to 40% between the seed sources and with needle age. For example, photosynthesis was significantly reduced by up to 40% in needles which had been exposed to UV-B for an entire season, but only 18% on recently expanded needles. These reductions, however, were only transient in some plants because they could not be detected following the winter dormant period. This suggests that UV-B repair mechanisms may exist which could mitigate UV-B damage. Measurements of chlorophyll fluorescence and the photosynthetic response to light indicated that the quantum yield was significantly reduced in some cases by direct effects on photosystem II. No significant effects were observed on stomatal conductance or transpiration, and chlorophyll concentrations were not generally altered by UV-B radiation.

In vitro studies, using isolated chloroplasts, indicate that UV-B radiation-induced damage to photochemical reactions is greater in C_3 plants *(Dolichoas lablab, Phaseolus mungo*, and *Triticum vulgare)* than in C_4 plants *(Amaranthus gangeticus, Zea mays, and Pennisetum typhoides)*. Such differences are associated with the polypeptide composition of the thylakoids *[Kulandaivelu et al., 1991]*.

Studies in growth chambers with the ozone filter for attenuating solar UV-B radiation showed significant reductions in net photosynthesis (measured under saturating light conditions) on a leaf area and whole plant basis in sunflower seedlings, when grown for three weeks at a daily maximum temperature of 28°C or 32°C under a 20% higher UV-B radiation level compared to controls (5.1 kJ m^{-2} day^{-1} UV-B_{BE} vs. 3.6 kJ m^{-2} day^{-1}). These represent average values from May 1990 to August 1990 and are equivalent to approximately a 10% ozone depletion. In contrast, net photosynthesis was lower in maize seedlings only during the earliest stages of development at both temperatures *[Tevini et al., 1991c]*.

UV-Radiation and Abiotic and Biotic Factors

In assessing the effect of UV radiation on plants, it is important to keep in mind that other factors may ameliorate or aggravate the response to UV radiation. Thus the response of the plant to multiple biotic and abiotic factors should be investigated for a more accurate assessment of the impact of global climate changes.

Temperature

In addition to higher levels of UV-B radiation, increases in temperature due to the greenhouse effect are also anticipated in our future environment. The following study simulated a 4°C difference in the daily temperature course in combination with UV-B radiation.

Seedlings of four plant species (sunflower, maize, rye, and oat) were grown for three weeks in growth chambers (placed in Portugal 38°N) using the ozone filter technique, which simulated a 20% UV-B radiation difference between the chambers and with daily maximum temperatures of 32°C or 28°C, respectively. Growth of seedlings (measured as plant height, leaf area and dry weight) was greater at 32°C than at 28°C, except for oat seedlings which did not grow well at higher temperatures. Leaf area and size of 3 week old sunflower seedlings irradiated with a 20% higher UV-B level were significantly reduced at both temperature regimes. Maize and rye seedlings grown at the higher temperature regime (32°C) could compensate for the growth reduction normally found at 28°C. Dry weight reduction normally found at 28°C in sunflower and maize did not occur at 32°C. Oat and rye seedlings responded differently. These results indicate that higher temperature regimes can ameliorate UV-B effects on at least some plant species.

Heavy Metals

The rise in toxic pollutants, including heavy metals, from both industrialized and developing countries is cause for concern. It has been shown that plants, in particular, may be adversely affected by the additional stresses beyond enhanced UV-B radiation. This approach to multiple effects is important, because it has been shown that even with low doses of UV-B radiation, the addition of another factor may substantially affect the plant.

When seedlings of Norway spruce (*Picea abies* L. Karst) were exposed to UV-B_{BE} of only 6.17 kJ m^{-2} day^{-1} together with 5 millimolar cadmium chloride for a period of 10 weeks, rates of net photosynthesis decreased by 33% in plants under the combined treatment of enhanced UV-B radiation and cadmium (relative to controls). The enhanced levels of UV-B radiation and cadmium applied simultaneously also decreased dry weight, height of seedlings, and chlorophyll content to a greater extent than found for UV treatment given alone *[Dubé and Bornman, 1991]*. Therefore, unless the effects of simultaneous multiple stresses are taken into account, one may underestimate the different environmental pressures on plants.

Carbon Dioxide

Current atmospheric levels of CO_2 may double from 340 ppm to 700 ppm by the middle of the 21st century. A number of field and greenhouse experiments have shown that growth and photosynthesis in a wide range of cultivated and native plant species will be substantially altered by such a CO_2 doubling. However, few studies have examined the combined effects of increases in CO_2 and UV-B radiation. Teramura et al. *[1990b]* grew wheat, rice, and soybean in a factorial greenhouse experiment utilizing two levels of CO_2 (350 ppm and 650 ppm) and two levels of UV-B (8.8 and 15.7 kJ m^{-2} UV-B_{BE}). Seed yield and total plant biomass increased significantly in all three species when grown in elevated CO_2. However, with concurrent increases in UV-B, these CO_2-induced increases remained in soybean, but were statistically eliminated in rice and wheat. Therefore, the combined effects of CO_2 and UV-B are species specific, but do indicate that UV-B may modify CO_2-induced increases in photosynthesis and yield. Recently, L.H. Ziska and A.H. Teramura *[1991]* further examined the interactions of two rice cultivars, IR-36 and Fujiyama-5, under similar combined UV-B radiation and CO_2 conditions as above. An analysis of gas exchange and chlorophyll fluorescence data indicated that the predominant limitation to photosynthesis with increased UV-B radiation was the capacity to regenerate RuBP in IR-36 and a decline in carboxylation efficiency in Fujiyama-5. Therefore, increased CO_2 may not compensate for the direct effects which UV-B has on the photosynthetic apparatus in rice.

Plant Diseases

It has also been shown that certain diseases may become more severe in plants exposed to enhanced UV-B radiation, possibly by an interaction of these factors. Sugar beet *(Beta vulgaris)* plants infected with *Cercospora beticola*, and receiving 6.9 kJ m^{-2} day^{-1} UV-B_{BE}, showed large reductions in leaf chlorophyll content, and fresh and dry weight of total biomass *[Panagopoulos et al., 1991]*. The study also showed that there was an increase in free radicals under the combined treatments.

In another study, three cucumber *(Cucumis sativus)* cultivars were exposed to a daily UV-B dose of 11.6 kJ m^{-2} UV-B_{BE} in a greenhouse before and/or after infection with *Colletotrichum lagenarium* or *Cladosporium cucumerinum*, and analyzed for disease development *[Orth et al., 1990]*. Two of the three cultivars were disease resistant and the other was disease susceptible. Pre-infection treatment with UV-B radiation led to greater disease development in the susceptible cultivar and in one of the disease resistant cultivars. Post-infection treatment did not alter disease development. The increased disease development in

UV-B irradiated plants was found only on the cotyledons and not on true leaves, suggesting that the effects of UV-B radiation on disease development in cucumber vary according to the cultivar, timing of UV-B exposure, and tissue age.

CONCLUSION

Although continuing research shows the potential importance of solar UV-B radiation as an environmental factor, caution must be exercised in making predictions on the consequences of stratospheric ozone change for agriculture and natural ecosystems. This is partially due to the complexities of the manner in which increased UV-B radiation interacts with other biotic and abiotic factors in influencing plant growth. Furthermore, plant research has been limited to only a few continuing projects.

Progress has been made in several technical areas including improved irradiation systems with both artificial and natural solar UV radiation. Progress has also been made in making direct measurements of the penetration of UV into plant organs giving an indication of both quality and quantity of the radiation environment within plant tissues.

Mechanistic studies are also providing improved insight into repair and tolerance processes in plants. Nevertheless, recent studies also indicate the complexities in which plant responses to UV-B may be modified by other environmental factors. These complications, and the very limited number of field studies which have been conducted with realistic UV-B supplements, greatly constrain quantitative predictions.

Most of the research to date deals with temperate-latitude agricultural species. Little is known at present about the manner in which agricultural and native plants at tropical latitudes cope with the intense solar UV-B flux already present in these regions, nor the degree to which these species can adapt to the still greater flux that would occur with ozone depletion.

Although much has been learned in the past two decades since the threat of ozone layer reduction first emerged, the global implications of the changing UV-B climate for terrestrial vegetation is far from resolved.

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CHAPTER 4

AQUATIC ECOSYSTEMS

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1991 REPORT SUMMARY

Aquatic ecosystems contribute more biomass (104 Gt/a) than all terrestrial ecosystems (100 Gt/a) combined. Recent work on UV-B effects has concentrated on inhibition mechanisms and field studies in the subpolar waters of Antarctica, because of its high productivity and the occurrence of the ozone hole over this region.

Phytoplankton organisms orient within the water column using external factors. However, mobility and orientation mechanisms are impaired by UV-B radiation. Because most organisms do not possess UV-B receptors, they cannot avoid deleterious wavelength radiation that (according to new measurements) penetrates deeper into the water column than what has been previously measured. New action spectra indicate that, in addition to DNA, other targets absorb UV-B radiation including intrinsic proteins of the photoreceptor and photosynthetic apparatus.

The inability to adjust their position within the water column causes massive inhibition of photosynthesis, measured both in field and laboratory studies. Only in a few cases have potential UV-B-inducible screening pigments been identified.

A large share of the nitrogen consumed by higher plants is made available by bacterial microorganisms, which have been found to be very sensitive to UV-B radiation. Losses in nitrogen fixation could be compensated by additional nitrogen fertilization. However, such actions could stress the capabilities of developing nations.

The role of DMS, released from plankton and macroalgae as aerosol and cloud nuclei, is of major concern. Most importantly, a UV-B-induced decrease in phytoplankton populations may have an impact on cloud patterns and concomitant global climate changes.

An increased understanding of Antarctic trophic dynamics suggests that the likelihood of direct UV-B radiation effects on consumers is small. Rather, it is the possibility of indirect effects that may significantly affect the Antarctic trophic structure, such as different species sensitivities to UV-B radiation, or decreases in total available primary production. Because more than 30% of the world's animal protein for human consumption comes from the sea, the human populations may also be affected by the direct and indirect consequences of increased solar UV-B radiation on aquatic food webs.

Another potential consequence of a decrease in marine primary productivity would be a reduction in the capacity of the ocean to absorb carbon dioxide. A hypothetical loss of 10% of the marine phytoplankton would reduce the oceanic annual uptake of carbon dioxide by about 5 Gt (an amount equal to the annual emissions of carbon dioxide from fossil fuel consumption). Uncertainties regarding the magnitude of increased levels of UV-B radiation on aquatic systems still remain, including problems of extrapolating laboratory findings to the open sea, and the nearly complete absence of data on long-term effects and ecosystem responses. Uncertainties and future research needs include adaptive strategies and the effects of cumulative UV-B radiative doses. Additional information is needed in several areas before a more reliable assessment of risks is possible.

1989 REPORT SUMMARY

Current data suggest that predicted increases in UV-B radiation could have important negative effects on the marine environment. However, uncertainties regarding the magnitude of these effects still remain, including problems of extrapolating laboratory findings to the open ocean, and the nearly complete absence of data on long-term effects and ecosystem responses.

Planktonic marine organisms account for over half of the total global amount of carbon fixed annually (10^{11} tons). Any reduction in this productivity will undoubtedly affect global food supply and global climate. Both primary production and subsequent steps in biological food webs are sensitive to current UV-B levels, and are potentially endangered by expected increases in UV-B radiation.

UV-B radiation affects 1) adaptive strategies (e.g., motility, orientation), 2) impairs important physiological functions, (i.e., photosynthesis and enzymatic reactions), and 3) threatens marine organisms during their developmental stages (e.g., the young of finfish, shrimp larvae, crab larvae). In addition to DNA damage, UV-B radiation affects enzymes and other proteins, eliciting photodynamic responses. These effects can have a number of possible consequences for aquatic ecosystems:

- Reduction in biomass production, resulting in a reduced food supply to humans;
- Change in species composition and biodiversity;
- Decreased nitrogen assimilation by prokaryotic microorganisms, possibly leading to a drastic nitrogen deficiency for higher plant ecosystems, such as rice paddies; and
- Reduced sink capacity for atmospheric carbon dioxide, thereby augmenting the greenhouse effect.

However, additional information is needed before more reliable assessments of the UV-B radiative risks posed to the marine environment will be possible.

INTRODUCTION

Since the release of the UNEP Environmental Effects Panel Report of 1989 *[UNEP, 1989]*, UV-B aquatic research has concentrated on phytoplankton and the Antarctic ecosystem. It is estimated that phytoplankton convert 104 billion tons of carbon into organic material annually, which is slightly more than the 100 billion tons from all terrestrial ecosystems combined *[Houghton and Woodwell, 1989] (Figure 4.1)*. Phytoplankton, at the base of the aquatic food chain/trophic structure, serve as food for primary consumers (e.g., larvae of fish and shrimp), which in turn are consumed by secondary and tertiary consumers (e.g., fish). The final consumers of this trophic web are large fish, birds, and mammals, including man. Thus, any changes in the size and composition of phytoplankton communities will directly affect man's marine food sources.

A decrease in springtime concentrations of stratospheric ozone of over 50% have been clearly documented in the Antarctic. Within the Antarctic ecosystem, biomass is concentrated as an aquatic component, as opposed to the terrestrial environment. Concentrations of phytoplankton in subpolar waters may be 10^3 to 10^4 times greater than concentrations of phytoplankton found in tropical and subtropical seas *[Jeffery and Humphrey, 1975]*. Any significant increase in UV-B radiation, due to thinning of the ozone layer, could well diminish growth and productivity of phytoplankton, subsequently affecting all higher trophic levels in the aquatic food web. Therefore, it is not surprising that a majority of recent research has looked at the effects of increased UV-B radiation in Antarctic waters. Ongoing research activities include investigations of both direct (physiological and behavioral) and indirect effects (trophic implications).

Because of their requirement for solar energy, phytoplankton dwell in the top layers of the water column, the photic zone *[Ignatiades, 1990]*. Their position within the column is maintained by precise orientation strategies using light, gravity, and other external factors as guides. Phytoplankton, in the photic zone, would be exposed to any increase in solar ultraviolet radiation. Most phytoplankton organisms (studied up to now) do not have UV-B photoreceptors to guide them away from harmful radiation, a situation similar to humans. Previous work demonstrated that mobility/orientation mechanisms in response to light are impaired by solar ultraviolet radiation *[Häder and Worrest, 1991]* penetrating deep into the photic zone *[Baker and Smith, 1982]*. The ability of phytoplankton to adjust their position within the water column, in response to constantly changing conditions, may be affected at even ambient UV-B levels. In fact, ambient UV-B fluxes may cause damage to some species of phytoplankton. However, it should be emphasized that there are uncertainties regarding the magnitude of these effects, including problems of extrapolating laboratory findings to the open sea, and the nearly complete absence of data on long-term effects and ecosystem responses. Likewise, there is a need to investigate adaptation mechanisms. Before effects of exposure to solar UV-B radiation can be predicted, information is required on seasonal abundances and vertical distributions of marine organisms, vertical mixing, and the penetration of UV-B radiation into appropriate water columns.

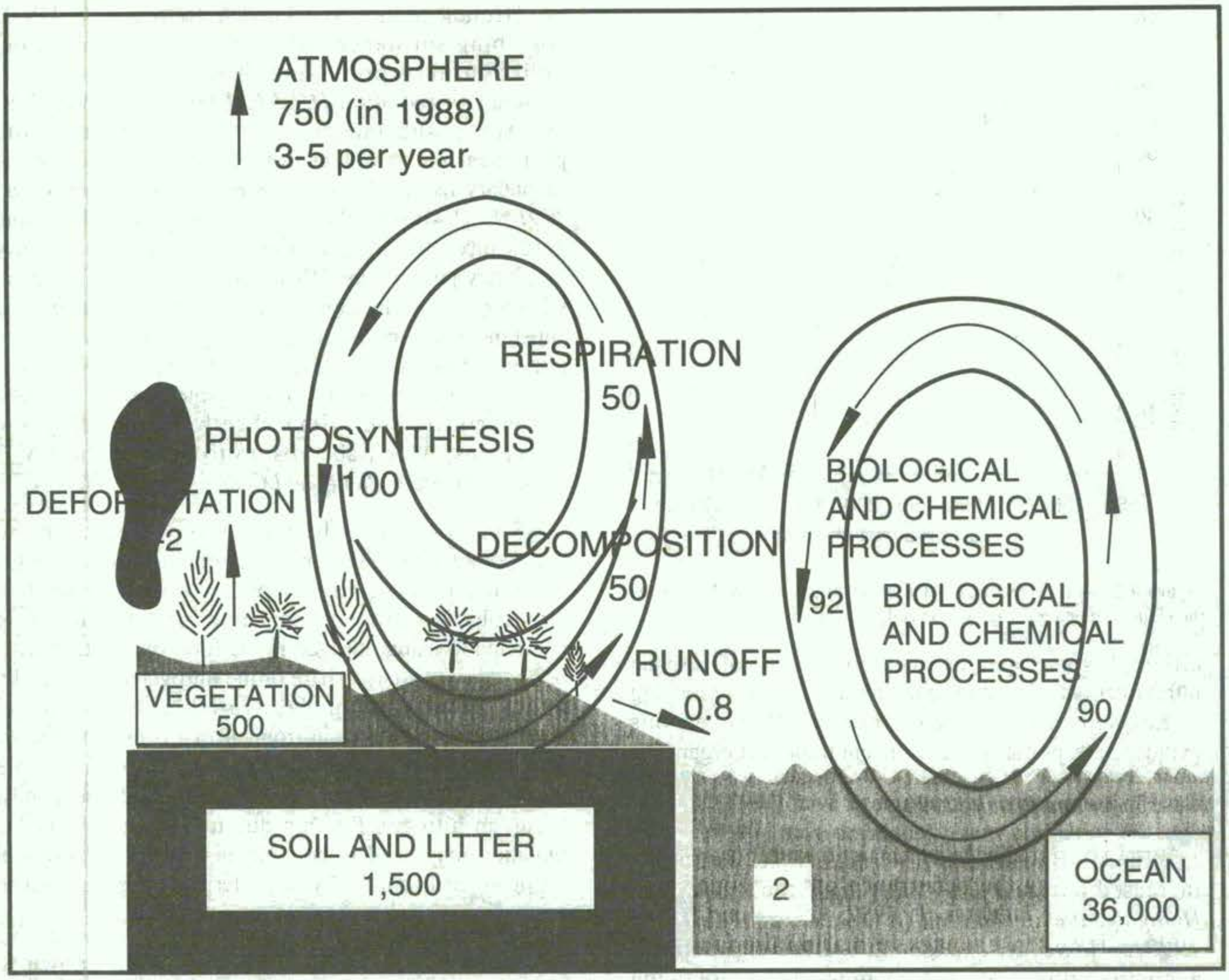

Figure 4.1 Major biospheric processes, pools, and fluxes in the carbon cycle (pools and fluxes are in gigatons carbon) *[Adapted from IPCC, 1990]*.

In their natural habitats, organisms are exposed to a wide range of UV-B radiative doses. This radiation has been shown to affect growth, photosynthesis, nitrogen incorporation, and enzyme activity *[Döhler and Alt, 1989; Döhler, 1990]*. Even a small increase in global UV-B radiation would intensify maximal irradiation levels, as well as increase long-term exposure doses.

NEW INFORMATION AND RECENT DEVELOPMENTS

Primary Producers

Recent results indicate that orientation mechanisms responsive to both light and gravity are affected by solar ultraviolet radiation in a number of ecologically significant phytoplankton groups *[Häder and Liu, 1991]*. Action spectra inhibitory effects are different from the DNA absorption spectrum and the action spectra calculated for higher plants, indicating that UV radiation affects these organisms by a totally different mechanism *(Figure 4.2)*. Recent data indicate that proteins essential for specific functions in orientation and photosynthesis are the primary targets of UV-B radiation.

Biochemical analyses, conducted to reveal the molecular targets of UV-B inhibition, show that specific photoreceptor proteins are degraded by ultraviolet radiation. Simultaneously, photosynthetic pigments (responsible for converting solar energy) are bleached and destroyed by radiation. The results of these biochemical studies are further supported by spectroscopic investigations showing losses in pigmentation.

In order to evaluate the effects of enhanced ultraviolet radiation, the vertical movement of natural phytoplankton was analyzed in 3-m long Plexiglas columns *[Eggersdorfer and Häder, 1991]*. Most organisms moved to the surface during daytime hours,

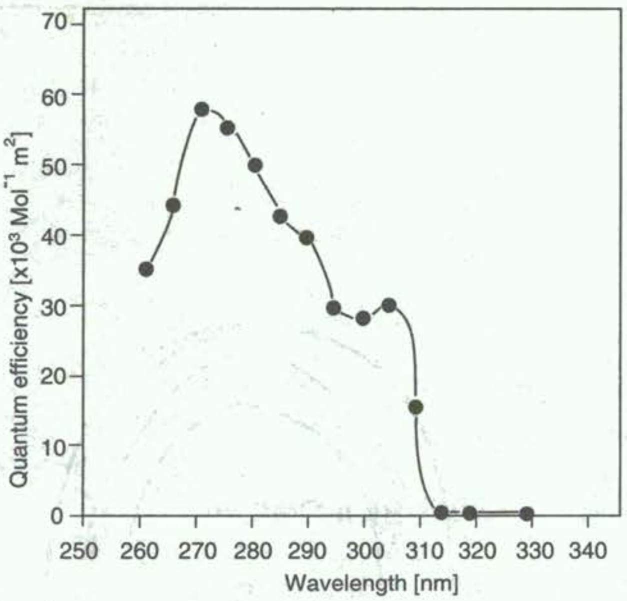

Figure 4.2 Action spectrum of the inhibition of motility in the flagellate Euglena gracilis by ultraviolet radiation.

although some species avoided periods of intense ultraviolet radiation during the midday hours by moving slightly down in the water column. However, this avoidance response is not sufficient to protect organisms under conditions of increased UV-B irradiation *[UNEP, 1989; Yoder and Bishop, 1990]*.

The UV-B irradiance in Antarctic waters drastically increased during the occurrence of the ozone hole *[Bidigare, 1989; Lubin et al., 1989; Karentz and Lutze, 1990]*. However, changes in marine productivity accompanying UV flux changes have not been determined. Recent measurements show that UV-B penetrates 65 meters deep in clear Antarctic waters *[Gieskes and Kraay, 1990]*. Consequently, measurements of photosynthetic biomass production in Antarctic waters under the ozone hole show a pronounced decrease of productivity by up to 25% *[Holm-Hansen, 1990]*. ATP content of Antarctic phytoplankton cells (a reflection of energetic state), significantly decreased in the presence of the ozone hole *[Vosjan et al., 1990; Karentz et al., 1991a]*.

Field studies indicate that photosynthesis is impaired first, followed by decreases in protein concentration and changes in pigment composition. As a result, a dramatic decrease in photosynthetic oxygen production can be measured after exposure to solar radiation *[Smith et al., 1980; Zündorf and Häder, 1991]*. It should be mentioned that other spectral bands, such as UV-A and visible radiation, may contribute to photosynthetic inhibition *[Smith et al., 1980; Mitchell, 1990]*. Likewise, photosynthetic inhibition has been detected in macroalgae at their natural depth *[Bittersmann et al., 1988; Nultsch et al., 1990]*.

Higher plants are known to produce UV-B absorbing substances when exposed to ultraviolet radiation, thus protecting them from solar short-wavelength radiation *[UNEP, 1989]*. Recently, UV-absorbing substances have been isolated from phytoplankton, as well as from a number of primary and secondary feeders *[Carretto et al., 1990; Karentz et al., 1991b]*. However, all of these mycosporine-like amino acids have maxima in the UV-A range and only secondary peaks in the UV-B. In addition, it is not clear whether the production of these potentially screening substances can be induced by exposing organisms to ultraviolet radiation *[Raven, 1991]*. One exception is cyanobacteria where a UV-B inducible pigment has been found within the slime sheath surrounding the organisms, which absorbs up to 88% of the UV-B radiation *[Garcia-Pichel and Castenholz, 1991]*.

Some planktonic bacteria have the capability to incorporate atmospheric nitrogen into a form accessible to higher plants. Higher plants cannot assimilate atmospheric nitrogen themselves and are therefore restricted to using nitrogen in the form of nitrate, nitrite, or ammonia. A large share of the nitrogen consumed by higher plants is made available by bacterial microorganisms, (e.g., in tropical rice paddies) *[Kumar and Kumar, 1988]*. However, these microorganisms are highly sensitive to solar UV-B radiation. Consequently, losses in nitrogen fixation due to increases in UV-B radiation may need to be compensated for by artificial nitrogen fertilization. Cyanobacteria alone are estimated to produce 35 million tons of nitrogen annually.

Furthermore, many algal groups are known to produce dimethylsulphonio-propionate as an antifreeze and osmotic regulator. From this substance, dimethylsulphide (DMS) is cleaved enzymatically and emitted into the surrounding water *[Karsten et al., 1990]*. From there it is released into the atmosphere where it undergoes photochemical oxidation to sulphate and methane sulphonate. These substances are thought to act as nuclei in aerosol formation and cloud condensation. Forty million tons of sulphur are released by this mechanism annually, equaling about 50% of the sulphur emissions from anthropogenic sources. Therefore, there are concerns that a reduction in the phytoplankton could have an effect on global climate changes *[Andreae, 1986]*.

CONSUMERS

Recently, little work has been conducted on the direct effects of UV-B radiation on zooplankton. Over the last few years, however, a greater understanding of Antarctic trophic dynamics has developed. Furthermore, there is a growing appreciation for microorganisms (especially diatoms) found in the sea

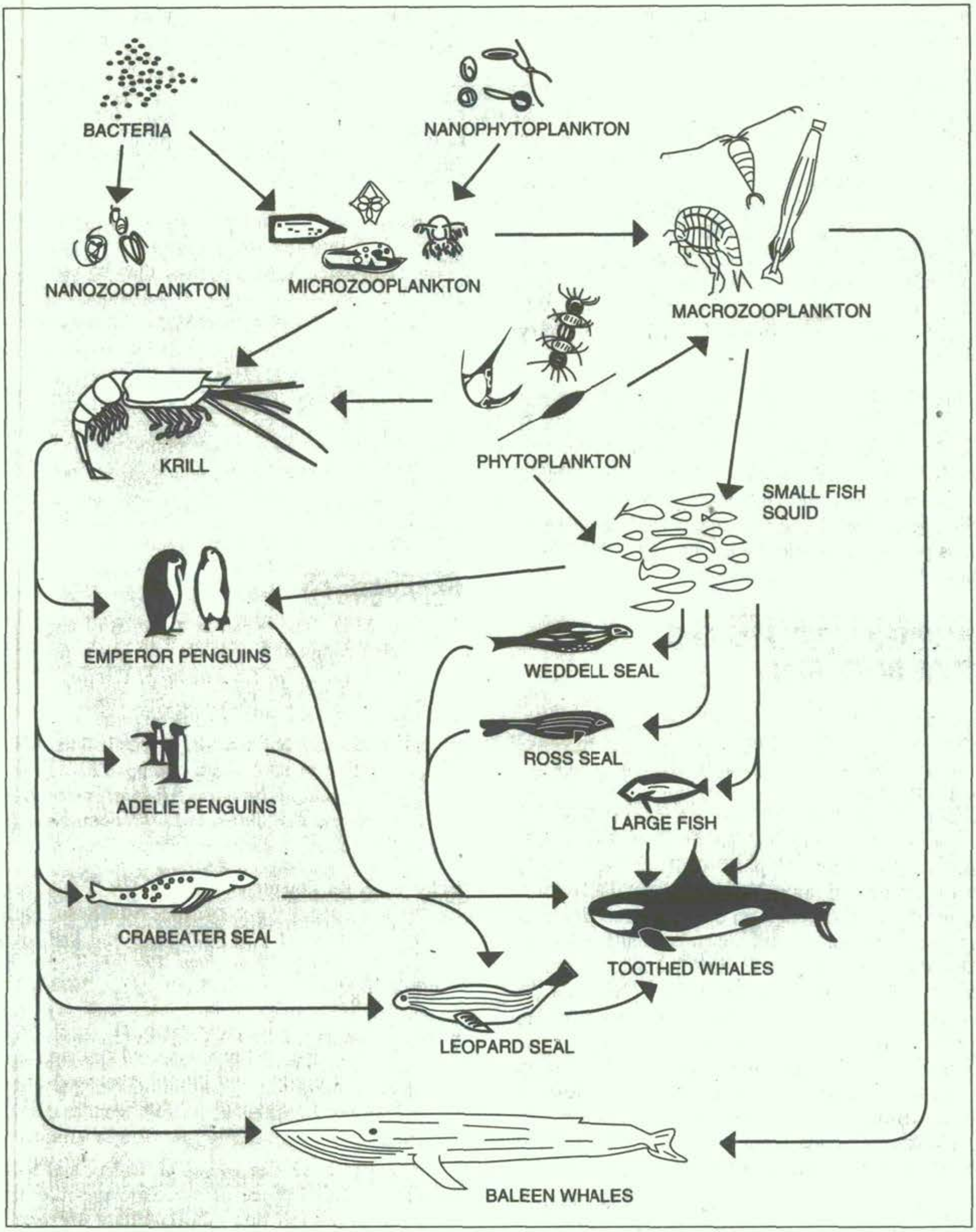

Figure 4.3 A representation of the Antarctic marine food web *[Adapted from Voytek, 1990, used with permission].*

ice *[Garrison et al., 1986]*. This community may be a significant factor for productivity in Antarctic waters, contributing to biomass and serving as an inoculum for spring phytoplankton blooms *[Voytek, 1990]*.

Figure 4.3 illustrates the nature of the Antarctic aquatic food web. Voytek *[1990]* suggests that it is inadequate to look only at primary production, but rather, the effects of increased UV-B radiation on each trophic component must be investigated. In general, direct effects from radiation on consumers is small, however, indirect effects (such as changes in the composition of phytoplankton assemblages) may significantly affect the Antarctic trophic structure. This effect is the result of species-specific sensitivity to UV-B radiation or decreases in total available primary production.

Human populations may also be affected by direct and indirect consequences of increased solar UV-B radiation on aquatic food webs. Because more than 30% of the world's animal protein for human consumption comes from the sea (in many developing countries this percentage is even larger), a substantial decrease in biomass production would diminish fishery resources in the face of growing world populations.

CONTINUED CONCERNS AND FUTURE RESEARCH

Another important consequence of a potential decrease in marine phytoplankton productivity would be the reduced ability of the ocean to serve as a sink for atmospheric carbon dioxide. Phytoplankton not only produce more than half of the biomass on our planet, but also absorb and fix more than half of the carbon dioxide from the atmosphere. Hypothetically, a loss of only 10% of the phytoplankton would prevent about 5 gigatons of carbon (in the form of carbon dioxide) from being removed from the atmosphere annually (which is equal to the amount of carbon dioxide emitted currently by fossil fuel utilization). Ten to twenty percent of the gross primary production from the oceans is estimated to occur in southern regions *[Voytek, 1990]*. Because carbon dioxide is a greenhouse gas, a reduction in oceanic carbon dioxide stores is an important consideration. UV-B-derived reductions in phytoplankton biomass are not presently incorporated into global climate change models.

Any sizable reduction in the population of nitrogen-fixing organisms may diminish the availability of nitrogen for higher plants (both naturally occurring species and crop plants). As a result, artificial nitrogen fertilization may be needed. However, such needs may stress the capabilities of developing countries.

A number of marine systems, particularly some fisheries (which are severely depleted due to over-harvesting and pollution), are presently stressed by anthropogenic factors. Coral reefs (important to both fisheries and tourism) are under stress and are experiencing declines from sedimentation, pollution, and perhaps temperature increases. Increased UV-B radiation may push some populations past their threshold by decreasing larval fish survival or increasing coral bleaching events.

Researchers continue to investigate UV-B penetration into the water column and through ice. Basic physical information could then be used in both laboratory and field research to determine their effects on phytoplankton and zooplankton. Adaptive strategies utilized by these communities, as well as the effects of interactive stresses (temperature, salinity, and cumulative doses received over the lifetime of the organisms, etc.) need to be studied over extended periods of time. As a result, plankton effects can be modeled into broader ecosystem dynamic patterns and can be fed into models of global carbon and nitrogen cycling.

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CHAPTER 5

TROPOSPHERIC AIR QUALITY

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1991 REPORT SUMMARY

New tropospheric modeling studies corroborate conclusions discussed in the 1989 UNEP Report. In particular, increased levels of UV-B were found to lead to tropospheric ozone depletion in remote regions, enhanced photochemical reactivity in areas affected by anthropogenic emissions, and increased hydrogen peroxide concentrations in all regions modeled (remote, marine, continental, and urban-influenced regions at mid and low latitudes). Recent decreases in Antarctic surface ozone support model predictions of increased destruction of remote tropospheric ozone by UV-B. Hydrogen peroxide results, and surface-layer calculations in general, remain uncertain due to limitations in current tropospheric models.

1989 REPORT SUMMARY

In the troposphere, the rates of some important chemical reactions depend directly on the amount of UV-B radiation. If stratospheric ozone levels decrease, the resulting increase in UV-B near the earth's surface should increase the production of some very reactive radical molecules, potentially increasing the chemical reactivity of the troposphere. In rural and urban areas with sufficient NO_x concentrations (above 0.5 ppb v/v), this enhanced reactivity is calculated to result in greater levels of tropospheric ozone and other potentially harmful oxidized products, such as hydrogen peroxide and acids.

The extent of potential changes will depend on the amount of NO_x and hydrocarbon compounds available locally, along with the location of an area and time of year (the amount of UV-B change). Urban areas with large man-made emissions and little emission controls have the greatest potential for change, but even urban areas with extensive emission control programs could be affected since increased chemical reactivity could make planned control programs less effective than anticipated. Because rural ozone levels are currently much lower than in urban areas, even a small increase would be a large percentage increase and could affect agricultural productivity and exacerbate biological stress. Some rural areas that receive transported urban air could become significantly more urban-like.

Few studies have focused on oxidized products other than tropospheric ozone. Hydrogen peroxide is potentially more sensitive to stratospheric ozone changes, and the effects on acid and aerosol production are virtual speculation. In addition, the potential increases in global chemical reactivity related to stratospheric ozone loss could be either enhanced or diminished, depending on the extent and manifestation of possible changes to global climate.

NEW INFORMATION AND RECENT DEVELOPMENTS

Since the last UNEP Report in 1989, additional studies have investigated the impact of decreased stratospheric ozone on tropospheric chemistry. Thompson et al. *[1990 and 1991]* used a one-dimensional photochemical model and Isaksen et al. *[1989]* a two-dimensional model to calculate the effects of a 10% loss of stratospheric ozone. The modeled scenarios were for future conditions in different types of chemically coherent regions of the global troposphere, ranging from pristine to urban-influenced. The model results for tropospheric ozone, hydrogen peroxide (H_2O_2), and the free radicals OH and HO_2, agreed with and expanded upon previous findings.

These model calculations suggest that, for regions of the troposphere directly or even indirectly influenced by human emissions, the chemical response to increased UV-B may be quite different from that found in remote regions. Given added UV-B, photochemical activity is expected to increase and operate for longer periods of time. Principally, this was thought to be due to higher concentrations of oxides of nitrogen (NO_x) in urban influenced regions. However, in concentrated urban areas, the added influence of hydrocarbons could produce more photochemical smog (as described in the 1989 UNEP Report). Such conditions constitute a unique chemical system that has not been directly described in the above models.

In remote regions (probably including portions of the free troposphere above the urban-influenced boundary layer), these modeling studies predict that a 10% loss of stratospheric ozone would decrease tropospheric ozone levels due to increased tropospheric ozone photolytic rates (with enhanced UV-B). Although photolytic enhancement would produce additional hydroxyl radicals (OH), these remote regions lack high enough concentrations of precursor chemicals (mostly anthropogenic) required to compensate for ozone loss via photochemical production. However, all tropospheric region models showed that increased photochemical activity (caused by the enhanced UV-B) would produce substantial increases in tropospheric HO_2 and H_2O_2.

The occurrence of stratospheric ozone loss in the Antarctic springtime is a well-documented phenomenon. One characteristic of the ozone hole is significantly enhanced UV-B near the earth's surface *[see Chapter 1 of UNEP, 1989]*. Model simulations predict that enhanced UV-B in remote tropospheric regions should induce a coincidental loss of surface ozone. Thompson *[1990]* demonstrated this by simulating an extreme case of increased UV-B over the southern ocean (48°S) during the December breakup of the 1985 ozone hole. An airmass of extremely low ozone (<240 Dobson) was calculated to cause nearly twice the rate of surface ozone photolysis (to $O(^1D)$) that would normally occur for typical December ozone column densities. Simulation results projected a decrease in surface ozone by nearly 30%, with a concomitant increase of surface OH (30%) and hydrogen peroxide (15%).

Recent measurements at the South Pole *[Schnell et al., 1991]* provided the first observable confirmation of surface ozone loss in remote regions. A decrease of 17% in surface ozone concentrations was reported for periods during the austral spring and summer from 1976 to 1989. Schnell and co-workers calculated that enhanced photochemistry could account for surface ozone depletion, assuming a 10% decrease in the overhead ozone column. Such changes in the ozone column agree with observed trends in total ozone, taken from a Total Ozone Mapping Spectrometer (TOMS) onboard the Nimbus 7 satellite *[Stolarski et al., 1991]*.

CONTINUING CONCERNS AND FUTURE RESEARCH

Although the observed decline in South Pole surface ozone confirms model calculations (under the relatively understandable conditions of the Antarctic), additional observations of both UV-B and tropospheric chemical species must be initiated to assess potential effects and evaluate atmospheric models. Initial attempts should focus on regions where impacts are most likely to occur. TOMS observations indicate statistically significant negative ozone trends extending outward from both poles (see Chapter 1 of this report). Episodes of stratospheric ozone depletions are known to persist for days to weeks over southern Australian and, occasionally, South American cities (after the breakup of the ozone hole). Thompson *[1991]* suggested the possibility of detecting tropospheric ozone losses in the southern hemisphere through appropriate surface and balloon measurements. However, such studies must be carefully designed, due to the difficulty correlating stratospheric ozone loss with tropospheric changes at lower latitudes. This is because stratospheric ozone loss is less dramatic over these regions and the tropospheric chemistry is complicated by the influence of human emissions.

A second item that requires immediate improvement is the level of detail in mathematical models used to describe both chemical and physical processes of the troposphere. Current work is more detailed than previous work, but the results must still be considered in the context of global-scale models. Specifically, this work focuses on decoupled, chemically similar regions of the entire troposphere (from 0 to 15 km); furthermore, the results are probably most valid for the more homogeneous regions of the troposphere (marine, remote, and non-surface regions). More detailed calculations are needed to: (1) improve the calculation of deposition, emission, mass transfer, radiative transfer, and the complex chemical processes that occur in the surface layer, and (2) expand the vertical linkages between surface, free troposphere, and stratosphere, as well as the transfer of mass between different regions in the horizontal direction.

Such work is needed to improve our understanding of the potential effects of emissions-dominated photochemistry in urban and continental regions. Although surface regions represent only a small percentage of the entire tropospheric volume, accurate descriptions of the impacts in such regions are important for determining exposures to humans and other portions of the biosphere.

Concurrent with model improvements, emissions and air quality data for hydrocarbons, NO_x, sulfur-containing species, and greenhouse gases must be expanded to include all areas of the earth. In addition, new model calculations for effects (due to stratospheric ozone loss) must include projected future conditions of trace gas and emissions increases caused by population growth, the effects of changing global climate, and all important mass- and radiative-transfer linkages (between atmospheric, terrestrial, and marine regions). It is probable that current models and scenarios have not considered all important effects caused by potential changes in water vapor levels, cloud cover, temperature, flow, and dilution patterns. Finally, it may be necessary to investigate the effect of increased UV-B on condensed phase processes. In areas with significant cloud cover, there is a greater probability for enhanced photocatalytic processes and increased source strengths for dissolved free radicals and excited state molecules *[Graedel, 1990]*.

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CHAPTER 6

MATERIALS DAMAGE

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1991 REPORT SUMMARY

Exposure to solar ultraviolet (UV) radiation causes degradation of materials such as wood and plastics, limiting their useful lifetimes in outdoor applications. Plastics are compounded with light stabilizers to overcome this problem. Increases in the UV radiation levels in sunlight as a consequence of partial ozone depletion will cause faster light-induced degradation of materials leading to shorter outdoor lifetimes. Increasing the levels of conventional light stabilizers in plastics may overcome this problem, but the effectiveness of these stabilizers under high UV sunlight conditions is not known. This strategy using known stabilizers, the development and use of alternative stabilizers, or more frequent replacement of materials used in outdoor applications, might all be used to address the problem. Each response, however, leads to increased cost of using plastics outdoors.

Assessment of the economic impacts of ozone depletion in the materials area requires the knowledge of both the damage estimates and of the effectiveness of stabilizers under altered sunlight conditions. Estimates of light-induced damage to materials might be based on action and activation spectral data for the relevant materials. Data available in the literature pertain to polymer compositions not typically used outdoors, and are based on measurements not directly relevant to modes of damage of practical interest. Available data are summarized in a table. No data exist on stabilizer effectiveness under spectrally altered sunlight exposure conditions. This lack of data precludes the reliable estimate of damage under different ozone depletion scenarios. Estimates based on available data (such as on rates of discoloration) do not reflect structural damage and therefore tend to underestimate the effects of exposure.

Exposure in near-equator locations which experience high levels of UV-B radiation under present conditions, presents a valuable opportunity to study the behavior of materials under partial ozone depletion conditions. On-going work in Saudi Arabia and China may generate data on the weathering behavior of selected plastics under desert exposure conditions. Future data from these studies might be used to better understand the problem and perhaps to generate reliable estimates of damage to materials.

1989 REPORT SUMMARY

Exposure to solar ultraviolet (UV) radiation is the primary cause of degradation of materials, particularly plastics used outdoors. To maintain useful lifetimes at acceptable levels, chemical additives are generally employed as light stabilizers in plastics intended for outdoor application. A partial depletion of stratospheric ozone leading to increased UV radiation levels will increase the rate at which plastic products degrade outdoors. Products designed (stabilized) to withstand current outdoor exposure conditions will suffer reduced lifetimes under such altered conditions.

Only a limited amount of reliable technical data is available on the issue of materials damage from UV radiation, particularly relating to action spectra for commercially relevant plastic products. In the case of rigid poly(vinyl chloride), PVC (a high volume plastic used outdoors), the discoloration is extremely sensitive to both the wavelength and the intensity of UV radiation. Even a small change in short wavelength UV radiation will lead to a substantial increase in the rates of yellowing PVC materials. This undesirable discoloration also is indicative of structural damage in PVC materials. Other plastics have not been studied in sufficient detail from a similar point of view.

The most damaging effects to materials due to partial depletion of stratospheric ozone (increased UV radiation) will be felt primarily in the near-equator regions of the world due to high ambient temperatures and sunshine levels. It is important to investigate the degradation and stabilization techniques applicable to plastics weathering under these extreme environmental conditions. While some research is currently underway, much more emphasis on this aspect of the subject is desirable.

INTRODUCTION

Plastics and wood are used extensively in outdoor applications, particularly in the building industry. The lifetimes of materials involved in routine exposure to outdoor conditions are generally determined by their light stability. Plastic formulations intended for outdoor use generally employ light stabilizers to ensure adequately long lifetimes. Wood is either surface treated or painted for protection against light and moisture.

Partial depletion of the stratospheric ozone layer will lead to increased ultraviolet (UV) radiation levels in terrestrial sunlight. The wavelengths affected, the 280 nm to 315 nm band or UV-B region of the electromagnetic spectrum, are the most damaging to materials. Consequent increases in light-induced degradation rates will result in significantly shorter outdoor lifetimes and require faster replacement of such products.

The extent to which the lifetimes of materials used outdoors is shortened, as a result of ozone layer depletion, depends upon the increment of UV-B in sunlight and the susceptibility of the particular type of material to light-induced degradation.

The most damaging effects of a partial ozone depletion, demonstrated in terms of increased UV levels in sunlight, will be felt primarily in the near-equator regions of the world. The net change in the ozone column at these locations is expected to be small relative to those at higher latitudes. Near-equator regions currently experience the highest insolation as well as very high ambient temperatures. Any further increase in the intensity of UV radiation or in ambient temperature will result in dramatic increases in the rates of degradation of materials at these locations. This will be further exacerbated if ozone depletion causes shorter wavelength radiation (currently filtered out by ozone) to reach the earth's surface.

Little is known about the susceptibility of key plastic formulations (and different types of wood) to photodegradation. Most reported data pertain to studies carried out on pure polymers *[Hirt and Searle, 1967; Searle, 1990; Searle et al., 1989; Fueki and Torikai, 1990]*. Work on poly(vinyl chloride) (PVC) materials, a plastic used in siding, pipe, window frame, and other applications, has indicated that these materials discolor upon exposure to UV light *[Andrady, et al., 1989; Andrady, et al., 1990]*. Shorter wavelength light is particularly effective in causing discoloration, which is indicative of structural damage to the plastic. Even a small increase in the shorter wavelength UV component in sunlight is expected to cause a substantial increase in damage to PVC materials *[Andrady et al., 1989; Andrady et al., 1990]*. The same is true for polycarbonates used in glazing applications *[Andrady et al., 1991]*.

Lack of quantitative information on spectral sensitivity and light susceptibility of relevant plastic compounds seriously limits the assessment of damage related to different scenarios of partial ozone depletion. A first response to shortened service lifetimes might be to increase the level of currently used stabilizers to compensate for the increase in the UV content of sunlight. This will involve increased costs, not only due to higher stabilizer demand, but possibly from certain processing considerations of the new formulations. Even so, the effectiveness of currently used stabilizers against spectrally altered sunlight has not been demonstrated. There is insufficient data available to determine if the required stabilizer levels are impractically high or if alternate stabilizer compounds need to be identified.

NEW INFORMATION AND RECENT DEVELOPMENTS

Spectral Sensitivity of Materials

To realistically estimate the damage to a particular class of plastic or wood products due to increased UV radiation levels in sunlight in the future, it is crucial to have information on the wavelength sensitivity (or action spectra) of the material. An action spectrum is a measure of light-induced damage, expressed as a function of the wavelength of the radiation to which it was exposed. Most of the spectral sensitivity data in the research literature fall short of this requirement for action spectral information because of (a) the use of pure polymers (or formulations) as opposed to typical plastic mixes used in actual applications *[Hirt and Searle, 1967; Searle, 1990; Searle et al., 1989; Fueki and Torikai, 1990]*, and (b) the use of material properties measurements which cannot be easily related to the types of damages relevant to field exposure conditions *[Munro and Allaker, 1985; Reinisch et al., 1966]* in their elucidation. Some publications identify the region of the sunlight spectrum (under present sunlight conditions) where the photodegradation is at a maximum, which is usually referred to as an activation spectrum *[Trubiroha, 1989; Searle, 1989]*.

As such, any new information on spectral sensitivities is a valuable addition to the scientific literature. This update summarizes the available data on the spectral sensitivity of materials and relates to the most damaging spectral regions of sunlight. Only those experiments where the tested property is relevant to the applications of material are listed *(see Table 6.1)*.

The table is an updated, expanded summary of the data given in the Environmental Effects Panel Report *[UNEP, 1989]*. The data relating to wood pulp as well as some of the polyethylene and polystyrene data are new. The data on the two polymers are estimates since they are based on a grade of polymer which contains additives to accelerate photodegradation *[Society of Plastics Industry, 1989]*. This allowed the action spectra to be conveniently generated in a short period of time. However, inclusion of the data herein assumes that the mechanism of degradation is essentially unchanged (merely accelerated) by the presence of a pro-oxidant additive. New spectral sensitivity studies on polycarbonates showed the 290 nm to 300 nm band to be very effective in bringing about yellowing. Any inclusion of light with a wavelength shorter than 290 nm, possibly due to ozone depletion, is likely to cause weakening, as well as a marked increase in the yellowing of polycarbonates. The data on wood pulp (unbleached newsprint paper) are for a light-induced yellowing of mechanical pulp, which has the same composition as the pine wood *(Pinus taeda)* used in its manufacture. The available spectral sensitivity data are based on discoloration and yellowing of plastics, rather than on mechanical properties, such as strength and brittleness, which are of practical relevance. Basing damage estimates on action spectra for yellowing possibly underestimates the extent of damage due to partial ozone depletion.

Light Stabilizer Effectiveness

The understanding of the mechanisms and kinetics of light stabilization of commercial plastics has advanced during the last few years. This is particularly true of the new types of stabilizers such as the hindered amine light stabilizers (HALS) *[Crouzel et al., 1989]*. However, the reported research has not included studies to determine the effectiveness of these stabilizers under exposure to sunlight with altered spectral irradiance distributions. The durability of the stabilizers themselves might be compromised under such conditions; commercial HALS are known to be photolyzed by very short wavelength UV radiation *[Chen et al., 1988]*. Also, the intensity dependence of stabilizer effectiveness has not been studied in any detail.

Table 6.1 Reported Data on Spectral Sensitivity of Commodity Thermoplastics to Yellowing and Strength Variations.

Material	Formulation	Wavelength* Range (nm)	Mode of Degradation	Action Spectrum	Activation Spectrum	Reference
PVC	rigid, white	310-325	yellowing	yes	yes	Andrady et al., 1989, 1990
	base polymer	320	yellowing	no	yes	Hirt and Searle, 1967
PC	clear	(280-600)**	yellowing	yes	no	Andrady, 1991a
	clear	300-320	yellowing	no	yes	Trubioroha, 1989
	clear	<300, 310-340	yellowing	no	yes	Andrady and Searle 1991
PP	molded sheet	315-330	tensile properties	no	no	Andrady and Searle, 1990
	molded sheet	290-400	color	no	no	Searle, 1990
PE	laminate#	~330	tensile properties	no	no	Andrady et al., 1990
	film	~310	color	no	no	Searle, 1990
PS	foam#	320-345	yellowing	no	yes	Andrady et al., 1990
ABS	laminate	300-380	yellowing	no	no	Searle, et al., 1991
Wood Pulp	newsprint	(260-600)**	yellowing	yes	yes	Andrady et al., 1990, 1991b

* Wavelength range is that where maximum damage was observed in full or partial activation spectra.

** No activation spectra available, the range is the wavelength range used in experiments.

\# Enhanced photodegradable material. The polymer was modified chemically or a prodegradant used to accelerate the photodegradation.

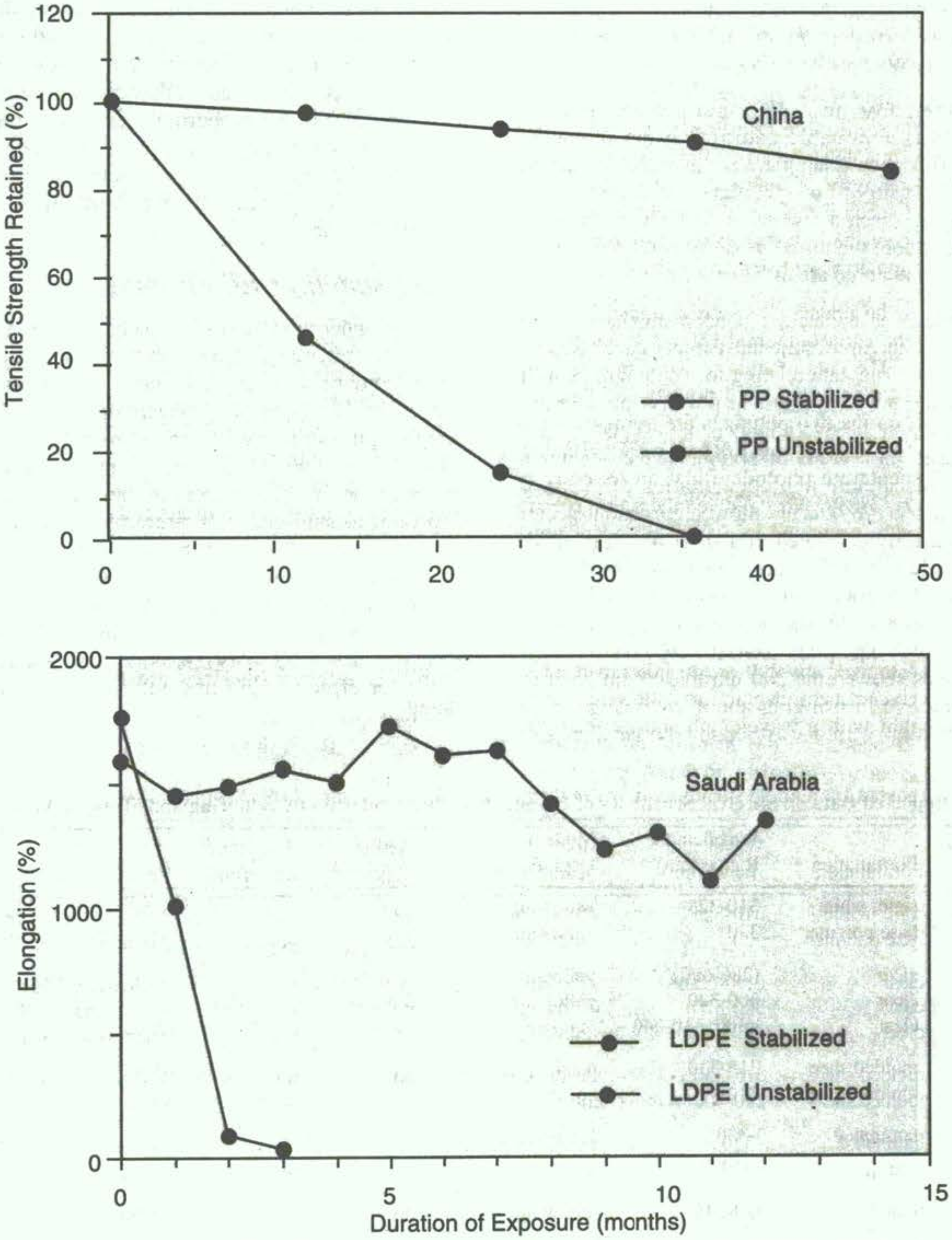

Figure 6.1 Effect of light stabilizer on weathering of polypropylene (PP) and polyethylene (PE) laminates at two (desert and tropical) locations *[Lee et al., 1991a]*

This is not surprising, as the general problem addressed by material scientists has been the extension of outdoor service life of selected plastics in the most cost-effective manner. The assumption is that the exposure conditions, with respect to the nature of light, its intensity, ambient temperature, and rainfall, have remained essentially unaltered in the long-run.

Understanding the Performance of Plastics and Wood Under Extreme Environments

In view of the extremely high levels of UV radiation, as well as temperatures associated with the near-equator regions *[Hamid et al., 1988]*, which is further increased in the event of a partial ozone layer depletion, the performance of materials at such exposure locations is of particular interest. While data which allow the separation of the photodegradation component from thermal degradation effects are needed for the present purpose, any exposure data relating to the performance of commercially relevant plastic compositions are useful. Very limited data are available in this subject area.

A significant new source of data is the research currently in progress at the Research Institute (KFUPM), Dhahran, Saudi Arabia. Studies involving plastic greenhouse films, mulch films, container samples, and pipe sections, are aimed at studying degradation under various outdoor conditions relevant to Saudi Arabia.

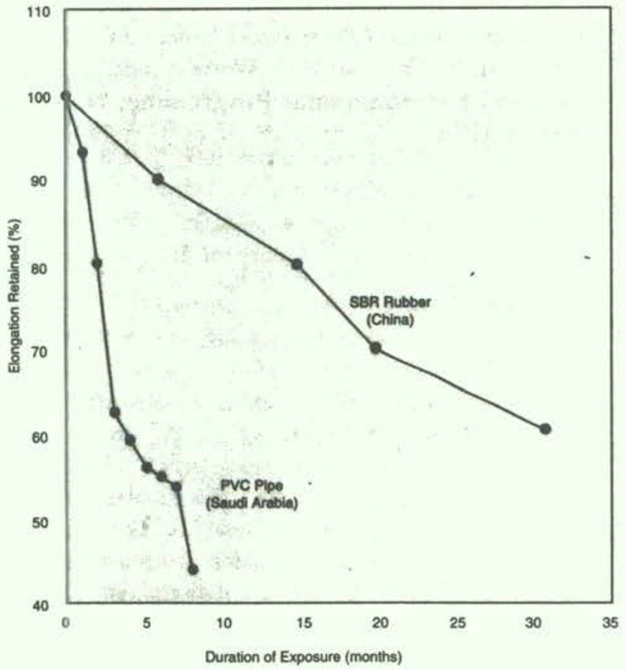

Figure 6.2 Weathering of PVC pipe sections and styrene-butadiene rubber sheets under desert and tropical exposure conditions.

The study currently generates useful data, but it is premature to draw general conclusions. The preliminary data emphasize particularly harsh weathering environments and the need for stabilizer formulations specially selected for optimum performance at different sites in the country *[Amin et al., 1991]*. Similar studies are also in progress in China.

Figure 6.1 illustrates the rapid change in tensile properties of polyolefin laminates exposed at two desert/tropical locations, Dhahran, Saudi Arabia *[Hamid, 1991]* and Hainan, China *[Lee et al., 1991]*. Data illustrate the role played by light stabilizers in current polymer formulations. *Figure 6.2* shows the weathering of plastic pipe section and a rubber formulation *[Lee et al., 1991b]* at these locations which shows the rapid degradation rates obtained. The weathering behavior of the same material at different latitudes can be used as a basis for estimating damage due to increased UV radiation. Quantitative information of this nature is available only for a few specialized plastic formulations at special pairs of locations such as Dubai and Garston, England *[Crowder and Ali, 1985]*. Even less quantitative data are available for wood materials at comparable exposure locations. The ongoing study does not include any wood or coatings as test materials. While coatings represent a low-volume use for polymers, they are nevertheless important because they protect surfaces which can be expensive to otherwise maintain or replace.

CONCLUSION

Recently reported research relating to weathering and stabilization of materials were not designed to generate data on the susceptibility of materials to spectrally altered, UV-rich sunlight. Consequently, the realistic assessment of the increased damage to materials under different scenarios of partial ozone layer depletion remains a difficult exercise.

However, several important new contributions, such as relevant action and activation spectra on materials of commercial interest, have been published. An ongoing study in Saudi Arabia designed to generate data on the weathering of actual plastic products under desert exposure is also expected to provide useful data in the coming years.

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CHAPTER 7

RESEARCH NEEDS

GENERAL RESEARCH NEEDS

- A panel should be established to evaluate specifications including wavelength span and resolution, error limits, and minimum detectable effects, as they relate to the ozone depletion problem.
- Action spectra need to be developed for various types of ocular damage (preferably in primates), biological responses, and material degradation.
- Secondary effects of ozone depletion, e.g., effects of air quality degradation, CFC substitutes, materials break down, and, in turn, their effects on the biosphere, need to be characterized.
- Studies should be undertaken on the availability of protective mechanisms and responses in organisms potentially affected by solar UV-B radiation.

SOLAR INTERACTIONS

- There is a need for global monitoring of UV-B radiation, with particular attention to long-term instrument stability, representative geographical deployment, and collocation with other measurements of atmospheric optical characteristic.
- Numerical modeling of current and future global UV-B climatology is needed, with emphasis on the assimilation of satellite and ground-based data (for ozone, clouds, aerosols, etc.) to quantify the optical state of the atmosphere.

HUMAN HEALTH

Identifed below are a number of areas that require further research.

- Studies of animal models of infectious disease with UV-B radiation.
- Studies of infectious disease epidemiology, including diseases shared by animals and man, in conjunction with UV monitoring, especially in tropical areas.
- Studies of vaccination processes in humans and animals in conjunction with UV-B exposure to evaluate whether stratospheric ozone depletion could have an impact on vaccination processes.
- Detailed exposure studies of people at various stages of life and in various activities to determine life-stage related doses of UV-B.
- Detailed studies of melanoma induction in animal and *in vitro* models to determine the dose-response relationship, action spectrum, and mechanism of transformation.
- Additional studies on the effects of UV-B on human skin, including immune function.
- Further characterization of the latitudinal distribution of important diseases, vectors, and agents.

TERRESTRIAL PLANTS

- Studies are needed to elucidate how UV-B effects are modified by additional biotic and abiotic factors, such as carbon dioxide, temperature, water and nutrient stress, heavy metals, diseases, and pests.
- The manner and magnitude of adaptation to increased UV-B, such as by increased screening pigments or enhanced DNA damage repair capacity, need to be investigated both as adaption capacity of individual plants and as genetically based changes in plant populations. The latter also provides a basis for plant breeding interventions for agricultural and tree species.
- Studies have to be made on UV-B effects on plant species composition, productivity, and plant chemical composition as these influence herbivores, pathogens, litter decomposition, and nutrient cycling.
- There is a need for sufficient information of agricultural and native plant productivity and other responses using realistic UV-B enhancements under field conditions.

- Although future relative increases in UV-B radiation are projected to be quite small in tropical latitudes, in absolute terms these regions receive the greatest UV-B flux of any location in the world. The effects of UV-B radiation on tropical crops or native plants should be addressed.

AQUATIC ECOSYSTEMS

- Research priorities continue to relate to UV-B penetration into the water column and through ice. This basic physical information should then be used both in laboratory and field research to determine effects on phytoplankton and zooplankton.
- Adaptive strategies of the plant and plankton communities need to be studied over extended periods of time as well as the effects of interactive stresses (temperature, salinity, etc.) and cumulative doses received over the lifetime of the organisms.
- Plankton effects should be modeled into broader ecosystem dynamic patterns, which will feed into models of global carbon and nitrogen cycling.

TROPOSPHERIC AIR QUALITY

- Additional measurement programs are needed to detect surface chemical changes caused by increased UV-B. This is particularly critical in populated areas of high latitude where significant stratospheric ozone depletion has been observed. The information is needed not only to set priorities in areas of significant change, but to further develop and evaluate mathematical models of the atmosphere.
- Mathematical models of the atmosphere require significant further improvement of both calculation detail and scope to ensure that all important feedback processes are included. In addition, the use of these models to predict surface conditions requires more detailed chemistry, and expanded radiative- and mass-transfer calculations.
- Additional modeling studies are needed to assess the effects of increased UV-B on specific areas of tropospheric air quality. Particular issues would include the following: (1) the impacts of urban air quality and anticipated air quality management programs, (2) changes in high latitude areas, and (3) assessment of the effects of climate changes, population growth changes, and global feedback processes.

MATERIALS DAMAGE

- Relatively little information is available on the lifetimes of plastics and wood in near-equator exposure. A comparative study of environmental photodegradation of relevant plastic materials under near-equator and far-equator conditions is needed. The study should involve exposure to (a) natural sunlight, (b) filtered sunlight, (c) UV-excluded sunlight, and (d) natural sunlight under controlled temperature conditions.
- Several important classes of materials other than plastics also will be affected by partial depletion of the ozone layer.

  a. Paints and coatings;

  b. Rubber products (tires, roofing membranes);

  c. Wood and paper products; and

  d. Textiles.

  The deleterious effect of UV radiation on these materials is generally known. But little quantitative data on their weathering behavior are available, making it impossible to produce meaningful economic projections. Such basic data need to be generated.
- Action spectra for degradation of commodity plastics formulations, as well as their dose-response information, are currently unavailable. This useful information can be obtained by exposure of plastics to a light-source in the wavelength range of 280 nm to 500 nm.

  In the case of poly(vinyl chloride), PVC, where action spectra for yellowing are available, refinements of experimental methodology are needed to account for factors such as dark reactions and temperature cycling. Experiments on degradation in UV-enriched light sources also are important to predict the effect of UV in sunlight reliably and unambiguously.
- The most likely initial response to increased UV-B content in sunlight, and consequent shortening of outdoor lifetimes of plastics, will be the use of conventional stabilizers at higher levels to further protect the plastic material. Effectiveness of these stabilizers under enhanced UV-B exposure conditions is essentially not known. The effectiveness of this strategy must be established at least for the widely used commodity plastic materials.

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APPENDIX C

UNITED NATIONS ENVIRONMENT PROGRAMME **(UNEP)**

MONTREAL PROTOCOL ON SUBSTANCES THAT DEPLETE THE OZONE LAYER

*AS ADJUSTED AND AMENDED BY THE SECOND MEETING OF THE PARTIES**

LONDON, 27-29 JUNE 1990

*NOTE: Portions of the Protocol that have changed are printed in bold type.

MONTREAL PROTOCOL ON SUBSTANCES THAT DEPLETE THE OZONE LAYER AS ADJUSTED AND AMENDED BY THE SECOND MEETING OF THE PARTIES, LONDON, 27-29 JUNE 1990

The Parties to this Protocol,

Being Parties to the Vienna Convention for the Protection of the Ozone Layer,

Mindful of their obligation under that Convention to take appropriate measures to protect human health and the environment against adverse effects resulting or likely to result from human activities which modify or are likely to modify the ozone layer,

Recognizing that world-wide emissions of certain substances can significantly deplete and otherwise modify the ozone layer in a manner that is likely to result in adverse effects on human health and the environment,

Conscious of the potential climatic effects of emissions of these substances,

Aware that measures taken to protect the ozone layer from depletion should be based on relevant scientific knowledge, taking into account technical and economic considerations,

Determined to protect the ozone layer by taking precautionary measures to control equitably total global emissions of substances that deplete it, with the ultimate objective of their elimination on the basis of developments in scientific knowledge, taking into account technical and economic considerations **and bearing in mind the developmental needs of developing countries,**

Acknowledging that special provision is required to meet the needs of developing countries [for these substances], **including the provision of additional financial resources and access to relevant technologies, bearing in mind that the magnitude of funds necessary is predictable, and the funds can be expected to make a substantial difference in the world's ability to address the scientifically established problem of ozone depletion and its harmful effects,**

Noting the precautionary measures for controlling emissions of certain chlorofluorocarbons that have already been taken at national and regional levels,

Considering the importance of promoting international co-operation in [Research and development of science and technology] **research, development and transfer of alternative technologies** relating to the control and reduction of emissions of substances that deplete the ozone layer, bearing in mind in particular the needs of developing countries,

HAVE AGREED AS FOLLOWS:

ARTICLE 1: DEFINITIONS

For the purposes of this Protocol:

1. "Convention" means the Vienna Convention for the Protection of the Ozone Layer, adopted on 22 March 1985.

2. "Parties" means, unless the text otherwise indicates, Parties to this Protocol.

3. "Secretariat" means the Secretariat of the Convention.

4. "Controlled substance" means a substance [listed] in Annex A **or in Annex B** to this Protocol, whether existing alone or in a mixture. **It includes the isomers of any such substance, except as specified in the relevant Annex**, but [it] excludes, [however] any [such] **controlled** substance or mixture which is in a manufactured product other than a container used for the transportation or storage of [the] **that** substance.

5. "Production" means the amount of controlled substances produced, minus the amount destroyed by technologies to be approved by the Parties **and minus the amount entirely used as feedstock in the manufacture of other chemicals. The amount recycled and reused is not to be considered as "production".**

6. "Consumption" means production plus imports minus exports of controlled substances.

7. "Calculated levels" of production, imports, exports and consumption means levels determined in accordance with Article 3.

8. "Industrial rationalization" means the transfer of all or a portion of the calculated level of production of one Party to another, for the purpose of achieving economic efficiencies or responding to anticipated shortfalls in supply as a result of plant closures.

9. **"Transitional substance" means a substance in Annex C to this Protocol, whether existing alone or in a mixture. It includes the isomers of any such substance, except as may be specified in Annex C, but excludes any transitional substance or mixture which is in a manufactured product other than a container used for the transportation or storage of that substance.**

ARTICLE 2: CONTROL MEASURES

1. (Incorporated in Article 2A as per the adjustments made in Second Meeting of the Parties in London in 1990).

2. Replaced by Article 2B.

3 and 4. Replaced in Article 2A.

5. **Any Party may, for one or more control periods, transfer to another Party any portion of its calculated level of production set out in Articles 2A to 2E, provided that the total combined calculated levels of production of the Parties concerned for any group of controlled substances do no exceed the production limits set out in those Articles for that group. Such transfer of production shall be notified to the Secretariat by each of the Parties concerned, stating the terms of such transfer and the period for which it is to apply.**

6. Any Party not operating under Article 5, that has facilities for the production of **Annex A** or **Annex B** controlled substances under construction, or contracted for, prior to 16 September 1987, and provided for in national legislation prior to 1 January 1987, may add the production from such facilities to its 1986 production of such substances for the purposes of determining its calculated level of production for 1986, provided that such facilities are completed by 31 December 1990 and that such production does not raise that Party's annual calculated level of consumption of the controlled substances above 0.5 kilograms per capita.

7. Any transfer of production pursuant to paragraph 5 or any addition of production pursuant to paragraph 6 shall be notified to the Secretariat, no later than the time of the transfer or addition.

8. (a) Any Parties which are Members States of a regional economic integration organization as defined in Article 1 (6) of the Convention may agree that they shall jointly fulfil their obligations respecting consumption under this Article **and Articles 2A to 2E** provided that their total combined calculated level of consumption does not exceed the levels required by this Article **and Articles 2A to 2E**.

(b) The Parties to any such agreement shall inform the Secretariat of the terms of the agreement before the date of the reduction in consumption with which the agreement is concerned.

(c) Such agreement will become operative only if all Members States of the regional economic integration organization and the organization concerned are Parties to the Protocol and have notified the Secretariat of their manner of implementation.

9. (a) Based on the assessments made pursuant to Article 6, the Parties may decide whether:

(i) Adjustments to the ozone depleting potentials specified in Annex A **and/or Annex B** should be made and, if so, what the adjustments should be; and

(ii) Further adjustments and reductions of production or consumption of the controlled substances [from 1986 levels] should be undertaken and, if so, what the scope, amount and timing of any such adjustments and reductions should be;

(b) Proposals for such adjustments shall be communicated to the Parties by the Secretariat at least six months before the meeting of the Parties at which they are proposed for adoption;

(c) In taking such decisions, the Parties shall make every effort to reach agreement by consensus. If all efforts at consensus have been exhausted, and no agreement reached, such decisions shall, as a last resort, be adopted by a two-thirds majority vote of the Parties present and voting representing [at least fifty per cent of the total consumption of the controlled substances of the Parties;] **a majority of the Parties operating under Paragraph 1 of Article 5 present and voting and a majority of the Parties not so operating present and voting.**

(d) The decisions, which shall be binding on all Parties, shall forthwith be communicated to the Parties by the Depositary. Unless otherwise provided in the decisions, they shall enter into force on the expiry of six months from the date of the circulation of the communication by the Depositary.

10. [(a)] Based on the assessments made pursuant to Article 6 of this Protocol and in accordance with the procedure set out in Article 9 of the Convention, the Parties may decide:

(i) Whether any substances, and if so which, should be added to or removed from any annex to this Protocol; and

(ii) The mechanism, scope and timing of the control measures that should apply to those substances;

[(b) Any such decisions shall become effective, provided that it has been accepted by a two-thirds majority vote of the Parties present and voting.]

11. Notwithstanding the provisions contained in this Article **and Articles 2A to 2E** Parties may take more stringent measures than those required by this Article **and Articles 2A to 2E**.

INTRODUCTION TO THE ADJUSTMENTS

The Second Meeting of the Parties to the Montreal Protocol on Substances that Deplete the Ozone Layer decides, on the basis of assessments made pursuant to Article 6 of the Protocol, to adopt adjustments and reductions of production and consumption of the controlled substances in Annex A to the Protocol, as follows, with the understanding that:

(a) References in Article 2 to "this Article" and throughout the Protocol to "Article 2" shall be interpreted as references to Articles 2, 2A and 2B;

(b) References throughout the Protocol to "paragraphs 1 to 4 of Article 2" shall be interpreted as references to Articles 2A and 2B; and

(c) The reference in paragraph 5 of Article 2 to "paragraphs 1, 3 and 4" shall be interpreted as a reference to Article 2A.

ARTICLE 2A: CFCs

1. Each Party shall ensure that for the twelve-month period commencing on the first day of the seventh month following the date of entry into force of this Protocol, and in each twelve-month period thereafter, its calculated level of consumption of the controlled substances in Group I of Annex A does not exceed its calculated level of consumption in 1986. By the end of the same period, each Party producing one or more of these substances shall ensure that its calculated level of production of the substances does not exceed its calculated level of production in 1986, except that such level may have increased by no more than ten per cent based on the 1986 level. Such increase shall be permitted only so as to satisfy the basic domestic needs of the Parties operating under Article 5 and for the purposes of industrial rationalization between Parties.

2. Each Party shall ensure that for the period from 1 July 1991 to 31 December 1992 its calculated levels of consumption and production of the controlled substances in Group I of Annex A do not exceed 150 per cent of its calculated levels of production and consumption of those substances in 1986; with effect from 1 January 1993, the twelve-month control period for these controlled substances shall run from 1 January to 31 December each year.

3. Each Party shall ensure that for the twelve-month period commencing on 1 January 1995, and in each twelve-month period thereafter, its calculated level of consumption of the controlled substances in Group I of Annex A does not exceed, annually, fifty percent of its calculated level of consumption in 1986. Each Party producing one or more of these substances shall, for the same periods, ensure that its calculated level of production of the substances does not exceed, annually, fifty per cent of its calculated level of production in 1986. However, in order to satisfy the basic domestic needs of the Parties operating under paragraph 1 of Article 5, its calculated level of production may exceed that limit by up to ten per cent of its calculated level of production in 1986.

4. Each Party shall ensure that for the twelve-month period commencing on 1 January 1997, and in each twelve-month period thereafter, its calculated level of consumption of the controlled substances in Group I of Annex A does not exceed, annually, fifteen per cent of its calculated level of consumption in 1986. Each Party producing one or more of these substances shall, for the same periods, ensure that its calculated level of production of the substances does not exceed, annually, fifteen per cent its calculated level of production in 1986. However, in order to satisfy the basic domestic needs to the Parties operating under paragraph 1 of Article 5, its calculated level of production in 1986.

5. Each Party shall ensure that for the twelve-month period commencing on 1 January 2000, and in each twelve-month period thereafter, its calculated level of consumption of the controlled substances in Group I of Annex A does not exceed zero. Each Party producing one or more of these substances shall, for the same periods, ensure that its calculated level of production of the substances does not exceed zero. However, in order to satisfy the basic domestic needs of the Parties operating under paragraph 1 of Article 5, its calculated level of the production may exceed that limit by up to fifteen per cent of its calculated level of production in 1986.

6. In 1992, the Parties will review the situation with the objective of accelerating the reduction schedule.

ARTICLE 2B: HALONS

1. Each Party shall ensure that for the twelve-month period commencing on 1 January 1992, and in each twelve-month period thereafter, its calculated level of consumption of the controlled substances in Group II of Annex A does not exceed, annually, its calculated level of consumption in 1986. Each Party producing one or more of these substances shall, for the same periods, ensure that its calculated level of production of the substances does not exceed, annually, its calculated level of production in 1986. However, in order to satisfy the basic needs of the Parties operating under paragraph 1 of Article 5, its calculated level of production may exceed that limit by up to ten per cent of its calculated level of production in 1986.

2. Each Party shall ensure that for the twelve-month period commencing on 1 January 1995, and in each *twelve-month period thereafter, its calculated level of consumption of the controlled substances in Group II of Annex A does not exceed, annually, fifty per cent of its calculated level of consumption in 1986. Each Party producing one or more of these substances shall, for the same periods, ensure that its calculated level of production of the substances does not exceed, annually, fifty per cent of its calculated level of production in 1986. However, in order to satisfy the basic domestic needs of the Parties operating under paragraph 1 of Article 5, its calculated level of production may exceed that limit by up to ten per cent of its calculated level of production in 1986. This paragraph will apply save to the extent that the Parties decide to permit the level of production or consumption that is necessary to satisfy essential uses for which no adequate alternatives are available.*

3. Each Party shall ensure that for the twelve-month period commencing on 1 January 2000, and in each twelve-month period thereafter, its calculated level of consumption of the controlled substances in Group II of Annex A does not exceed zero. Each Party producing one or more of these substances shall, for the same periods, ensure that its calculated level of production of the substances does not exceed zero. However, in order to satisfy the basic domestic needs of the Parties operating under paragraph 1 of Article 5, its calculated level of production may exceed that limit by up to fifteen per cent of its calculated level of production in 1986. This paragraph will apply save to the extent that the Parties decide to permit the level of production or consumption that is necessary to satisfy essential uses for which no adequate alternatives are available.

4. By 1 January 1993, the Parties shall adopt a decision identifying essential uses, if any, for the purposes of paragraphs 2 and 3 of this Article. Such decision shall be reviewed by the Parties at their subsequent meetings.

ARTICLE 2C: OTHER FULLY HALOGENATED CFCs

1. Each Party shall ensure that for the twelve-month period commencing on 1 January 1993, and in each twelve-month period thereafter, its calculated level of consumption of the controlled substances in Group I of Annex B does not exceed, annually, eighty per cent of its calculated level of consumption in 1989. Each Party producing one or more of these substances shall, for the same periods, ensure that its calculated level of production of the substances does not exceed, annually, eighty per cent of its calculated level of production in 1989. However, in order to satisfy the basic domestic needs of the Parties operating under paragraph 1 of Article 5, its calculated level of production may exceed that limit by up to ten per cent of its calculated level of production in 1989.

2. Each Party shall ensure that for the twelve-month period commencing on 1 January 1997, and in each twelve-month period thereafter, its calculated level of consumption of the controlled substances in Group I of Annex B does not exceed, annually, fifteen per cent of its calculated level of consumption in 1989. Each Party producing one or more of these substances shall, for the same periods, ensure that its calculated level of production of the substances does not exceed, annually, fifteen per cent of its calculated level of production in 1989. However, in order to satisfy the basic domestic needs of the Parties operating under paragraph 1 of Article 5, its calculated level of production may exceed that limit by up to ten per cent of its calculated level of production in 1989.

3. Each Party shall ensure that for the twelve-month period commencing on 1 January 2000, and in each twelve-month period thereafter, its calculated level of consumption of the controlled substances in Group I of Annex B does not exceed zero. Each Party producing one or more of these substances shall, for the same periods, ensure that its calculated level of production of the substances does not exceed zero. However, in order to satisfy the basic domestic needs of the Parties operating under paragraph 1 of Article 5, its calculated level of production may exceed that limit by up to fifteen per cent of its calculated level of production in 1989.

ARTICLE 2D: CARBON TETRACHLORIDE

1. Each Party shall ensure that for the twelve-month period commencing on 1 January 1995, and in each twelve-month period thereafter, its calculated level of consumption of the controlled substance in Group II of Annex B does not exceed, annually, fifteen per cent of its calculated level of consumption in 1989. Each Party producing the substance shall, for the same periods, ensure that its calculated level of production of the substance does not exceed, annually, fifteen per cent of its calculated level of production in 1989. However, in order to satisfy the basic domestic needs of the Parties operating under paragraph 1 of Article 5, its calculated level of production may exceed that limit by up to ten per cent of its calculated level of production in 1989.

2. Each Party shall ensure that for the twelve-month period commencing on 1 January 2000, and in each twelve-month period thereafter, its calculated level of consumption of the controlled substance in Group II of Annex B does not exceed zero. Each Party producing

the substance shall, for the same periods, ensure that its calculated level of production of the substance does not exceed zero. However, in order to satisfy the basic domestic needs of the Parties operating under paragraph 1 of Article 5, its calculated level of production may exceed that limit by up to fifteen per cent of its calculated level of production in 1989.

ARTICLE 2E: 1,1,1 - TRICHLOROETHANE (METHYL CHLORORFORM)

1. Each Party shall ensure that for the twelve-month period commencing on 1 January 1993, and in each twelve-month period thereafter, its calculated level of consumption of the controlled substance in Group III of Annex B does not exceed, annually, its calculated level of consumption in 1989. Each Party producing the substance shall, for the same periods, ensure that its calculated level of production of the substance does not exceed, annually, its calculated level of production in 1989. However, in order to satisfy the basic domestic needs of the Parties operating under paragraph 1 of Article 5, its calculated level of production may exceed that limit by up to ten per cent of its calculated level of production in 1989.

2. Each Party shall ensure that for the twelve-month period commencing on 1 January 1995, and in each twelve-month period thereafter, its calculated level of consumption of the controlled substance in Group III of Annex B does not exceed, annually, seventy per cent of its calculated level of consumption in 1989. Each Party producing the substance shall, for the same periods, ensure that its calculated level of production of the substance does not exceed, annually, seventy per cent of its calculated level of consumption in 1989. However, in order to satisfy the basic domestic needs of the Parties operating under paragraph 1 of Article 5, its calculated level of production may exceed that limit by up to ten per cent of its calculated level of production in 1989.

3. Each Party shall ensure that for the twelve-month period commencing on 1 January 2000, and in each twelve-month period thereafter, its calculated level of consumption of the controlled substance in Group III of Annex B does not exceed, annually, thirty per cent of its calculated level of consumption in 1989. Each Party producing the substance shall, for the same periods, ensure that its calculated level of production of the substances does not exceed, annually, thirty per cent of its calculated level of production in 1989. However, in order to satisfy the basic domestic needs of Parties operating under paragraph 1 of Article 5, its calculated level of production may exceed that limit by up to ten per cent of its calculated level of production in 1989.

4. Each Party shall ensure that for the twelve-month period commencing on 1 January 2005, and in each twelve-month period thereafter, its calculated level of consumption of the controlled substance in Group III of Annex B does not exceed zero. Each Party producing the substance shall, for the same periods, ensure that its calculated level of production of the substance does not exceed zero. However, in order to satisfy the basic domestic needs of the Parties operating under paragraph 1 of Article 5, its calculated level of production may exceed that limit by up to fifteen per cent of its calculated level of production in 1989.

5. The Parties shall review, in 1992, the feasibility of a more rapid schedule of reductions than that set out in this Article.

ARTICLE 3: CALCULATION OF CONTROL LEVELS

For the purposes of Articles 2, **2A to 2E** and 5, each Party shall, for each group of substances in Annex A or Annex B, determine its calculated levels of:

(a) Production by:

(i) Multiplying its annual production of each controlled substance by the ozone depleting potential specified in respect of it in Annex A or **Annex B**;

(ii) Adding together, for each such Group, the resulting figures;

(b) Imports and exports, respectively, by following, mutatis mutandis, the procedure set out in subparagraph (a); and

(c) Consumption by adding together its calculated levels of production and imports and subtracting its calculated level of exports as determined in accordance with subparagraphs (a) and (b). However, beginning on 1 January 1993, any export of controlled substances to non-Parties shall not be subtracted in calculating the consumption level of the exporting Party.

ARTICLE 4: CONTROL OF TRADE WITH NON-PARTIES

[1. Within one year of the entry into force of this Protocol, each Party shall ban the import of controlled substances from any State not Party to this Protocol.

2. Beginning on 1 January 1993, no Party operating under paragraph 1 of Article 5 may export any controlled substance to any State not Party to this Protocol.

3. Within three years of the date of entry into force of this Protocol, the Parties shall, following the procedure in Article 10 of the Convention, elaborate in an annex a list of products containing controlled substances. Parties that have not objected to the annex in accordance with those procedures shall ban, within one year of the annex having become effective, the import of those products from any State not party to this Protocol.]

[4. Within five years of the entry into force of this Protocol, the Parties shall determine the feasibility of banning or restricting, from States not party to this Protocol, the import of products produced with, but not containing, controlled substances. If determined feasible, the Parties shall, following the procedures in Article 10 of the Convention, elaborate in an annex a list of such products. Parties that have not objected to it in accordance with those procedures shall ban or restrict, within one year of the annex having become effective, the import of those products from any State not party to this Protocol.

5. Each Party shall discourage the export, to any State not party to this Protocol, of technology for producing and for utilizing controlled substances.]

1. As of January 1990, each party shall ban the import of the controlled substances in Annex A from any State not Party to this Protocol.

1 bis. Within one year of the date of the entry into force of this paragraph, each Party shall ban the import of the controlled substances in Annex B from any State not party to this Protocol.

2. As of 1 January 1993, each Party shall ban the export of any controlled substances in Annex A to any State not party to this Protocol.

2 bis. Commencing one year after the date of entry into force of this paragraph, each Party shall ban the export of any controlled substances in Annex B to any State not party to this Protocol.

3. By 1 January 1992, the Parties shall, following the procedures in Article 10 of the Convention, elaborate in an annex a list of products containing controlled substances in Annex A. Parties that have not objected to the annex in accordance with those procedures shall ban, within one year of the annex having become effective, the import of those products from any State not party to this Protocol.

3 bis. Within three years of the date of the entry into force of this paragraph, the Parties shall, following the procedures in Article 10 of the Convention, elaborate in an annex a list of products containing controlled substances in Annex B. Parties that have not objected to the annex in accordance with those procedures shall ban, within one year of the annex having become effective, the import of those products from any State not party to this Protocol.

4. By 1 January 1994, the Parties shall determine the feasibility of banning or restricting, from States not party to this Protocol, the import of products produced with, but not containing, controlled substances in Annex A. If determined feasible, the Parties shall, following the procedures in Article 10 of the Convention, elaborate in an annex a list of such products. Parties that have not objected to the annex in accordance with those procedures shall ban, within one year of the annex having become effective, the import of those products from any State not party to this Protocol.

4 bis. Within five years of the date of the entry into force of this paragraph, the Parties shall determine the feasibility of banning or restricting, from States not party to this Protocol, the import of products produced with, but not containing, controlled substances in Annex B. If determined feasible, the Parties shall, following the procedures in Article 10 of the Convention, elaborate in an annex a list of such products. Parties that have not objected to the annex in accordance with those procedures shall ban or restrict, within one year of the annex having become effective, the import of those products from any State not party to this Protocol.

5. Each Party undertakes to the fullest practicable extent to discourage the export to any State not party to this Protocol of technology for producing and for utilizing controlled substances.

6. Each Party shall refrain from providing new subsidies, aid, credits, guarantees or insurance programmes for the export to States not party to this Protocol of products, equipment, plants or technology that would facilitate the production of controlled substances.

7. Paragraphs 5 and 6 shall not apply to products, equipment, plants or technology that improve the containment, recovery, recycling or destruction of controlled substances, promote the development of alternative substances, or otherwise contribute to the reduction of emissions of controlled substances.

8. Notwithstanding the provisions of this Article, imports referred to in paragraphs 1, **1 bis**, 3, **3 bis**, 4, **and 4 bis and exports referred to Paragraphs 2 and 2 bis** may be permitted from, or to, any State not party to this Protocol if that State is determined, by a meeting of the Parties, to be in full compliance with Article 2, **Articles 2A to 2E** and this Article, and [has] have submitted data to that effect as specified in Article 7.

9. For the purposes of this Article, the term "State not Party to this Protocol" shall include, with respect to a particular controlled substance, a State or regional economic integration organization that has not agreed to be bound by the control measures in effect for that substance.

ARTICLE 5: SPECIAL SITUATION OF DEVELOPING COUNTRIES

1. Any Party that is a developing country and whose annual calculated level of consumption of the controlled substances **in Annex A** is less that 0.3 kilograms per capita on the date of the entry into force of the Protocol for it, or any time thereafter [within ten years of the date of entry into force of the Protocol] **until 1 January 1999** shall, in order to meet its basic domestic needs, be entitled to delay **for ten years** its compliance with the control measures set out in **Articles 2A to 2E** [paragraphs 1 to 4 of Article 2 by ten years after that specified in those paragraphs]. [However, such Party shall not exceed an annual calculated level of consumption of 0.3 kilograms per capita. Any such Party shall be entitled to use either the average of its annual calculated level of consumption for the period of 1995 to 1997 inclusive or a calculated level of consumption of 0.3 kilograms per capita, whichever is the lower, as the basis for its compliance with the control measures].

[2. The Parties undertake to facilitate access to environmentally safe alternative substances and technology for Parties that are developing countries and assist them to make expeditious use of such alternatives.]

[3. The Parties undertake to facilitate bilaterally or multilaterally the provision of subsides, aid, credits, guarantee or insurance programmes to Parties that are developing countries for the use of alternative technology and for substitute products.]

2. However, any Party operating under paragraph 1 of this Article shall exceed neither an annual calculated level of consumption of the controlled substances in Annex A of 0.3 kilograms per capita nor an annual calculated level of consumption of controlled substances of Annex B of 0.2 kilograms per capita.

3. When implementing the control measures set out in Articles 2A to 2E, any Party operating under paragraph 1 of this Article shall be entitled to use:

(a) For controlled substances under Annex A, either the average of its annual calculated level of consumption for the period 1995 to 1997 inclusive or a calculated level of consumption of 0.3 kilograms per capita, whichever is the lower, as the basis for determining its compliance with the control measures.

(b) For controlled substances under Annex B, the average of its annual calculated level consumption for the period 1998 to 2000 inclusive or a calculated level of consumption of 0.2 kilograms per capita, whichever is the lower, as the basis for determining its compliance with the control measures.

4. If a Party operating under paragraph 1 of this Article, at any time before the control measures obligations in Articles 2A to 2E become applicable to it, finds itself unable to obtain an adequate supply of controlled substances, it may notify this to the Secretariat. The Secretariat shall forthwith transmit a copy of such notification to the Parties, which shall consider the matter at their next Meeting, and decide upon appropriate action to be taken.

5. Developing the capacity to fulfil the obligations of the Parties operating under paragraph 1 of this Article to comply with the control measures set out in Articles 2A to 2E and their implementation by those same Parties will depend upon the effective implementation of the financial co-operation as provided by Article 10 and the transfer of technology as provided by Article l0A.

6. Any Party operating under paragraph 1 of this Article may, at any time, notify the Secretariat in writing that, having taken all practicable steps it is unable to implement any or all of the obligations laid down in Articles 2A to 2E due to the inadequate implementation of Articles 10 and l0A. The Secretariat shall forthwith transmit a copy of the notification to the Parties, which shall consider the matter at their next Meeting, giving due recognition to paragraph 5 of this Article and shall decide upon appropriate action to be taken.

7. During the period between notification and the Meeting of the Parties at which the appropriate action referred to in paragraph 6 above is to be decided, or for a further period if the Meeting of the Parties so decides, the non-compliance procedures referred to in Article 8 shall not be invoked against the notifying Party.

8. A Meeting of the Parties shall review, not later than 1995, the situation of the Parties operating under paragraph 1 of this Article, including the effective implementation of financial co-operation and transfer of technology to them, and adopt such revisions that may be deemed necessary regarding

the schedule of control measures applicable to those Parties.

9. Decisions of the Parties referred to in paragraphs 4, 6 and 7 of this Article shall be taken according to the same procedure applied to decision-making under Article 10.

ARTICLE 6: ASSESSMENT AND REVIEW OF CONTROL MEASURES

Beginning in 1990, and at least every four years thereafter, the Parties shall assess the control measures provided for in Article 2 **and Articles 2A to 2E, and the situation regarding production, imports and exports of the transitional substances in Group I of Annex C** on the basis of available scientific, environmental, technical and economic information. At least one year before each assessment, the Parties shall convene appropriate panels of experts qualified in the fields mentioned and determine the composition and terms of reference of any such panels. Within one year of being convened, the panels will report their conclusions, through the Secretariat, to the Parties.

ARTICLE 7: REPORTING OF DATA

1. Each Party shall provide to the Secretariat, within three months of becoming a Party, statistical data on its production, imports and exports of each of the controlled substances **in Annex A** for the year 1986, or the best possible estimate of such data where actual data are not available.

[2. Each Party shall provide statistical data to the Secretariat on its annual production (with separate data on amounts destroyed by technologies to be approved by the Parties), imports, and exports to Parties and non-Parties, respectively, of such substances for the year during which it becomes a Party and for each year thereafter. It shall forward the data no later than nine months after the end of the year to which the data relate.]

2. Each Party shall provide to the Secretariat statistical data on its production, imports and exports of each of the controlled substances in Annex B and each of the transitional substances in Group I of Annex C, for the year 1989, or the best possible estimates of such data where actual data are available, not later than three months after the date when the provisions set out in the Protocol with regard to the substances in Annex B enter into force for that Party.

3. Each Party shall provide statistical data to the Secretariat on its annual production (as defined in paragraph 5 of Article 1), and, separately,

- **amounts used for feedstocks,**
- **amounts destroyed by technologies approved by the Parties,**
- **imports and exports to Parties and non-Parties respectively,**

of each of the controlled substances listed in Annexes A and B as well as of the transitional substances in Group I of Annex C, for the year during which provisions concerning the substances in Annex B entered into force for that Party and for each year thereafter. Data shall be forwarded not later than nine months after the end of the year to which the data relate.

4. For Parties operating under the provisions of paragraph 8 (a) of Article 2, the requirements in paragraphs 1, 2 and 3 of this Article in respect of statistical data on imports and exports shall be satisfied if the regional economic integration organization concerned provides data on imports and exports between the organization and States that are not members of that organization.

ARTICLE 8: NON-COMPLIANCE

The Parties, at their first meeting, shall consider and approve procedures and institutional mechanisms for determining non-compliance with the provisions of this Protocol and for treatment of Parties found to be in non-compliance.

ARTICLE 9: RESEARCH, DEVELOPMENT, PUBLIC AWARENESS AND EXCHANGE OF INFORMATION

1. The Parties shall co-operate, consistent with their national laws, regulations and practices and taking into account in particular the needs of developing countries, in promoting, directly or through competent international bodies, research, development and exchange of information on:

(a) Best technologies for improving the containment, recovery, recycling, or destruction of controlled **and transitional substances** or otherwise reducing their emissions;

(b) Possible alternatives to controlled substances, to products containing such substances, and to products manufactured with them; and

(c) Costs and benefits of relevant control strategies.

2. The Parties, individually, jointly or through competent international bodies, shall co-operate in

promoting public awareness of the environmental effects of the emissions of controlled substances and other substances that deplete the ozone layer.

3. Within two years of the entry into force of this Protocol and every two years thereafter, each Party shall submit to the Secretariat a summary of the activities it has conducted pursuant to this Article.

[ARTICLE 10: TECHNICAL ASSISTANCE

1. The Parties shall in the context of the provisions of Article 4 of the Convention, and taking into account in particular the needs of developing countries, co-operate in promoting technical assistance to facilitate participation in and implementation of this Protocol.

2. Any Party of Signatory of this Protocol may submit a request to the Secretariat for technical assistance for the purposes of implementing or participating in the Protocol.

3. The Parties, at their first meeting, shall begin deliberations on the means of fulfilling the obligations set out in Article 9, and paragraphs 1 and 2 of this Article, including the preparation of workplans. Such workplans shall pay special attention to the needs and circumstances of the developing countries. States and regional economic integration organizations not party to the Protocol should be encouraged to participate in activities specified in such workplans.]

ARTICLE 10: FINANCIAL MECHANISM

1. The Parties shall establish a mechanism for the purposes of providing financial and technical co-operation, including the transfer of technologies, to Parties operating under paragraph 1 of Article 5 of this Protocol to enable their compliance with the control measures set out in Articles 2A to 2E of the Protocol. The mechanism, contributions to which shall be additional to other financial transfers to Parties operating under that paragraph, shall meet all agreed incremental costs of such Parties in order to enable their compliance with the control measures of the Protocol. An indicative list of the categories of incremental costs shall be decided by the meeting of the Parties.

2. The mechanism established under paragraph 1 shall include a Multilateral Fund. It may also include other means of multilateral, regional and bilateral co-operation.

3. The Multilateral Fund shall:

(a) Meet, on a grant or concessional basis as appropriate, and according to criteria to be decided upon by the Parties, the agreed incremental costs;

(b) Finance clearing-house functions to:

(i) Assist Parties operating under paragraph 1 of Article 5, through country specific studies and other technical co-operation, to identify their needs for co-operation;

(ii) Facilitate technical co-operation to meet these identified needs;

(iii) Distribute, as provided for in Article 9, information and relevant materials, and hold workshops, training sessions, and other related activities, for the benefit of Parties that are developing countries; and

(iv) Facilitate and monitor other multilateral, regional and bilateral co-operation available to Parties that are developing countries;

(c) Finance the secretarial services of the Multilateral Fund and related support costs.

4. The Multilateral Fund shall operate under the authority of the Parties who shall decide on its overall policies.

5. The Parties shall establish an Executive Committee to develop and monitor the implementation of specific operational policies, guidelines and administrative arrangements, including the disbursement of resources, for the purpose of achieving the objectives of the Multilateral Fund. The Executive Committee shall discharge its tasks and responsibilities, specified in its terms of reference as agreed by the Parties, with the co-operation and assistance of the International Bank for Reconstruction and Development (World Bank), the United Nations Environment Programme, the United Nations Development Programme or other appropriate agencies depending on their respective areas of expertise. The members of the Executive Committee, which shall be selected on the basis of a balanced representation of the Parties operating under paragraph 1 of Article 5 and of the Parties not so operating, shall be endorsed by the Parties.

6. The Multilateral Fund shall be financed by contributions from Parties not operating under paragraph 1 of Article 5 in convertible currency or, in certain circumstances, in kind and/or in national currency, on the basis of the United Nations scale of assessments. Contributions by other Parties shall be encouraged. Bilateral and, in particular cases agreed by a decision of the Parties, regional co-operation may, up to a percentage and consistent with any criteria to be specified by decision of the Parties, be considered as a contribution to the Multilateral

Fund, provided that such co-operation, as a minimum:

(a) Strictly relates to compliance with the provisions of this Protocol;

(b) Provides additional resources; and

(c) Meets agreed incremental costs.

7. The Parties shall decide upon the programme budget of the Multilateral Fund for each fiscal period and upon the percentage of contributions of the individual Parties thereto.

8. Resources under the Multilateral Fund shall be disbursed with the concurrence of the beneficiary Party.

9. Decisions by the Parties under this Article shall be taken by consensus whenever possible. If all efforts at consensus have been exhausted and no agreement reached, decisions shall be adopted by a two-thirds majority vote of the Parties present and voting, representing a majority of the Parties operating under paragraph 1 of Article 5 present and voting and a majority of the Parties not so operating present and voting.

10. The financial mechanism set out in this Article is without prejudice to any future arrangements that may be developed with respect to other environmental issues.

ARTICLE 10A: TRANSFER OF TECHNOLOGY

Each Party shall take every practicable step, consistent with the programmes supported by the financial mechanism, to ensure:

(a) That the best available, environmentally safe substitutes and related technologies are expeditiously transferred to Parties operating under paragraph 1 of Article 5; and

(b) That the transfers referred to in subparagraph (a) occur under fair and most favourable conditions.

ARTICLE 11: MEETINGS OF THE PARTIES

1. The Parties shall hold meetings at regular intervals. The Secretariat shall convene the first meeting of the Parties not later than one year after the date of the entry into force of this Protocol and in conjunction with a meeting of the Conference of the Parties to the Convention, if a meeting of the latter is scheduled within that period.

2. Subsequent ordinary meetings of the parties shall be held, unless the Parties otherwise decide, in conjunction with meetings of the Conference of the Parties to the Convention. Extraordinary meetings of the Parties shall be held at such other times as may be deemed necessary by a meeting of the Parties, or at the written request of any Party, provided that within six months of such a request being communicated to them by the Secretariat, it is supported by at least one third of the Parties.

3. The Parties, at their first meeting, shall:

(a) Adopt by consensus rules of procedure for their meetings;

(b) Adopt by consensus the financial rules referred to in paragraph 2 of Article 13;

(c) Establish the panels and determine the terms of reference referred to in Article 6;

(d) Consider and approve the procedures and institutional mechanisms specified in Article 8; and

(e) Begin preparation of workplans pursuant to paragraph 3 of Article 10.

4. The functions of meetings of the Parties shall be to:

(a) Review the implementation of this Protocol;

(b) Decide on any adjustments or reductions referred to in paragraph 9 of Article 2;

(c) Decide on any addition to, insertion in or removal from any annex of substances and on related control measures in accordance with paragraph 10 of Article 2;

(d) Establish, where necessary, guidelines on procedures for reporting of information as provided for in Article 7 and paragraph 3 of Article 9;

(e) Review requests for technical assistance submitted pursuant to paragraph 2 of Article 10;

(f) Review reports prepared by the Secretariat pursuant to subparagraph (c) of Article 12;

(g) Assess, in accordance with Article 6, the control measures **and the situation regarding transitional substances** [provided for in Article 2];

(h) Consider and adopt, as required, proposals for amendment of this Protocol or any annex and for any new annex;

(i) Consider and adopt the budget for implementing this Protocol; and

(j) Consider and undertake any additional action that may be required for the achievement of the purposes of this Protocol.

5. The United Nations, its specialized agencies and the International Atomic Energy Agency, as well as any State not party to this Protocol, may be represented at meetings of the Parties as observers. Any body or agency, whether national or international, governmental or non-governmental, qualified in fields relating to the protection of the ozone layer which has informed the Secretariat of its wish to be represented at a meeting of the Parties as an observer may be admitted unless at least one third of the Parties present object. The admission and participation of observers shall be subject to the rules of procedure adopted by the Parties.

ARTICLE 12: SECRETARIAT

For the purposes of this Protocol, the Secretariat shall:

(a) Arrange for and service meetings of the Parties as provided for in Article 11;

(b) Receive and make available, upon request by a Party, data provided pursuant to Article 7;

(c) Prepare and distribute regularly to the Parties reports based on information received pursuant to Articles 7 and 9;

(d) Notify the Parties of any request for technical assistance received pursuant to Article 10 so as to facilitate the provision of such assistance;

(e) Encourage non-Parties to attend the meetings of the Parties as observers and to act in accordance with the provisions of this Protocol;

(f) Provide, as appropriate, the information and request referred to in subparagraphs (c) and (d) to such non-party observers; and

(g) Perform such other functions for the achievement of the purposes of this Protocol as may be assigned to it by the Parties.

ARTICLE 13: FINANCIAL PROVISIONS

1. The funds required for the operation of this Protocol, including those for the functioning of the Secretariat related to this Protocol, shall be charged exclusively against contributions from the Parties.

2. The Parties, at their first meeting, shall adopt by consensus financial rules for the operation of this Protocol.

ARTICLE 14: RELATIONSHIP OF THIS PROTOCOL TO THE CONVENTION

Except as otherwise provided in this Protocol, the provisions of the Convention relating to its protocols shall apply to this Protocol.

ARTICLE 15: SIGNATURE

This Protocol shall be open for signature by States and by regional economic integration organizations in Montreal on 16 September 1987, in Ottawa from 17 September 1987 to 16 January 1988, and at United Nations Headquarters in New York from 17 January 1988 to 15 September 1988.

ARTICLE 16: ENTRY INTO FORCE

1. This Protocol shall enter into force on 1 January 1989, provided that at least eleven instruments of ratification, acceptance, approval of the Protocol or accession thereto have been deposited by States or regional economic integration organizations representing at least two-thirds of 1986 estimated global consumption of the controlled substances, and the provisions of paragraph 1 of Article 17 of the Convention have been fulfilled. In the event that these conditions have not been fulfilled by that date, the Protocol shall enter into force on the ninetieth day following the date on which the conditions have been fulfilled.

2. For the purposes of paragraph 1, any such instrument deposited by a regional economic integration organization shall not be counted as additional to those deposited by member States of such organization.

3. After the entry into force of this Protocol, any State or regional economic integration organization shall become a Party to it on the ninetieth day following the date of deposit of its instrument of ratification, acceptance, approval or accession.

ARTICLE 17: PARTIES JOINING AFTER ENTRY INTO FORCE

Subject to Article 5, any State or regional economic integration organization which becomes a Party to this Protocol after the date of its entry into force, shall fulfil forthwith the sum of the obligations under Article 2, as well as under **Articles 2A to 2E**, and Article 4, that apply at that date to the States and regional economic integration organizations that became Parties on the date the Protocol entered into force.

ARTICLE 18: RESERVATIONS

No reservations may be made to this Protocol.

[ARTICLE 19: WITHDRAWAL

For the purposes of this Protocol, the provisions of Article 19 of the Convention relating to withdrawal shall apply, except with respect to Parties referred to in paragraph 1 of Article 5. Any such Party may withdraw from this Protocol by giving written notification to the Depositary at any time after four years of assuming the obligations specified in paragraphs 1 to 4 of Article 2. Any such withdrawal shall take effect upon expiry of one year after the date of its receipt by the Depositary, or on such later date as may be specified in the notification of the withdrawal.]

ARTICLE 19: WITHDRAWAL

Any Party may withdraw from this Protocol by giving written notification to the Depositary at any time after four years of assuming the obligations specified in paragraph 1 of Article 2A. Any such withdrawal shall take effect upon expiry of one year after the date of its receipt by the Depositary, or on such later date as may be specified in the notification of the withdrawal.

ARTICLE 20: AUTHENTIC TEXTS

The original of this Protocol, of which the Arabic, Chinese, English, French, Russian and Spanish texts are equally authentic, shall be deposited with the Secretary-General of the United Nations.

IN WITNESS WHEREOF THE UNDERSIGNED, BEING DULY AUTHORIZED TO THAT EFFECT, HAVE SIGNED THIS PROTOCOL.

DONE AT MONTREAL THIS SIXTEENTH DAY OF SEPTEMBER, ONE THOUSAND NINE HUNDRED AND EIGHTY SEVEN.

Annex A

CONTROLLED SUBSTANCES

Group	Substances	Ozone Depleting Potential*/
Group I		
$CFCl_3$	(CFC-11)	1.0
CF_2Cl_2	(CFC-12)	1.0
$C_2F_3Cl_3$	(CFC-113)	0.8
$C_2F_4Cl_2$	(CFC-114)	1.0
C_2F_5Cl	(CFC-115)	0.6
Group II		
CF_2BrCl	(halon-1211)	3.0
CF_3Br	(halon-1301)	10.0
$C_2F_4Br_2$	(halon-2402)	6.0

*/ These ozone depleting potentials are estimates based on existing knowledge and will be reviewed and revised periodically.

Annex B

CONTROLLED SUBSTANCES

Group	Substances	Ozone Depleting Potential
Group I		
CF_3Cl	(CFC-13)	1.0
C_2FCl_5	(CFC-111)	1.0
$C_2F_2Cl_4$	(CFC-112)	1.0
C_3FCl_7	(CFC-211)	1.0
$C_3F_2Cl_6$	(CFC-212)	1.0
$C_3F_3Cl_5$	(CFC-213)	1.0
$C_3F_4Cl_4$	(CFC-214)	1.0
$C_3F_5Cl_3$	(CFC-215)	1.0
$C_3F_6Cl_2$	(CFC-216)	1.0
C_3F_7Cl	(CFC-217)	1.0
Group II		
CCl_4	carbon tetrachloride	1.1
Group III		
$C_2H_3Cl_3$*	1,1,1-trichloroethane (methyl chloroform)	0.1

* This formula does not refer to 1,1,2-trichloroethane.

Annex C

TRANSITIONAL SUBSTANCES

Group	Substance
Group I	
$CHFCl_2$	(HCFC-21)
CHF_2Cl	(HCFC-22)
CH_2FCl	(HCFC-31)
C_2HFCl_4	(HCFC-121)
$C_2HF_2Cl_3$	(HCFC-122)
$C_2HF_3Cl_2$	(HCFC-123)
C_2HF_4Cl	(HCFC-124)
$C_2H_2FCl_3$	(HCFC-131)
$C_2H_2F_2Cl_2$	(HCFC-132)
$C_2H_2F_3Cl$	(HCFC-133)
$C_2H_3FCl_2$	(HCFC-141)
$C_2H_3F_2Cl$	(HCFC-142)
C_2H_4FCl	(HCFC-151)
C_3HFCl_6	(HCFC-221)
$C_3HF_2Cl_5$	(HCFC-222)
$C_3HF_3Cl_4$	(HCFC-223)
$C_3HF_4Cl_3$	(HCFC-224)
$C_3HF_5Cl_2$	(HCFC-225)
C_3HF_6Cl	(HCFC-226)
$C_3H_2FCl_5$	(HCFC-231)
$C_3H_2F_2Cl_4$	(HCFC-232)
$C_3H_2F_3Cl_3$	(HCFC-233)
$C_3H_2F_4Cl_2$	(HCFC-234)
$C_3H_2F_5Cl$	(HCFC-235)
$C_3H_3FCl_4$	(HCFC-241)
$C_3H_3F_2Cl_3$	(HCFC-242)
$C_3H_3F_3Cl_2$	(HCFC-243)
$C_3H_3F_4Cl$	(HCFC-244)
$C_3H_4FCl_3$	(HCFC-251)
$C_3H_4F_2Cl_2$	(HCFC-252)
$C_3H_4F_3Cl$	(HCFC-253)
$C_3H_5FCl_2$	(HCFC-261)
$C_3H_5F_2Cl$	(HCFC-262)
C_3H_6FCl	(HCFC-271)