#### UNITED NATIONS ENVIRONMENT PROGRAMME





# ENVIRONMENTAL EFFECTS 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)

One of Four Assessment Panel Reports

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Copies of the report are available from:

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#### **EXECUTIVE SUMMARY**

# ENVIRONMENTAL EFFECTS OF OZONE DEPLETION

In accordance with the provisions of the Montreal Protocol on Substances that Deplete the Ozone Layer, the United Nations Environment Programme (UNEP) developed a set of reports to provide an assessment of current knowledge of scientific, environmental, technical, and economic matters relevant to the implementation of the Protocol.

The present report on the environmental effects of ozone depletion deals mainly with the direct effects of increased ultraviolet-B (UV-B) radiation on man and the environment. The report was written in 1989, the year that the Montreal Protocol came into effect. The Parties to the Protocol have agreed to specified limits on the production of certain gases that endanger the ozone layer. It was widely realized that the threat to the ozone shield was no longer theory. Occurrence of a "hole" in the ozone layer has been observed in the Antarctic region. At the time that the Protocol was signed, there were scientific data indicating that the limitations for the substances agreed upon were not sufficient for a recovery of the ozone layer. Parties advocated stricter limits and the inclusion of more gases.

This report reviews and integrates scientific information on potential effects associated with various levels of stratospheric ozone decrease in an effort to assist decision makers, particularly those involved in the policy process. Clearly, the report would be the most useful if it could provide clear-cut quantitative predictions of the effects to be expected from the different policy options under consideration. The actual situation is rather far from that goal.

The scientists involved in effects research can at best derive tentative conclusions with regard to the impact of ozone depletion. The principal limitation is insufficient information. Investigations have shown that ultraviolet radiation has a multitude of effects on man, animals, plants and materials; most of these effects are damaging. The knowledge required for quantitative predictions, however, is available for only a few areas.

For each area, there is a need to know 1) the dependence of the specific effect on the wavelength of the radiation, 2) the relationship between dose and effect, and 3) modifying factors, such as adaptation and interactions between organisms.

The change of both the quantity and quality of UV-B radiation is different for the various chlorofluorocarbon (CFC) control scenarios relevant to the Montreal Protocol and varies with time in every scenario. Moreover, the atmospheric models from which the decreases of ozone are computed are still being improved. Every refinement may cause an adjustment of the UV-B radiation expected. In addition, the scenarios themselves may have to be changed to adapt to new policy decisions or to changes in projections for global production of CFCs and halons.

Investigators studying effects of increased levels of UV-B radiation deal with a range of expected UV-B increases, which is subject to change. Their experiments usually take several years and cannot readily be adapted to frequently changing scenarios. Most investigators have chosen to examine the effect that is expected from a particular decrease of total column ozone or a limited set of decreases.

Studies have been conducted on effects of increased UV-B irradiance on human health, plants, aquatic organisms, air quality, and man-made materials. Significant changes are likely in each of these areas. With regard to a few effects areas, investigators feel confident enough with the results to provide quantitative predictions. In other areas, the findings give reason for concern, but the effects cannot yet be quantified or confirmed. This difference in certainty and specification of the conclusions reflects the complexity of the issues and the state of the relevant scientific knowledge, rather than the potential importance of the effects. For example, a prediction of the influence of increased UV-B on world food supply would be very difficult. Broad systems, such as agriculture and fisheries, are so complex that many influences would be expected to occur and to interact with each other, making the research problem difficult

to address. Yet, an overall negative influence of increased UV-B on food supply would be very important.

The information available for each of the areas of concern is summarized here. The individual chapters of the report provide a more detailed discussion of the state of the science and an assessment of results.

#### **Solar Interactions**

With depletion of the ozone layer, the atmosphere becomes more transparent to solar ultraviolet radiation. Ultraviolet-B radiation, in a wavelength range of 280 to 315 nanometers (nm), is most affected. Both the intensity and quality (wavelength composition) of the UV-B radiation are altered by changes in the ozone layer. The intensity increases and the wavelength composition is shifted to shorter wavelengths. Most effects of ultraviolet radiation depend strongly on the wavelength of the radiation. This is displayed in "action spectra," which are different for the various effects. Changes in the solar UV radiation climate of the earth pose a threat. What this portends for man and other organisms depends on the amount of ozone reduction, the time of year, the location on earth especially with respect to latitude, and the nature of the biological and other effects of the increased UV.

- The ozone hole over the Antarctic region in early spring has been firmly established and the resulting increase in UV-B radiation has been confirmed by measurements.
- At temperate latitudes (30-60°), the process of ozone layer depletion has already started.
- Based solely on ozone layer thickness, the absolute increments of effective UV-B at tropical latitudes are calculated to become at least as great as the increased UV-B associated with the Antarctic ozone hole.

#### Human Health

- Exposure to increased UV-B radiation can cause suppression of the immune system, which might lead to an increase in the occurrence or severity of infectious diseases and a possible decrease in the effectiveness of vaccination programs.
- Enhanced levels of UV-B radiation can lead to increased damage to the eyes, especially cataracts.
   A cataract is a clouding of the eye lens a condition that causes impaired vision and blindness in many people. Cataracts were estimated to increase by 0.6% per 1% ozone depletion. This increase would

amount to 100,000 additional blind persons worldwide. Another concern is the increase of keratoconjunctivitis, or snowblindness, which is a painful but usually transient condition of the eyes.

Non-melanoma skin cancer will increase with any long-term increase of the UV-B irradiance, without a threshold value. The percentage increase will not be one to one: every 1% decrease of total column ozone will result in a 3% rise of the incidence of non-melanoma skin cancer. There also is concern about an increase of the more dangerous cutaneous melanoma.

#### **Terrestrial Plants**

- Of the plant species investigated, about half were found to be sensitive to enhanced levels of UV-B radiation. Within species, varieties have different UV sensitivities.
- Sensitive plants are typically shorter and have smaller leaves when grown under enhanced UV-B. In some cases, these plants also show changes in their chemical composition, which can affect the food quality and the availability of mineral nutrients.
- In some soybean varieties, increased UV-B reduced food yield up to 25% for an exposure simulating a 25% ozone depletion.
- Increased UV-B may reduce the biodiversity of forests and other terrestrial ecosystems.

#### **Aquatic Ecosystems**

- Increased UV-B irradiance has been shown to have a negative influence on aquatic organisms, especially small ones such as phytoplankton, zooplankton, larval crabs and shrimp, and juvenile fish.
- Because many of these small organisms are at the base of the marine food web, increased UV-B exposure may have a negative influence on the productivity of fisheries.
- Increased exposure to UV-B radiation could lead to decreased nitrogen assimilation by prokaryotic microorganisms and, thereby, to a drastic nitrogen deficiency for higher plant systems such as rice paddies.
- Phytoplankton in the oceans is a major sink for carbon dioxide in the atmosphere. A decrease in phytoplankton would leave the atmosphere with higher carbon dioxide concentrations, and so contribute to the greenhouse effect.

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- The chemical reactivity in all regions of the lower atmosphere (troposphere) could increase if stratospheric ozone depletion leads to increased surface UV-B levels.
- Increases in potentially harmful oxidized compounds, including urban and rural ozone, hydrogen peroxide, acids, and possibly aerosols, could occur in most rural and urban regions. This would result in a decline in the percentage of remote (pollution free) areas and an increase in areas with urban-like pollution.
- Degradation of air quality will exacerbate problems related to human health and welfare, will probably increase stress in the biosphere, and could make current air quality goals more difficult to attain.

#### **Materials Damage**

- Exposure to UV radiation is the primary cause of degradation of materials, particularly plastics used outdoors. Increased UV radiation levels will increase the rate at which plastic products degrade, reducing the outdoor lifetime of the products.
- The increased damage will be more severe at locations near the equator, where the degradation may be enhanced by high ambient temperatures and sunshine levels. Developing countries in these areas are particularly susceptible because of the growing use of plastics in building.
- Virtually no relevant data on other important classes of materials are available, limiting the ability to develop comprehensive economic projections. Such materials include rubber products, paints/coatings, wood, paper, and textiles, all of which will be affected by increased levels of UV-B radiation.

#### **Summary of Major Concerns**

Additional research is needed to gain a more complete understanding of these primary effects, especially in tropical and subtropical areas. Even with the present state of knowledge, it is clear that some of these effects cause a significant threat, including the following:

- Decreased food production from UV-B impacts on agriculture or the oceans' productivity would significantly affect people in areas where shortages occur even now, mainly developing countries.
- Damage to the eyes and possible increases in incidence or severity of infectious diseases would be serious, primarily for people in tropical and subtropical

- areas, where UV-B irradiance is already much higher than elsewhere.
- Skin cancer would affect mainly people with little protective pigment in their skin.
- Polar and circumpolar areas receive comparatively little UV-B radiation, but the increases already apparent are more dramatic than elsewhere. Organisms in these areas may be least adapted to deal with increases in UV-B radiation.
- Because phytoplankton fix carbon dioxide in photosynthesis, damage to phytoplankton by increased UV-B radiation would indirectly contribute to predicted global warming induced by greenhouse gases.

Given this information, it is clear that the possible consequences of ozone depletion are truly global in nature, requiring global action to prevent or mitigate the damage.

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Given this information, it is clear that the possible consequences of ozone depletion are truly global in nature, requiring global action to prevent or mitigate the damage.



# OZONE REDUCTION AND INCREASED SOLAR ULTRAVIOLET RADIATION

M.M. Caldwell (USA), S. Madronich (USA), L.O. Björn (Sweden), and M. Ilyas (Malaysia)

#### SUMMARY:

With 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 thorter wavelengths. These changes must be evaluated with respect to biological responses and other phenomena affected by increased UV-B because these affects 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 in ozone of the upper and lower statosphere 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 at other seasons, and, at any time of year, it is much stronger at lower than higher latitudes.

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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 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 CPC release rates. The first is for CPC release as permitted by the Montreal Protocol agreements. The second scenario involves a thore stingent control whereby CPC 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 AND BACKGROUND

Changes in the solar ultraviolet (UV) radiation climate pose a threat to life on earth. What this portends for man and other organisms depends on the amount of ozone reduction, the time of year, the location on the earth especially with respect to latitude, and the nature

of the biological and other effects of the increased UV radiation.

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The effects of UV radiation depend not only on the intensity and length of exposure to the radiation, but also on the quality of the radiation. Therefore, changes

in quality as well as intensity of solar UV must be considered. The quality is expressed in physical terms as the wavelength composition of the radiation. The major types of solar radiation based on wavelength are: infrared radiation (> 700 nm), visible (400-700 nm), and ultraviolet (< 400 nm). Ultraviolet radiation is further subdivided into three parts, which are affected differently by reduction in stratospheric ozone. UV-A radiation (315-400 nm) is not affected by ozone reduction, whereas UV-B radiation (280-315 nm) is affected. UV-C radiation (< 280 nm) is completely absorbed by ozone and oxygen in the atmosphere. Even with severe ozone reduction, UV-C radiation would still be absorbed by the remaining ozone.

#### STATE OF THE SCIENCE

#### Factors Affecting the Present Solar UV Climate

There are large changes in solar UV as one progresses from the Equator toward the poles - much greater changes than for the total solar radiation. Apart from local conditions like cloud cover, there are two primary factors that determine the solar UV radiation. First is the amount of ozona ... the atmosphere above the earth at the location of interest, referred to as the total ozone column. More than 90% of the ozone is in the upper atmosphere (the stratosphere) but there can be considerable ozone in the lower atmosphere (the troposphere) especially in areas of air pollution. If ozone in the stratosphere is reduced, it can have effects on the amount of ozone in the troposphere (see Chapter 5). It is the net change in the total ozone column that is important for filtering UV radiation. The earth's ozone layer is not uniform. There are large differences in the stratospheric ozone layer at different latitudes. The layer is usually thinnest in the tropics and thickest toward the poles (Figure 1.1). There are also changes during the course of the year, except at tropical latitudes where the ozone tends to be essentially constant. The second major factor is the sun angle, because it determines the length of the path that the sun's rays take as they penetrate the atmosphere. When the sun is directly overhead, the sun's rays have the shortest path through the atmosphere. When the sun is lower in the sky, the path through the atmosphere is longer and the filtering action of the air is, therefore, increased. This is an important influence for all the solar radiation, but especially for the UV portion of sunlight. Therefore, the majority of the daily UV is received during the middle four hours of the day when the sun is high in the sky. During the remainder of the day, the UV flux is comparatively low - a lesson emphasized by dermatologists concerned about exposure of the skin to solar UV.

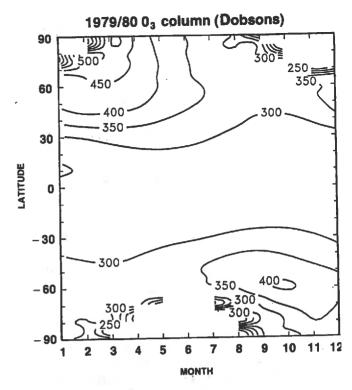


Figure 1.1
Total ozone column thickness as a function of latitude and time of year for 1979-1980. Ozone is represented in Dobson units, which were generated from the Total Ozone Mapping Spectrometer (see text). Because these satellite measurements cannot be conducted in darkness, no data exist during the polar nights, the absence of values during these times at very high latitudes. [From Madronich et al., 1989]

The change in ozone thickness with latitude and the differences in prevailing sun angles combine to produce a very large gradient in solar UV from the intense UV climate of the tropics to the very benign UV radiation received at high latitudes. As will be shown, the differences in solar UV with latitude may often be larger than the changes anticipated to occur at a given location due to ozone reduction.

The changes of solar UV with season are dominate by the changes in prevailing sun angles, but seasons ozone differences play a role as well. In the winte months at temperate and high latitudes, the sun tend to be lower in the sky and solar UV intensities are muc lower than in the summer. At the same latitude, th ozone layer tends to be greater in thickness in the sprin than in the autumn. Thus, even though sun angles at the same on March 21 and September 21, the difference in the ozone column result in more UV in the ear autumn than in the early spring. In the tropics, the rath constant ozone column and the similar sun anglithroughout the year mean that solar UV is about it same. Of course, cloud cover, such as with monsor weather, will modify this considerably.

Apart from the obvious effects of clouds, other atmospheric constituents such as haze, dust and air pollutants attenuate sunlight to varying degrees. Certain air pollutants, including sulphur dioxide and tropospheric ozone, are particularly effective UV attenuators.

Another dimension of global climate change apart from ozone reduction may also influence the solar UV climate. Increases of CO<sub>2</sub> and other gases, such as methane and CFCs, are generally considered to be causing a warming of the planet, known as the greenhouse effect. Although general warming is one consequence of this phenomenon, the planet will warm unevenly. This will cause differences in atmospheric pressure patterns and will, in turn, change the way storms develop and track across the globe, although the exact nature of these changes is, at present, not very predictable. Changes in weather patterns and cloud cover would have an obvious bearing on the sunlight climate.

#### **Nature of Biological Photoreactions**

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The influence of solar UV on biological and other phenomena depends not only on such factors as ozone layer thickness and sun angle, but also on the nature of the biological effects themselves. As sun angle and ozone in the atmosphere change, the intensity as well as the wavelength composition of the solar UV undergo change. Because biological reactions are wavelength dependent, these changes in quality have important consequences for the manner in which organisms are affected by sunlight.

With reduction of ozone or a move toward lower latitudes, the wavelength composition of sunlight shifts toward shorter wavelengths (i.e., shorter wavelengths are intensified more than the longer wavelengths). In general, the important destructive influences of UV radiation on organisms are greater at shorter than at longer wavelengths. Thus, a shift toward shorter wavelengths results in a larger biological effect. This means that an amplification of the radiation changes takes place because of the nature of biological reactions to the UV. This amplification effect is expressed as a radiation amplification factor (RAF), which is the percentage increase of biologically effective radiation caused by a given percentage change of total column ozone.

The relative effectiveness of different wavelengths in eliciting biological reactions and other photoreactions is shown by six examples in *Figure 1.2* (top left). These graphs, called action spectra, express the relative effect of radiation of the same intensity (in this case, the same photon flux density) at different wavelengths. They are all set equal to 1.0 at 300 nm wavelength; but because these are relative spectra, this is arbitrary. Note the

logarithmic scale in Figure 1.2. Two of these spectra are themselves derived from several action spectra and are meant to be general examples for 1) the response of higher plants to UV, and 2) the damaging effects on microorganisms mediated by nucleic acids, especially DNA (a prime molecule of inheritance and control in organisms) as the target of the radiation. A third spectrum is the response of a UV meter, the Robertson-Berger meter, designed to approximate the erythemal (sunburning) response of caucasian skin. The sensitivity of the meter does not exactly correspond to human erythema, but it has been used in a worldwide network for monitoring general biologically effective solar UV radiation. A recent action spectrum for the carcinogenic action of UV radiation is also included. Two additional spectra are included to represent non-biological effects of increased UV-B radiation: 1) the degradation of plastics, and 2) the photolysis of ozone in the troposphere that would result from greater penetration of solar UV-B through the stratosphere. Although this chapter emphasizes the importance of biological responses, these non-biological responses can be considered in the same vein. In most of these examples, the increasing effectiveness of the radiation with decreasing wavelength is quite apparent.

To incorporate the importance of changes in solar UV radiation quality due to ozone reduction or latitude. these action spectra are used as weighting functions. That is, the relative effectiveness (as represented in Figure 1.2), is multiplied by the intensity (flux density) of radiation at each wavelength to indicate the importance of the quality of the radiation. In the calculations, the weighted radiation values are summed over the appropriate wavelength range and the resulting value is a biologically effective dose, or the reaction rate for non-biological responses. These values incorporate both the complex ways that radiation changes with wavelength as a result of changes in atmospheric ozone or sun angle and the biological importance for these changes. As mentioned previously, a radiation amplification factor can be derived from the weighted radiation values. The RAF values are determined both by the action spectra used and other factors, particularly solar angle. In Figure 1.2, the RAF values are shown for three action spectra as a function of latitude and time of year. Many of the RAF values range between 1.0 and 2.5. This indicates that with such action spectra a 1% decrease of the total ozone column leads to an increase of the biologically effective irradiance by usually more than 1%. This is the reason for speaking of an "amplification."

All the UV-B radiation values subsequently presented in this Chapter are in the form of calculated biologically effective radiation using three action spectra.

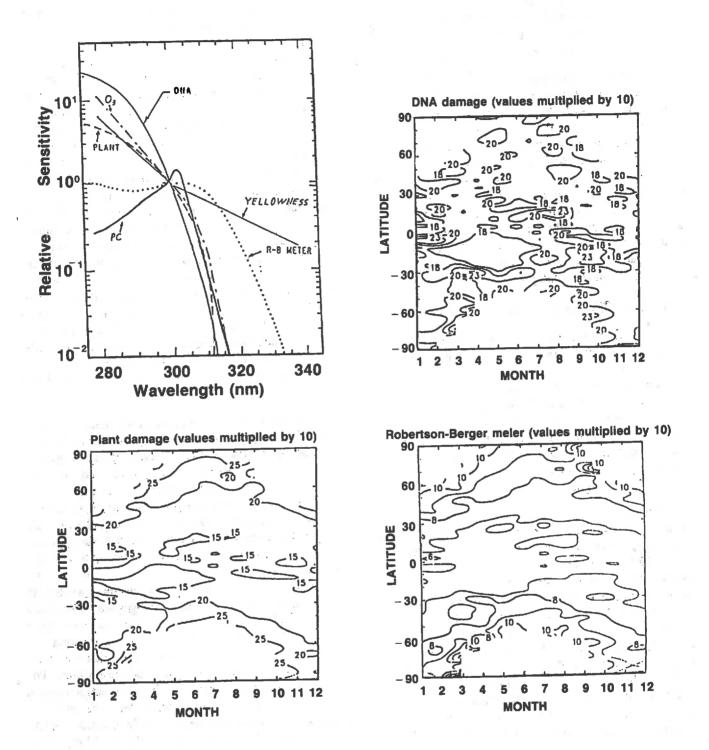


Figure 1.2
Action spectra used as weighting functions to calculate biologically effective UV-B radiation and UV-B effective in some non-biological responses. These are a generalized action spectrum for the response of plants to UV-B [from Caldwell, 1971], a generalized spectrum describing damage to nucleic acids (DNA) [from Setlow, 1974], the sensitivity curve of the Robertson-Berger (R-B) meters used to measure sunlight effective in erythema (sunburning), a photocarcinogensis spectrum for hairless mice [from Sterenborg and Slaper, 1987], a spectrum for photolysis of ozone [from DeMore et al., 1987], and a spectrum for degradation of PVC plastics expressed as yellowing [from Andrady et al., 1989]. All curves are arbitrarily set equal to 1.0 at 300 nm (upper left). The radiation amplification factors (RAF) for three spectra are shown as a function of latitude and time of year. These amplification factors give the percentage increase of effective irradiance for a 1% decrease of total column ozone. RAF factors are multiplied by 10 in these figures (upper right, bottom left and right).

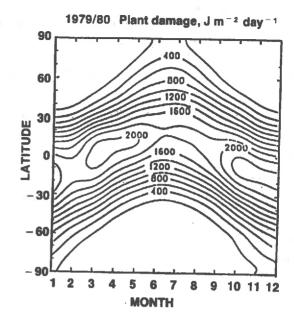
#### Latitude and Time of Year

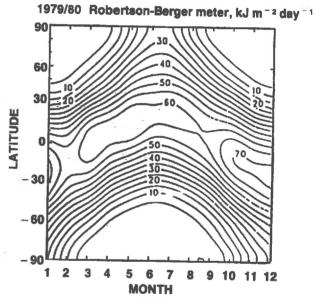
The magnitude of variation in biologically effective UV presently experienced with latitude and time of year provides a useful background against which to evaluate anticipated changes in solar UV due to ozone reduction. These radiation values can be plotted as effective radiation in relative units using the DNA-damage action spectrum, a generalized plant response action spectrum, and the Robertson-Berger meter response spectrum as weighting functions (Figure 1.2). Because these are plotted as relative units, the values of effective radiation using the different weighting functions cannot be compared with each other. Thus, the higher numerical values of R-B-weighted radiation in the following figures have no particular meaning. The purpose is to portray changes and differences for a particular biological weighting function. The three spectra chosen for this chapter cover a range of characteristics of UV-B action spectra.

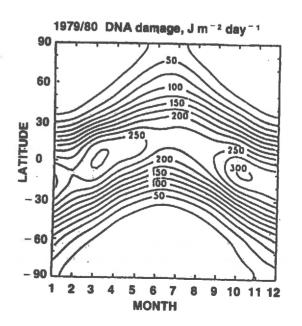
All calculations of UV-B shown subsequently in this Chapter are for cloudless conditions. The assumption is that cloud cover patterns would be the same following ozone reduction as they are at present. As discussed earlier, this may not be the case as the planetary climate changes, but alterations of cloud cover are difficult to predict at present. Cloud cover certainly influences UV-B, but this Chapter is focusing on the changes in UV-B specifically due to changes of atmospheric ozone. Thus, the clear-day cases presented best portray the potential increases in UV-B radiation. Effects of cloud cover on ground-level UV-B radiation can be accounted for only as averages over time. The effect of a partial cloud cover depends not only on the degree of coverage, but also on whether the sun is covered or not. The attenuation by a complete cloud cover may vary, depending on the type of cloud and the solar angle, between 56% [Büttner, 1938] and 90% [Josefsson, 1986]. Several formulas for taking clouds into account have been suggested. For example, Ilyas [1987] has recently shown that a rather simple formula developed by Büttner [1938] is useful in evaluating solar UV-B under average cloud cover conditions.

The daily effective UV-B radiation for different latitudes and times of the year for 1980 are portrayed in Figure 1.3 for cloudless days. These have been calculated for three action spectra as weighting functions. At

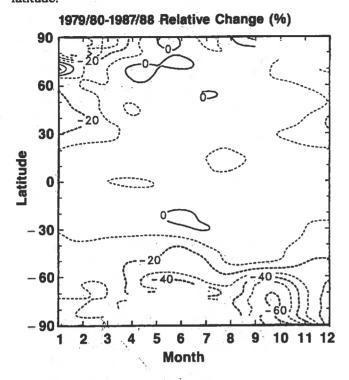
Figure 13
Calculated daily effective UVB for 1979/1980 on cloudless days as a function of latitude and time of year using three action spectra as weighting functions. The apparent differences in magnitude of effective UVB calculated with the different spectra are a result of the action spectrum used and the normalization wavelengths of these spectra. Values should only be compared if calculated with the same spectrum. [From Madronich et al., 1989]







temperate latitudes, sun angle is the most important factor determining the large differences in solar effective UV as seasons change during the year. Sun angle combined with differences in ozone, as explained earlier, determine the very large differences in effective UV with latitude.



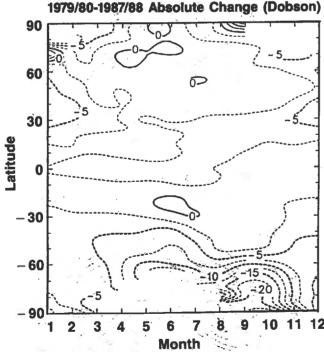


Figure 1.4
The change in global ozone between 1979/1980 and 1987/1988 from TOMS (Total Ozone Mapping Spectrometer) data corrected with Dobson measurements. This is portrayed both as a relative change (%) and as absolute change in Dobson units. [From Madronich et al., 1989]

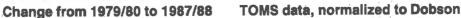
#### Recent Changes in Ozone and UV-B Radiation

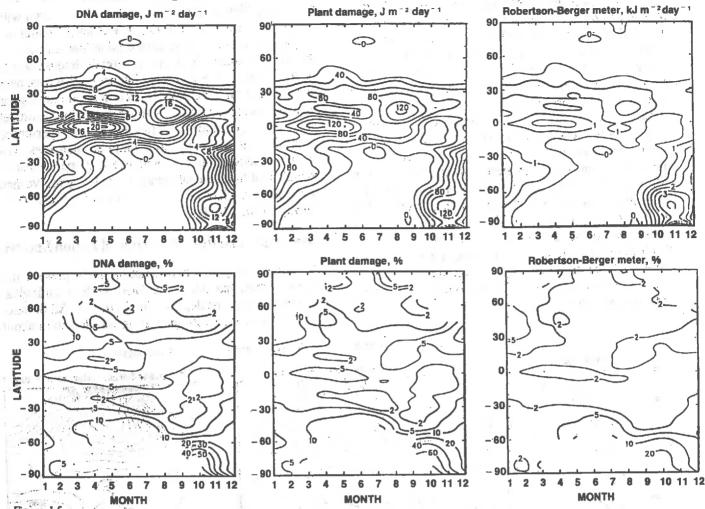
Measured changes in total column atmospheric ozone from satellite sensing using backscattered UV radiation (with the Total Ozone Mapping Spectrometer, TOMS) provides the picture of ozone change in the 8-year period from 1979/1980 to 1987/1988. (To compute the change of this 8-year period, 2-year averages were calculated to avoid the year-to-year changes that occur with the normal so-called quasi-biennial oscillation of ozone in the atmosphere. For example, in 1987 there was a very pronounced ozone hole over Antarctica, but only a small depression during 1988.) The change over the 8-year period is expressed both as relative change and also as incremental change in Dobson units (Figure 1.4). (A Dobson unit is the thickness of the ozone layer if condensed to standard pressure and temperature in units of hundredths of a millimeter.) The calculated changes in effective UV-B radiation corresponding with these ozone changes are shown in Figure 1.5. The pronounced ozone hole over Antarctica in the early spring is prominently reflected in increased effective UV-B. However, increases in effective UV-B at other latitudes in both hemispheres should have also occurred according to these calculations. Apart from the Antarctic ozone hole, the greatest relative increases in UV-B have occurred at temperate latitudes (30° to 60°) during the colder months of the year.

However, the greatest absolute increases in effective UV-B have occurred at tropical latitudes. In all cases, both the relative and absolute increases are much less pronounced when the effective radiation is calculated with the less steep action spectrum as a weighting function. Scotto et al. [1988] were unable to find a trend of increasing UV-B between 1974 and 1985 from the network of Robertson-Berger meters in the United States. They ruled out instrument drift and attributed the lack of increased UV-B to other factors, such as possible changes in climatic, meteorological and environmental factors in the troposphere. However, because the sensitivity spectrum of these meters is not very steep, they cannot be expected to be highly sensitive to ozone change.

#### **Future Solar UV Climate**

Future changes in solar UV radiation will be determined largely by changes in the total ozone, although other influences such as changes in cloud cover patterns mentioned earlier may play a sizeable role, at least in local environments. Changes in global temperatures may increase cloud cover in one location and decrease it in another.





Calculated increases in effective UV-B for the period 1979/1980 to 1987/1988 corresponding to the ozone change data of Figure 1.4. This is computed using three action spectra as weighting of functions and shows both relative and absolute changes of effective UV-B. [From Madronich et al., 1989]

Future levels of atmospheric ozone will be influenced by quantities of ozone-depleting chemicals, principally CFCs, and also by other gases whose concentrations are changing due in part to man's activities. These include gases such as CO<sub>2</sub>, methane and nitrogen oxides. In the following projections of UV-B radiation increases owing to changes in total column ozone, the model calculations did not include the effect on stratospheric ozone arising from temperature feedback from greenhouse gases. Also, predictions of total ozone column by different models may differ according to the manner in which they treat future trends of tropospheric ozone, which is a significant percent (10%) of the total ozone column. Tropospheric ozone predictions are highly sensitive to assumed chemical models and future trends in emissions of methane and nitrogen oxides. Additional feedbacks also exist. For example, when stratospheric ozone is reduced, UV-B penetrates more effectively into the troposphere and affects the hydrocarbon/NO<sub>x</sub> photochemistry and, therefore, the formation

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of tropospheric ozone (see Chapter 5). Differences can be expected when other models are used.

Model results are most useful in comparing the effects of reducing CFC release to different levels. Two scenarios of ozone reduction are considered.

- Al For the products covered by the Montreal Protocol, a constant flux into the atmosphere after 1985 is assumed, using 1986 production estimates as the annual release into the atmosphere.
- D1 This scenario is essentially the same as A1 except that between the years 1996 and 2000, the release of Montreal Protocol products would be scaled down to 5% and remain at this level after the year 2000.

The predicted ozone reduction by the year 2060 using the two CFC release scenarios would lead to increases in effective UV-B as portrayed in *Figures 1.6* and 1.7 for the A1 and D1 cases, respectively. This is

shown both as relative increase and as incremental change in the relative effective UV-B units for a particular action spectrum weighting. The relative reduction in ozone is greater at high latitudes than at low latitudes and is also more pronounced in winter than in summer. When translated into changes in effective UV-B (Figures 1.6 and 1.7), the relative increase in UV-B is further amplified at higher latitudes because the radiation amplification factors mentioned earlier are often greater at higher latitudes than they are at lower latitudes (Figure 1.2). For both ozone reduction scenarios, the largest relative increases in effective UV-B are at high latitudes in the spring months. The greatest absolute increments in effective UV-B often occur at temperate and high latitudes in the late spring and early summer months, but the patterns are complicated. These model calculations do not incorporate details of heterogeneous chemistry that lead to calculations of polar ozone hole(s). Clearly, there are large differences in the amount of increased effective UV-B that would result from the two ozone reduction scenarios.

Although ozone reduction may lead to greater absolute and relative increments of effective UV-B at temperate and high latitudes than in the tropics, even with the Al scenario, the resulting UV-B levels would not surpass those currently experienced at low latitudes. In the tropics, solar UV-B that is already intense would be much more so, and surpass intensities that have been experienced on the earth's surface in recent geological history. Species adapted to temperate and high latitudes would be exposed to intensities not before experienced in these locations, even though higher intensities exist at low latitudes. There is evidence that species native to higher latitudes are inherently more UV sensitive than those at lower latitudes [e.g., Caldwell et al., 1982; Barnes et al., 1987].

#### Postscript: The Role of Biological Action Spectra

Biologically effective radiation in the present and future climate has been calculated by three biological weighting functions depicted in *Figure 1.2*. All of these functions decrease with increasing wavelength in about

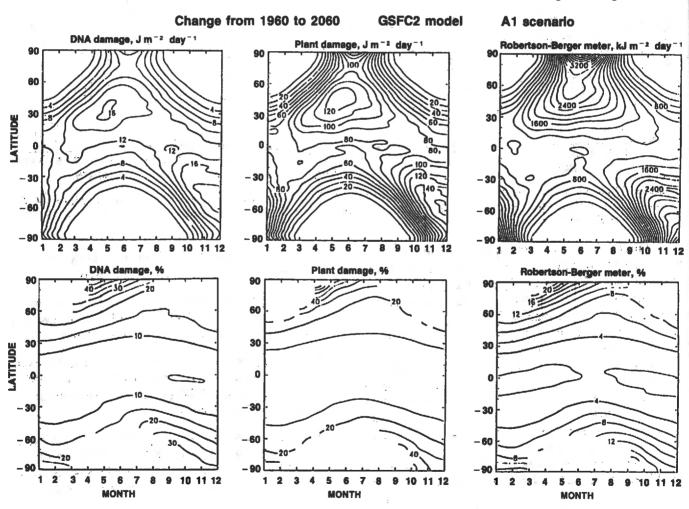
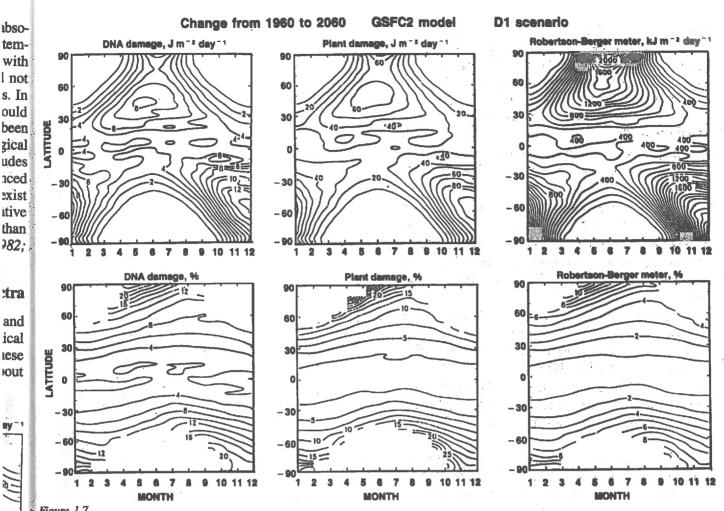


Figure 1.6

The predicted change in effective UV-B between the years 1960 and 2060 following the ozone changes resulting from the Al ozone reduction scenario as computed by the Goddard Space Flight Center model (GSFC2). [From Madronich et al., 1989]



The predicted change in effective UV-B between the years 1960 and 2060 following the ozone changes resulting from the DI ozone reduction scenario as computed by the Goddard Space Flight Center model (GSFC2). [From Madronich et al., 1989]

the same wavelength region. However, they result in different patterns of radiation change in the present solar UV climate (Figure 1.3). Variations with latitude and season are more pronounced for effective radiation calculated with action spectra, such as for DNA damage that drops steeply with increasing wavelength, than for effective radiation calculated with less steep action spectra such as the R-B meter spectrum. With ozone reduction, the radiation amplification factors (RAF) are also much greater for steeper spectra (Figure 1.2). This is reflected in greater changes in effective radiation for the ozone reduction that has already occurred (Figure 1.5) and for future ozone reduction scenarios (Figures 1.6 and 1.7). A single correct action spectrum used as a weighting function for biological organisms does not exist, but direct and indirect evidence suggests that steeper functions apply to many important biological responses to UV. The R-B meter used in a world-wide network of solar UV monitoring has a spectrum that is less sensitive to ozone and sun angle changes. Thus, measurements with this meter network would not be expected to exhibit as much of a pronounced increase in solar UV as ozone is diminished.

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### **HUMAN HEALTH**

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#### 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 are cataracts. The relationship between UV-B exposure and two forms of cataracts — cortical 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 cataracta. 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 relatively 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 carcinomas - appears to be one of increased risk with increased total lifetime dose 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 hir skinned individuals are more susceptible than dark-akinged individuals receiving the same ambient exposure. The relationship between UV-B exposure and melanoma akin cancer is probably more complex; it is certainly less well taderstood. Some data suggest that intermittent severe exposures, 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 andies, it is estimated that a 1% decrease in stratospheric ozone will result in a 3% increase in non-inclanoma skin cancer, and a lower but still significent increase in melanoma.

#### INTRODUCTION AND BACKGROUND

UV-B radiation has many influences on the human body. Some are positive, such as the formation of vitamin D<sub>3</sub> in the skin, which helps in the maintenance of bone tissue. In phototherapy, doctors utilize the beneficial effects of UV-B radiation on certain skin diseases. On the other hand, many effects of UV-B radiation are

damaging, such as sunburn, snowblindness (a form of photokeratitis), cataracts, aging of the skin, and skin cancer. There also are effects which by themselves cannot be called beneficial or damaging, but which influence other reactions of the body. This applies, for instance, to the influences of UV-B radiation on the immune system. UV-B radiation suppresses allergic reactions of the skin, as well as the immune defense

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against tumours initiated in the skin by UV-B radiation. There are indications of a suppression of the resistance of the skin, and indeed, of the whole organism, against certain infections.

This Chapter will discuss the consequences for human health of an increase of the UV-B radiation in sunlight. The statement that all effects of UV-B radiation would be enhanced in proportion to the increasing irradiance would be too simple. One reason is that for most influences of UV-B radiation the relationship between dose and effect shows non-linear behaviour in certain areas of the dose-response curve. For instance, the formation of vitamin D<sub>3</sub> in the skin by UV-B radiation is self-limiting [Holick et al., 1982]. In other cases, adaptation of the skin to UV radiation will modify the effects. Exposure of the skin to UV-B radiation leads to thickening of the most superficial skin layers and to increased pigmentation. This increases the absorption of UV-B radiation in the superficial layers and provides the skin with an efficient protection against sunburn. The hyperproliferation of skin cells involved may, however, also render the skin more susceptible to skin cancer. In some instances, the modifying influences may be so strong that greater doses of radiation lead to smaller effects. Patients with photodermatoses have abnormal reactions of the skin to sunlight, and in many cases to the UV-B radiation in sunlight; the skin will react with papules, itching, swelling, etc. These diseases generally occur less and in less severe forms in the sunny areas of the world than in areas with limited sunlight and dark winters.

Due to such complications and the limited existing knowledge regarding some of the effects of UV-B radiation on man, the overall consequences of an increase of UV-B irradiance on health cannot be predicted in a straightforward manner. For some effects, sufficient data are available to allow quantitative predictions. In other respects, the consequences are rather uncertain. In most cases, something can be learned from comparisons of people living with different exposures to UV-B radiation regardless of any ozone depletion.

The State of the Science section that follows presents both qualitative and quantitative answers to the question of what may be the consequences for human health of stratospheric ozone depletion and its accompanying increase in UV-B. Quantitative estimates of how increased UV-B will affect health are presented for cataracts and non-melanoma and melanoma skin cancers. The issue of the impact on the immune system has been treated qualitatively. It should be stressed, however, that just because there are quantitative estimates for some effects and not for others that this does not imply a ranking of worth. Indeed, the quantitative estimates should be treated very cautiously because they

require a number of assumptions. In addition, the effects that can be assessed only qualitatively may well have the potential for a much greater impact.

#### STATE OF THE SCIENCE

## Ocular Damage: Effects on the Cornea, Lens and Retina, and Intraocular Melanoma

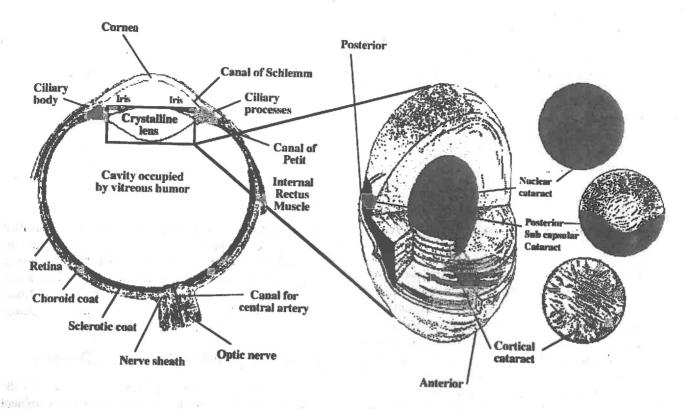
Current scientific evidence indicates that exposure to ultraviolet radiation may contribute to the development of a variety of eye disorders [USEPA, 1987; Pitts 1989; Engel et al., 1988; Taylor et al., 1988]. The UV-B portion of the spectrum can damage the cornea, lens and, to a lesser extent, the retina [Pitts, 1989]. Endpoints of concern include cataract, photokeratitis, retinal degeneration, arcus senilis and pterygia.

#### Damage to the Cornea

The initial response of the eye to exposure to UV-B radiation (280-315 nm) is the condition termed photokeratitis in which the front of the eye, the eyelids and the skin surrounding the eyes become reddened. This condition is commonly seen in skiers and also is called snowblindness. Unlike the skin, the eye does not develop a tolerance to UV but becomes more sensitive with repeated exposures. At wavelengths below 290 nm, damage is principally to corneal epithelium. Between 290 and 315 nm, the corneal stroma and endothelium begin to show damage as well. Doses as low as 0.21 J cm<sup>-2</sup> of 308 nm radiation (from a laser) could initiate damage to the cornea; 0.6 J cm<sup>-2</sup> at 300 nm produced demonstrable damage in the stroma and endothelium which was not fully repaired eight days post-exposure. Other data indicated that damage from UV radiation at these wavelengths is cumulative and additive among wavelengths [Pitts, 1989].

#### Damage to the Lens

Cataract, a disease of the lens, is the most prevalent form of ocular damage associated with UV exposure. Cataracts are opacities in the lens of the eye which impair vision. There are three major forms of cataracts: nuclear, posterior subcapsular and cortical. In nuclear cataracts, one sees a yellowing of nuclear proteins. In posterior subcapsular cataracts, abnormal and degenerate cells migrate and accumulate at the posterior surface of the lens. In cortical cataracts, gaps form in the cortex and fill with water and debris. Figure 2.1 shows a composite drawing of the eye which indicates the position of the lens and shows how the lens cortex, posterior capsule or nucleus may be affected by a cataract.



Cataract Formation. Cataracts involve changes in the structure of the eye's lens which affect vision. In nuclear cataracts, the nuclear proteins darken, scattering light. In cortical cataracts, gaps form in the cortex which fill with water and debris.

In developed countries, corrective surgery can prevent most cataracts from causing blindness; more than 1 million cataract operations were performed in the United States in 1988. Nevertheless, in the United States, cataract remains the third leading cause of legal blindness. In developing countries where such operations are not always available, cataracts result in a much higher incidence of blindness. The World Health Organization (WHO) estimated in 1985 that the greatest single cause of avoidable blindness was cataract. Cataracts were responsible for 17 million cases of blindness, accounting for more than one-half of all the blindness in the world [Maitchouk, 1985].

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In both the developed and the developing countries, cataracts represent a significant problem, which is anticipated to grow worse as life expectancy increases. In 1980 almost one-half of the world's 260 million elderly resided in the developed nations, whereas by the year 2000, an estimated two-thirds of the elderly (400 million) will reside in the now developing nations [Maitchouk, 1985]. Thus, cataract is expected to grow as a public health problem in the developing countries.

The exact mechanism of the formation of a cataract is still unknown, although it is clearly multifactorial. Epidemiological studies [USEPA, 1987; Taylor et al., 1988, Bochow et al., 1989] suggest that some cataracts,

particularly cortical and posterior subcapsular cataracts [Taylor et al., 1988; Bochow et al., 1989], are etiologically related to exposure to solar radiation, specifically UV-B [Hollows and Moran, 1981]. Studies in animals suggest that the active portion of the solar spectrum lies in the UV-B region [Pitts et al., 1986]. The cataracts induced in these studies were anterior subcapsular [Pitts et al., 1977]. Ultraviolet-A radiation and other causes, such as nutritional deficiency, also may contribute to cataract formation.

Table 2.1 presents the relationship between cataract incidence and amount of exposure to sunlight in Nepal [Brilliant et al., 1983]. Even more persuasive, however, is the finding in a recent epidemiologic study of occupationally exposed individuals that the incidence of cortical cataracts appears to be directly related to exposure to UV-B. A doubling of cumulative exposure increased the risk of cortical cataract by a factor of 1.6. Nuclear cataracts showed no such increased risk with UV-B exposures. When individuals were ranked as to their average annual UV-B exposure, those in the upper quarter of the ranking had a 3.3 fold increased risk of cortical cataract compared to those in the lowest quarter [Taylor et al., 1988]. A second recent case-control study examined the relationship between posterior subcapsular cataract and UV-B and found that cases had

Table 2.1 Cataract prevalence by average daily sunlight hours for full-time, residents [Brilliant et al., 1983]

Average Daily Hours	Cataract Cases	Prevalence (per 100)	Odds Ratio
7	13	1.26	1.0
8	54	2.00	1.6
9	66	1.88	1.5
10	85	1.45	1.2
11	136	3.08	2.5
12	476	4.63	3.8

a 23% higher cumulative exposure to UV-B [Bochow et al., 1989].

Given this evidence, reduction in the ozone layer and its associated increase in the amount of UV-B reaching the earth's surface will likely increase the incidence of cataracts. On the basis of earlier epidemiologic data [Hiller et al., 1983], the U.S. Environmental Protection Agency estimated that for every 1% decrease in stratospheric ozone, there will be between a 0.3 and 0.6% increase in cataracts. More recently, the work of Taylor and his colleagues [1988] has indicated that for every 1% decrease in stratospheric ozone there will be a 1.2% increase in cortical cataracts. Given that nuclear cataracts account for about 30% of all cataracts and that posterior subcapsular cataracts account for about 40% and apparently have approximately the same dose-response relationship as that observed for cortical cataracts, the EPA estimates might need to be revised upward slightly to 0.6-0.8% [Taylor, 1989]. Application of this range of estimated increases (0.6-0.8%) in cataracts to the number of cases of cataract blindness estimated for 1985 [17 million; Maitchouk, 1985] suggests that if the same population had lived with the ozone layer reduced by 1%, there would have been between 100,000 and 150,000 additional cases of cataract-induced blindness.

#### Damage to the Retina

UV reaching the retina causes both functional and morphological damage. Lenses that have been removed (aphakic), such as after a cataract operation, provide clear evidence of this occurence. The threshold for damage to the rabbit eye at 300 nm was 0.23 J m<sup>-2</sup>. A similar value (0.36 J m<sup>-2</sup>) was found for the primate eye at 325 nm (not UV-B); the aphakic threshold was about ten times lower. More research is needed to determine how these findings might apply to retinal damage in exposed human populations.

#### Intraocular Melanoma

Sunlight exposure has recently been implicated as

a risk factor for intraocular melanoma in a study that determined a latitude gradient for this tumour. Individuals born in the southern United States showed nearly a three-fold increase in risk. Blue-eyed individuals comprised the phenotype with the largest risk. Complexion and hair colour were not important risk factors [Tucker et al., 1985].

#### Immunologic Effects/Infectious Diseases

Ultraviolet radiation has profound effects on the immune system, particularly that of the skin. At ambient environmental levels, animal models have shown that UV radiation reduces the ability of the cell-mediated arm of the immune system1 to respond adequately to foreign substances, known as antigens [DeFabo and Kripke, 1979]. The skin often is the first point of contact with many foreign substances including infectious agents. In these instances, the skin's immune response is the body's first line of defense. However, when foreign substances (antigens) are given via the skin to UVtreated animals, they induce tolerance rather than inducing a protective response (immunity). The reason for this failure appears to be due to an increase in or elicitation of the activity of a class of lymphocytes termed suppressor T-cells (Ts cells). This occurs possibly in conjunction with the failure of a second part of the immune system: the antigen presenting cell [DeFabo and Noonan, 1983; Granstein, 1984; Baadsgaard, 1987]. Normally, if an antigen is introduced via the skin, a cellular immune response to it would be generated via the interaction of antigen-presenting cells and a class of lymphocytes termed effector T-cells. In UV-exposed skin, the loss of one type of antigen-presenting cell type the Langerhans cell - is associated with the subsequent appearance of T<sub>s</sub> cells [Elmet et al., 1983]. Such cells

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¹The immune system has two principal forms of defense against a foreign substance. One is achieved via a soluble molecule termed an antibody, the second is mediated via the activity of lymphocytes. Antibody-mediated immune responses are termed "humoural" while those in which lymphocytes play a role are termed "cell-mediated."

normally serve a regulatory function, preventing an animal from making inappropriate immune responses such as responding to its own proteins.

In the case of UV-treated skin, the T<sub>s</sub> cells prevent the animal from responding to antigens given at the same time or shortly after these cells appear in the skin. It is for this reason that in animal models, UV radiation-induced tumours are not controlled by the skin's immune system; they are not recognized as foreign. This observation has been explored in some detail in the context of the induction and development of tumours by UV radiation [Fisher and Kripke, 1974, 1981; Kripke, 1984]. However, it has important implications not only for carcinogenic processes but also for many infectious disease systems, where the inability of the host to respond to infectious agents in the skin may allow such infections to become established.

The skin cancer effects of UV radiation occur mainly in the white-skinned races. Most information suggests this is because the greater pigment (melanin) content of dark skin blocks UV radiation, preventing it from harming the cells of the skin. Were this same reasoning applied to the immune system effects, the conclusion would be that only the light-skinned populations would be at risk for adverse effects on the immune system. There are a limited number of studies that

address this issue. However, what little has been reported indicates that the effects of UV radiation on the immune system occurs irrespective of skin colour. Thus, in humans, the effect of UV radiation on the antigen presenting cell has been observed at very low doses not only in Caucasians but also in Asians and Aborigines [Scheibner, 1987]. On the basis of this information, the impacts on the immune response and its role in the control of infectious diseases may not be restricted to the white populations.

There are a large number of diseases that might be affected by UV-induced immunosuppression. At a minimum, these include all those diseases which have a stage involving the skin, and to which cell-mediated (as opposed to antibody-mediated) immunity is important. Examples include: 1) measles and other viral diseases that elicit a rash such as chicken pox and herpes, 2) parasitic diseases introduced via the skin such as malaria and leishmaniasis, 3) bacterial diseases such as tuberculosis (T-cell immunity is important), and 4) fungal infections such as candidiasis. Studies of animal models of some of these diseases confirm the potential for an effect of UV-B on the development of infectious disease processes [Howie, 1986a,b; Giannini, 1987; Taylor, 1988]. Figure 2.2 presents a model of how ultraviolet

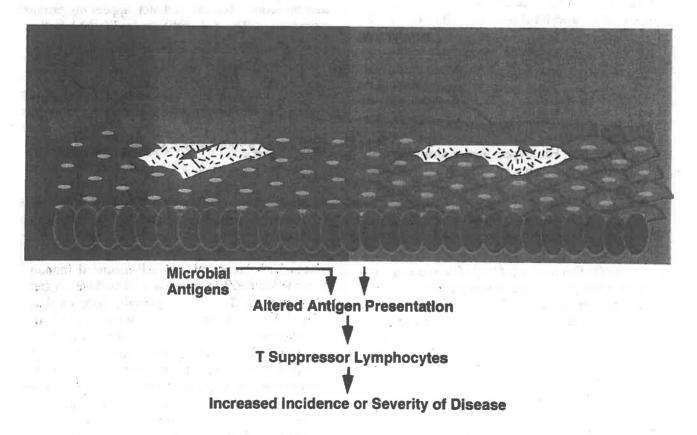


Figure 2.2

Model for the role of UV radiation in an increased incidence or severity of infectious disease.

radiation is thought to interact with skin inducing T<sub>s</sub> cells resulting in specific non-responsiveness to infectious agents that subsequently gain entry into the skin.

Figure 2.2 deals only with impaired local immunity (i.e., at the site of irradiation), which occurs following doses of UV that could be received in a normal sun-exposure scenario such as a week-long sunny vacation. Larger doses (i.e., several months of daily sunny exposure) could possibly induce impaired systemic immunity so that introduction of any organism might be met by a diminished host response.

Brief descriptions follow of several diseases (herpes, leishmaniasis, malaria, and bacterial and fungal infections) where preliminary results have shown that UV radiation has an impact. With the exception of herpes virus infections where UV-B irradiation has been shown to elicit reoccurrence of the virus in man, most of the data come from studies in animals. There are other diseases which also may be candidates for an impact of increased UV radiation by virtue of one of the traits identified above. Brief descriptions of two of these—tuberculosis and leprosy—are given below. However, experimental evidence to examine these hypothese needs to be gathered.

#### Herpes Viruses

Human herpes viruses comprise a class of viruses that include the varicella-zoster virus (the cause of chicken pox and herpes zoster), the herpes simplex virus (cold sores and genital herpes), cytomegalovirus, and the Epstein-Barr virus (Burkitt's lymphoma and infectious mononucleosis). These viruses have as a common characteristic the ability to exist in a carrier state which can last for extended periods of time. In the carrier stage, the infection has no symptoms, but a variety of stimuli can cause reactivation. For herpes simplex viruses, reoccurrences have been noted after fever, trauma, emotional upsets, gastrointestinal disorders, and exposure to UV. In humans, both multiple sub-erythemal doses (10 exposures, equivalent to 5 or 6 MED 2) or single doses equivalent to a mild sunburn (3 MED) have been shown to reactivate latent herpes simplex virus infections [Spruance, 1985; Perna et al., 1988]. The mechanism leading to reactivation of herpes in humans is unknown. Studies in mice, however, indicate that UV irradiation of mice at the site of cutaneous infection with herpes led to the development of T<sub>s</sub> cells that decreased the

activity of those T cells that would normally react to herpes-infected cells [Aurelian et al., 1988].

#### Leishmaniasis

Leishmaniasis is a parasitic protozoan infection transmitted by the sand-fly. Human leishmaniasis is caused by several different species and sub-species of protozoa and is present on every continent except Australia and Antarctica. The World Health Organization has estimated that there are 400,000 new cases of leishmaniasis each year [UNDP, 1980], with the majority of cases being found in Africa and Latin America. WHO also concluded that this was a gross underestimate.

In studies using a broad spectrum UV lamp, a dose of 150 J m<sup>-2</sup> UV-B reduced the size of the lesioninduced leishmania but did not change the distribution of leishmania parasites in an animal model of the skin [Giannini, 1986]; 79% of the lamp's output was in the 280-320 nm range, and the remainder was above 320 nm. In a subsequent study, Giannini and DeFabo [1987] used monochromatic UV-B light at 290 nm or 320 nm. They found that 720 J m<sup>-2</sup> of 290 nm (given in five, 1-hour exposures of about 145 J m<sup>-2</sup>) appeared to promote the dissemination of parasites but did not modify lesion development. In contrast, five exposures to 330  $J m^{-2}$  of 320 nm UV-B (total dose = 1650  $J m^{-2}$ ) reduced lesion size but did not appear to promote dissemination. These observations lead to the hypothesis that exposure to sunlight, particularly as it becomes enriched with the shorter wavelengths of UV-B due to ozone depletion could have an adverse impact on skin diseases such as leishmaniasis. These observations suggest that exposure to sunlight could result in a suppressed immune response to the parasite and predispose the individual to a more severe disease.

#### Malaria

Malaria in humans is caused by one of four *Plasmodium* parasites and is transmitted by the mosquito. The immune responses against the four strain-specific malarial infections differ. Generally, malarial infection induces both humoural and cell-mediated immunity [Braunwald, 1987]. Numerous studies have suggested that suppressor T-cells are normally induced during malarial infection, but their presence has not been demonstrated conclusively. Preliminary studies in a mouse model of malaria have indicated that UV irradiation at low doses can impair the ability of the host to control the infection [Taylor, pers. comm.]. However, more work in both human and animal systems is needed to determine if UV radiation may have a role in the development of or response to malaria in humans.

<sup>&</sup>lt;sup>2</sup>MED is defined as the "minimum erythema dose" of energy required to produce clearly marginated sunburn in the sun-exposed area of the skin [Parrish et al., 1983]. In humans, 1 MED is approximately equivalent to 200 J m<sup>-2</sup> of UV radiation at 297 nm.

#### Bacterial and Fungal Infections

Bacterial and fungal cells are in constant residence on the skin and are the cause of the majority of skin infections. As a general rule, such infections are relatively minor, but in immunosuppressed individuals they can be a major cause of morbidity. Some of the more commonly found microbial inhabitants of the skin are the yeast Candida albicans and the bacteria Staphlococcus aureus and Escherichia coli. Preliminary data have shown that animals given high doses of ultraviolet radiation (15 KJ m<sup>-2</sup>) have difficulty in clearing either S. aureus, E. coli, or C. albicans when given an intravenous dose [Chung et al., 1988].

#### Tuberculosis and Leprosy

Tuberculosis is increasingly becoming a problem in the United States and many other areas of the world. In the United States in 1987, there were 22,517 cases of tuberculosis reported to the Centers for Disease Control, an increase of about 3% compared to 1986 /CDC. 1988]. After chicken pox and food poisoning (salmonellosis), tuberculosis had the highest number of cases reported of any infectious disease not classified as sexually transmitted. Immunity to the mycobacteria that causes tuberculosis is T-cell dependent, has a cutaneous phase, and is best elicited via immunization in the skin. Therefore, tuberculosis has many of the same qualities that identify diseases whose immunity may be compromised by UV radiation. Preliminary studies in an animal model of immunity to tuberculosis (immunization with Bacillus Calmette-Guerin) also suggest that moderate doses of UV radiation may impair development of an immune response and retard recovery [Kripke, 1989].

Leprosy also is caused by a mycobacterium and has many other characteristics which are similar to those of tuberculosis. T-cell mediated immunity is important in a host's response to leprosy and there is a cutaneous stage of the disease. It seems plausible to consider this too as a candidate disease which may be affected by increases in UV radiation as a result of ozone depletion.

#### Other Concerns: Vaccination Programs

The potential effects of increased UV-B on infectious diseases include not only direct increases in morbidity and mortality but via interference with vaccination programs as well. If an individual is immunized through UV-treated skin, the potential exists for that treatment to render the individual more susceptible rather than less susceptible to the administered antigen. This could have serious ramifications for vaccination programs in lesser developed countries where the control of certain

infections (e.g., measles) depends on effective vaccination.

#### Skin Cancer

Skin cancer is the most common form of cancer in white populations. There are two types of skin cancer: 1) non-melanoma skin cancer (NMSC) which affects the keratinocytes in the skin, and 2) cutaneous malignant melanoma (CMM) which affects the pigmentproducing cells of the skin. The risk of developing or dying from these cancers varies significantly by race. American blacks have an incidence rate of nonmelanoma skin cancer that is 1% of the incidence rate for whites [Scotto, 1989], and an incidence rate of CMM which is 10% of that of whites [NCI, 1988]. During the period 1977 to 1985, CMM increased 57% in whites and decreased 10% in American blacks. Their average age-adjusted incidence rates (adjusted to the 1970 U.S. standard population) per 100,000 were 8.3 and 0.8 respectively [NCI, 1988]. Similar data for Asians in the United States are not readily available. However, for the period from 1971 to 1977, the age-adjusted melanoma mortality in Japan was about 10% of that observed for the 1973 to 1977 period in the United States (0.16 versus 1.9 per 100,000; age adjusted to the 1970 Japanese population census) [Takizawa, 1987; NCI, 1988].

#### Non-Melanoma Skin Cancer<sup>3</sup>

There are two main types of non-melanoma skin cancers: basal cell carcinoma (BCC) and squamous cell carcinoma (SCC). The data currently gathered on these tumours are highly variable. In many instances, these tumours are removed in physicians' offices, and histopathology to identify type and/or reporting to a cancer registry is not performed. In registries that record these tumours, a few include only SCC, whereas most record a combination of BCC and SCC incidence under the designation of non-melanoma skin cancer. Where good medical care is available, the overall mortality is less than 1%. Although BCC typically represents 80% of non-melanoma skin cancer, the mortality is mainly due to SCC.

Squamous cell carcinomas have a convincing and clear-cut relationship to UV-B radiation. The causative role of sunlight is supported by the following observations: 1) SCC occurs predominantly on the most sunexposed parts of the skin, face, neck and hands; and

<sup>&</sup>lt;sup>3</sup>Much of this section was taken from a position paper, "Effects of ozone depletion on human health," written by one of the present authors (J.C. van der Leun) for the World Health Organization, Regional Office for Europe, Copenhagen, October 1988. WHO gave permission for this extensive quoting; some material was added and some quantitative data were slightly adjusted, according to more recent information.

2) in comparable populations, the incidence of SCC is highest in locations with the most sunlight. SCC also occurs predominantly in fair-skinned people, presumably due to a lack of protective pigment. The risk of developing SCC is strongly related to the cumulative dose of sunlight received throughout life. Several experimental animals develop SCC from exposure to UV radiation. A wealth of data is available, particularly for mice. De Gruijl et al. [1983] determined the doseeffect relationship for SCC induced by UV-B radiation. The carcinogenic effect could be described in mathematical terms as a power function of the doses of UV-B radiation regularly received by the animals. The basic same dose-effect relationship can be traced back in human epidemiological data [Fears et al., 1977]. This adds confidence to the assumption underlying the use of experimental data in this connection; the processes of photocarcinogenesis in mouse and human are generally the same.

The wavelengths responsible for UV-carcinogenesis in mice are predominantly in the UV-B range [Roffo, 1934; Blum, 1959], indicating that a depletion of stratospheric ozone has the potential to increase the incidence of skin cancer. As discussed in Chapter 1, one piece of information required for a quantitative consideration of this effect is an action spectrum for UV-carcinogenesis. The action spectrum gives the carcinogenic effectiveness of UV radiation as a function of wavelength. Until recently, such a relationship has not

been available, and investigators had to work with hypothetical action spectra. It was assumed, for instance, that the unknown action spectrum would be the same as that for UV-erythema, the reddening of the skin by UV radiation; the latter action spectrum has a pronounced peak in the UV-B range. Support for this assumption came from the work of Cole et al. [1986]. These investigators found that experimental data on photocarcinogenesis in mice could be described satisfactorily if it were assumed that the action spectrum for UV-carcinogenesis would be the same as that for UV-induced edema in mouse skin. The latter action spectrum was very similar to that for UV-erythema in human skin.

A programme to determine the action spectrum for UV-carcinogenesis in mice was carried out by Sterenborg and van der Leun [1987] and Slaper [1987]. These investigators exposed groups of hairless mice to UV radiation from eight different combinations of lamps and filters; from the experimental results they computed an action spectrum for UV-carcinogenesis (Figure 2.3). The action spectrum consists of a limited number of straight line segments, which indicates that it still is a crude approximation. The curve is best defined in the UV-B range, where a comparatively greater amount of experimental information is available. In this wavelength range, which is important from the viewpoint of ozone depletion, the action spectrum shows a close correspondence to that for UV-erythema. This tends to support, at least in

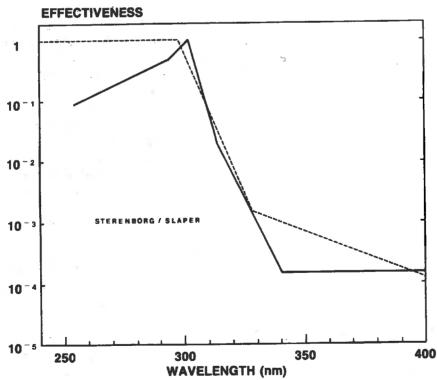


Figure 2.3
Action spectrum for photocarcinogenesis in hairless albino mice (full line); determined by Sterenborg and Slaper [Slaper, 1987]. The dashed line is a standardized action spectrum for UV- erythema, adopted by the Commission Internationale de l'Éclairage (CIE), 1987.

general, earlier predictions based on less complete data.

With both the dose-effect relationship and the action spectrum determined, more knowledge is available on the induction of squamous cell carcinoma by UV radiation than on any other potential consequence of ozone depletion. This has led to comparatively well-developed estimates of the increase of SCC with a decrease in stratospheric ozone. The estimates, which are being checked and refined, may also be of help in developing projections for other biological consequences. One conclusion is that the number of patients with SCC will increase more sharply than the rate at which the amount of ozone decreases. This is expressed in an "amplification factor," giving the percentage increase of the incidence caused by a 1% decrease of ozone. This percentage exceeds 1 as a result of the combined action of two amplifications: radiation amplification and biological amplification.

The radiation amplification, discussed in Chapter 1, represents the fact that a 1% decrease of ozone gives a stronger increase of the effective irradiance at the earth's surface. It depends on the wavelengths involved in the biological effect under consideration, because the increased penetration in the case of ozone depletion is wavelength dependent; it is greatest for the shortest wavelengths in the solar spectrum.

Figure 2.3 shows that in this wavelength range, especially in the wavelengths just above 300 nm, the carcinogenic effectiveness depends steeply on wavelength. This implies that an increase of irradiance in these wavelengths will have a comparatively large effect. Recent computations show that, with the Sterenborg-Slaper action spectrum, the radiation amplification factor has a value of 1.6 [Kelfkens and de Gruijl, 1989]. This is close to the values calculated before, on the basis of hypothetical action spectra; the values usually ranged between 1.7 and 2.0.

The biological amplification represents the fact that a 1% increase of the effective irradiance leads to a greater increase of the incidence of SCC. This amplification does not relate to the wavelengths responsible for carcinogenesis, but is due entirely to the steepness of the power relationship between the doses of UV radiation regularly received and the incidence of skin cancer. It may be concluded from epidemiological data in the United States [Scotto et al., 1981] that the biological amplification factor for SCC has a value of 2.9 [Slaper et al., 1986].

If the two amplifications are taken together, these data indicate that a 1% decrease of ozone will give a 1.6% increase of the effective irradiance; this will lead

to an increase of the incidence of SCC by  $1.6 \times 2.9 = 4.6\%$ . As SCC is a long-term reaction of the skin to chronic irradiation, it will take several decades for this increase to be fully realized.

For basal cell carcinoma, the situation is less clear. Although the body site distribution of BCC is similar to that for SCC, BCC has a latitudinal gradient that is less extreme. Furthermore, mice under UV lamps rarely develop BCC, so that an action spectrum specific to this tumour has not been determined. The clinical and epidemiological analogies between SCC and BCC are usually taken as an indication that BCC is also a consequence of solar UV-B radiation. If an additional assumption is made that the induction of BCC has the same action spectrum as the induction of SCC, it is possible to calculate the amplification factors. On this basis. the biological amplification factor for BCC becomes 1.7, and the overall amplification factor  $1.6 \times 1.7 = 2.7$ . It must be stressed that this latter value is more uncertain than the amplification factor for SCC. The amplification factors given here are in good agreement with those derived by others in a different way, but basically from the same data [Scotto et al., 1981].

The greater uncertainty is found in the most frequent form of non-melanoma skin cancer: basal cell carcinoma. The best-founded numbers refer to the more aggressive form: squamous cell carcinoma. For areas where only combined data on non-melanoma skin cancer are available, a value of 3 for the overall amplification factor appears to be the most appropriate. That means a 1% decrease of ozone will ultimately lead to a 3% increase of the incidence of non-melanoma skin cancer.

These calculations of increases of incidence to be expected for a 1% depletion of ozone form the basis for calculating the consequences of larger depletions. The depletion of total column ozone expected has varied over the years, with the improvement of atmospheric models. The expected depletions also will be influenced by real reductions of the use of CFCs, as agreed in the Montreal Protocol or by more stringent future limitations. These are sound reasons for giving the biological changes predicted "per percent of ozone depletion." In this way, the calculations of biological consequences can be readily adjusted to new data and new scenarios.

Should total column ozone be reduced by 5%, the carcinogenically effective UV-B irradiance would increase by  $5 \times 1.6 = 8\%$ . In the long run, this would lead to an increase of BCC by 14% and of SCC by 25%. The number of new patients affected may be estimated from data available on the present incidences. For the United States where comparatively good data are available, it is estimated that there are 500,000 new patients

with non-melanoma skin cancer per year, 80% of these having BCC and 20% SCC. The increases calculated for a 5% depletion of ozone would come down to 56,000 additional patients with BCC and 25,000 with SCC, or a total of 81,000 additional patients with non-melanoma skin cancer per year. Fewer data are available on the incidence of NMSC in many other parts of the world. It appears that a conservative estimate of the total number of non-melanoma skin cancer patients worldwide would be three times that in the United States. This would also lead to a three-fold increase, or about 240,000 additional patients with non-melanoma skin cancer per year worldwide.

The quantitative predictions for the incidence of non-melanoma skin cancer are based on comparatively solid data. However, they also are based on the assumption that the behaviour of human populations will not change. Human behaviour has important influence on the doses of UV radiation received, and a general change of behaviour could have a profound influence on the incidence of skin cancer. The rise of incidence expected from ozone depletion will come superimposed on any change of the incidence resulting from other causes.

#### Cutaneous Malignant Melanoma

Incidence rates of cutaneous malignant melanoma among white-skinned races throughout the world are rising at an alarming rate. During the period from 1974 to 1986, CMM incidence in the U.S. increased at an average yearly rate of 3 to 4%. For more than a decade, there has been serious concern that CMM is at least partially caused by exposure to sunlight and, in particular, by exposure to ultraviolet-B radiation [NAS, 1979, 1980, 1982]. However, several aspects of the scientific information about CMM have puzzled researchers and have contributed to uncertainty about the relationship of CMM to solar radiation and to UV-B. A brief overview of the biology of CMM is given below, followed by summaries of the information from human studies and animal models that must be considered in evaluating this relationship.

Cutaneous malignant melanoma is the result of the neoplastic transformation of melanocytes which are the pigment-producing cells in mammalian epidermis. Four different types of CMM have been evaluated for their relationships to sun exposure:

- Superficial spreading melanoma (SSM)
- Nodular melanoma (NM)
- Lentigo maligna melanoma (LMM), also known as Hutchinson's melanotic freckle
- Unclassified melanoma (UCM)

The two most common forms are SSM and LMM. It is thought that the role of sunlight in the induction of these tumours is very different. LMM shows a relationship similar to the cumulative dose relationship with BCC and SCC, whereas the relationship between solar exposure and SSM (and the other forms as well) may be related to peak exposures or possibly exposures early in life.

Evidence supporting a relationship between CMM and solar radiation, in particular UV-B, includes the following points [USEPA, 1987]:

- People who lack protective pigmentation, which reduces the penetration of solar radiation into the skin, have higher CMM incidence rates.
- Well-designed ecologic epidemiological studies show a correlation of higher CMM incidence rates with decreasing latitude and increasing radiation levels (UV-B in particular).
- Several case-control studies demonstrate an association between freckling and nevus formation (risk factors for CMM) and solar exposure.
- CMM rates differ between natives and immigrants to sunny climates.
- High rates of CMM in Xeroderma pigmentosum (XP) patients who are genetically deficient at repairing DNA damage induced by UV-B.
- Case-control studies indicate that sun exposure at early ages and of an intermittent and severe nature (e.g., sunburn) results in higher CMM risks.

In the past, the controversy with regard to the relationship between solar exposure and CMM other than LMM revolved around several observations that apparently contradict the kind of direct relationship between solar exposure and tumour development observed with non-melanoma skin cancer. Some of the key points include the following:

- Risk of the non-LMM form of CMM does not increase in individuals who spend much of their time outdoors
- Site-specific incidence of these forms of CMM does not favour those sites with the highest solar exposure
- Several ecologic epidemiologic studies failed to find an association between solar dose and CMM incidence (i.e., there was no latitudinal gradient)
- An animal model is lacking

Some of these issues have been resolved. For example, there are now two animal models (discussed below). At least one study [Pearl and Scott, 1984] has reanalyzed the site distribution data and suggests that on a surface area basis, CMM does occur on the more sun exposed areas. Clearly, however, CMM does not show the same propensity to develop on the head and hands that is demonstrated by non-melanoma skin cancer.

The U.S. Environmental Protection Agency completed a review of the available data and literature to assess the relationship of CMM to UV-B exposure [USEPA, 1987]. The salient conclusions of that review were the following: 1) the older literature, taken in conjunction with some very recent case-control epidemiologic studies, clearly indicated a role for sunlight in the etiology of all CMM, not just LMM; 2) based on animal studies, the active portion of the solar spectrum was most likely to be in the UV-B region, implicating UV-B in non-melanoma etiology and immunosuppression and on the sensitivity of XP patients; and 3) the dose-response relationships for incidence and mortality were estimated to be such that for every 1% decrease in stratospheric ozone there would be up to a 2% increase in CMM incidence and between 0.3 and 2% increase in CMM mortality.

Until recently, there were no animal models suitable to investigate the induction of melanomas by UV radiation. Thus, there was no possibility to check experimentally the suggestions based on epidemiology about the involvement of sunlight in the generation of melanomas, and no possibility to determine an action spectrum or a dose-effect relationship. Until such information is available, a high degree of uncertainty remains on any quantitative projections of an influence of ozone depletion on the incidence of melanomas. Recently, however, two promising animal models were found. Woodhead et al. [1988] reported on a small hybrid fish that developed melanomas after exposure to UV-B radiation. Lev [1988] found that UV-B radiation could induce melanomas in the marsupial Monodelphis domestica. Both models are new and publications have not yet appeared in print. It will take time before useful quantitative information is yielded by such models. But the emergence of these models supports the impression that UV-B radiation has a role in the induction of human melanomas.

#### Linkages

#### Global Warming

The relationships between weather parameters and human health are very complex, making it difficult to predict exactly what the impacts of global warming will be on health end-points. Potential concerns that have been identified, however, include the following [USEPA, 1989]:

- There may be an increase in the number of deaths associated with high summertime temperatures
- Global warming will make environments more favorable for vector-borne diseases, thereby increasing their incidence
- A warmer climate may lead to increases in perinatal mortality and pre-term birth, possibly due to increased infections
- Global warming may result in increased air pollution, thereby resulting in an increase in respiratory problems
- Disruption of agriculture due to changes in rainfall and temperature could result in additional famine and drought leading to widespread mortality from starvation as well as greatly decreased resistance to disease

Infectious diseases comprise a large area of potential overlap between the potential effects of global warming and stratospheric ozone depletion on human health. If the immunosuppressive effects of increased UV have an impact on infectious diseases, then this could have an additive or even synergistic effect on vector-borne diseases or perinatal infections. The two impacts could result in an increased incidence driven by climate change, occurring in populations made more susceptible by UV. Vaccination programs designed to deal with these infections could be compromised if vaccines are given to individuals with a high UV exposure. In addition, in the more northern countries where global warming will permit individuals to get out in the sun earlier in the season, the potential exists that a greater UV-B dose will be received under conditions of ozone depletion than would be received if the ozone level were maintained.

#### Air Pollution

Preliminary data suggest that stratospheric ozone depletion may result in increased levels of tropospheric ozone and other photochemical oxidants. Should this occur, asthmatics and other individuals who are sensitive to ozone levels are likely to encounter air pollution levels injurious to their health. The same prediction has been made vis a vis global warming. Thus, air pollution will be exacerbated by both global warming and ozone depletion thereby suggesting that a major interaction will be an increase in respiratory problems.

#### Animal Health

UV-B exposure is thought to be responsible for squamous cell cancer of the eye in Herefords and other cattle and has been shown to exacerbate infectious bovine keratoconjunctivitis (IBK) [Kopecky et al., 1979, 1980]. Thus, increases in UV are likely to increase these problems. Most animals, because of their heavy coats, are not likely to suffer the immunosuppressive effects of UV, but it is possible that global warming may change patterns of animal infectious disease via changes in the prevalence and distribution of insect vectors [Stem et al., 1988]. IBK is spread by the face fly; it could experience an augmentative impact both from ozone depletion and from global warming.

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## TERRESTRIAL PLANTS

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#### SUMMARY

Much of the research on the potential impacts of an increase in soinr UV-B radiation has centered on the effects on plant growth and physiology under artificial UV-B irradiation supplied to plant 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 radiaced UV-B for comparative purposes.

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Overall, the effectiveness of UV-B varies both among species and among cultivers of a given species. Of those plants which have been tested, a large proportion exhibit raduced growth (plant height, dry weight, leaf area, stc.), photosynthetic activity, and flowering. Computitive instructions also may be altered indirectly by differential growth suspenses. Photosynthetic activity may be reduced by direct effects on the photosynthetic process or metabolic pathways, or indirectly through

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 puter tissue layers, which presumably protect sensitive targets from UV damage. The key encympes in the biosymmetic 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 depistion. 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 AND BACKGROUND

The damaging effects of enhanced UV-B radiation resulting from a possible destruction of the stratospheric ozone layer by chlorofluorocarbons have been demonstrated by several research groups during the last 15 years. Reductions of leaf area, fresh and dry weight, lipid content and of photosynthetic activity were typically found in UV-B sensitive plant species. Additionally, alterations of leaf surface, epicuticular waxes, UV-absorbing pigments, and of the diffusion of water vapour through the stomata have been reported. For previous comprehensive publications see Caldwell [1981], Wellmann [1983], Teramura [1983], and Iwanzik et al. [1983].

#### STATE OF THE SCIENCE

#### **Artificial and Solar Radiation**

Most of our knowledge concerning the effects of UV-B radiation was obtained with artificial UV radiation sources supplementing either artificial white light in growth chambers, or solar radiation in greenhouses and in the field. Earlier growth chamber experiments demonstrated that UV-B damage was accentuated by low levels of white light (<200 μmol m<sup>-2</sup> s<sup>-1</sup> between 400-700 nm) [Warner and Caldwell, 1983; Mirecki and Teramura, 1984]. At present, perhaps the most appropriate radiation sources for growth chambers are xenon lamps (which can provide more than 1000 μmol m<sup>-2</sup> s<sup>-1</sup>) in combination with selective cut-off filters (Table 3.1).

Table 3.1 Stem length and leaf area in cucumber seedlings (Cucumis sativus cv Delikatess Robusta) after 18-days growth under artificial light (6000-W xenon lamp + 2 UV-B fluorescent tubes) using selected cut-off filters [Tevini et al., 1986]. Daily doses weighted according to the generalized plant weighting function [Caldwell, 1971] normalized at 300 nm. Locations calculated from Green et al. [1980] for day 127 of the year, according to equivalent daily doses.

• •					
Filters Used	Daily Dose (J m <sup>-2</sup> )	Simulated Location	Stem Length (cm)	Leaf Area (cm²)	
WG 295/2mm WG 305/2mm WG 305/3mm WG 305/4mm WG 305/5mm WG 320/2mm	14087 9532 5231 3695 2275 1016	0°N <sup>1</sup> 30°N <sup>2</sup> 49°N <sup>3</sup> 60°N <sup>4</sup> 65°N <sup>5</sup> 70°N <sup>6</sup>	4.41 5.74 6.74 6.97 7.66 7.28	5.28 6.27 7.45 9.04 9.06 9.59	

Location (ozone layer thickness):  $^{1}220$  D,  $^{2}280$  D,  $^{3}320$  D,  $^{4}300$  D,  $^{5}300$  D,  $^{6}>300$  D

In greenhouses or in the field where larger-scale experiments have been performed, cellulose acetate plastic films were used to shape the spectral distribution of radiation produced by low-pressure fluorescent sunlamps, eliminating harmful VV-C radiation (Figure 3.1). These fluorescent sunlamps were primarily Westinghouse FS-40 and Philips TL 40/12. This artificial UV-B radiation can be supplied to the plants in the field by adding a constant proportion of UV-B radiation in a modulated fashion while monitoring the ambient solar input [Caldwell et al., 1983], or by administering a fixed

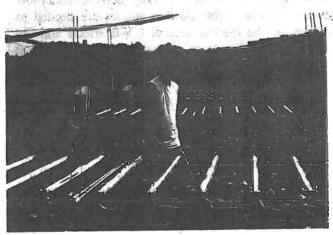


Figure 3.1
In field studies, fluorescent sun lamps provide supplemental UV-B radiation to plants. Lamps above control plants are filtered with plastic films which absorb UV-B radiation emitted from the lamps. Control plants receive only ambient levels of UV. In UV-B enhanced treatments, lamps are filtered with a UV-B transmitting plastic film. Therefore, these plants receive ambient UV plus a supplement from the lamps.

amount can be administered over a specified time period [Lydon et al., 1987]. In greenhouses, the UV-B component of artificial light sources is absorbed entirely by covering the lamps with Mylar plastic films; plants grown under these filtered lamps are considered as controls. In most greenhouse studies, control plants do not receive UV-B radiation at all, which is unrealistic for plants grown outdoors under a natural solar spectrum.

Because solar and artificial UV-B radiation sources have different spectral energy distributions, this radiation must be weighted according to its biological effectiveness. Most plant researchers use the generalized plant action spectrum [Caldwell, 1971] and/or the DNA action spectrum [Setlow, 1974] as weighting functions. (See Chapter 1 of this report for the description of weighting functions.)

Ideally, using a radiation source that perfectly simulates various ozone depletion scenarios would eliminate the need for using weighting functions at all. One technique to avoid weighting functions was demonstrated by Tevini et al. [1988a]. Two identical growth chambers were located at a southern latitude with naturally high ambient levels of solar UV-B radiation, and were covered with UV transmissible filters. Ambient UV-B radiation was reduced in one growth chamber by passing ozone through the filter on top. This simulated the lower UV-B radiation naturally found in more northern latitudes, which may serve as a reference or "control." The second filter contained only normal air, therefore plants beneath it received ambient UV-B radiation which is higher when compared to the control.

## Effects on Plant Growth, Competition and Flowering

#### Plant Growth

Growth characteristics such as plant height and leaf area are reduced in UV-B sensitive plants to various extents, depending on plant species and cultivar [Lydon et al., 1986; Murali and Teramura, 1980a]. A clear dose response relationship was demonstrated for plant height and leaf area of cucumber seedlings grown under enhanced artificial UV-B radiation in growth chambers (Table 3.1, Figure 3.2).

Both artificially and naturally supplied levels of UV-B radiation decreased stem length and leaf area in cucumber seedlings with increasing daily dose. The weighted daily doses listed in Table 3.1 are equivalent to the UV-B incident at different latitudes according to an empirical model [Green et al., 1980]. When the new ozone filter technique was used to simulate a 25% increase in solar UV-B irradiance (approximately equivalent to a 12% ozone depletion), reduced growth rates also were observed, which continued throughout the development of plants receiving higher levels of UV-B [Tevini et al., 1989b].

Growth studies with soybean (Glycine max L. cv Essex) in a greenhouse revealed that UV-B effects

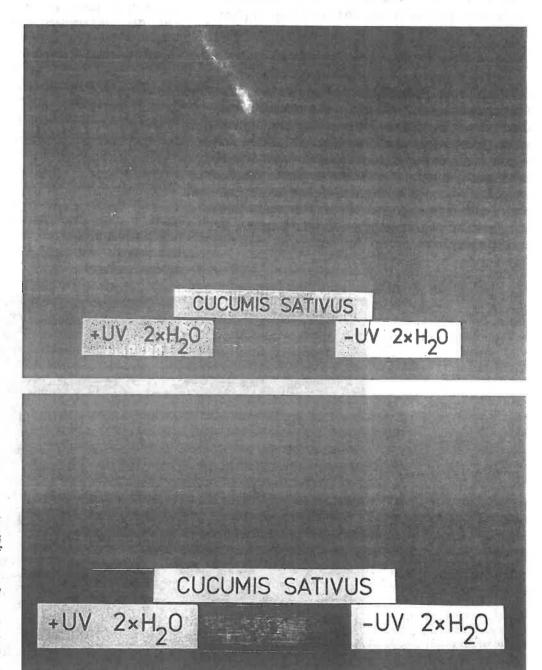


Figure 3.2
Cucumber seedlings grown under artificial UVB radiation using xenon lamps and cut-off filters; leaf area of seedlings (top), plant height (bottom). Control plants received ambient levels of UVB (-UV), whereas treated plants (+UV) received a UVB dose equivalent to a 12% ozone depletion at temperate latitudes.

(simulating a 25% ozone depletion) varied with plant growth stage; controls received no UV-B radiation. The most UV-effective period occurred during the transition time between vegetative and reproductive stages [Teramura and Sullivan, 1987]. Even intermediate levels of UV-B radiation (simulating a 10% ozone depletion) reduced plant height, leaf area and total dry weight at the end of the vegetative and reproductive phases. Furthermore, field studies with six soybean cultivars simulating a 16% and 25% ozone depletion, showed a UV-B dose dependent reduction in relative growth rate and plant size [Lydon et al., 1986]. In a six-year field study, reductions in plant height and leaf length were found both in wheat and wild oat when grown separately [Barnes et al., 1988]. These changes were not associated with reduced photosynthesis, and reductions in plant height or leaf area are not always correlated with total biomass reduction.

Besides differences among species, greenhouse and growth chamber studies have shown large response differences among cultivars of a single species. About 80 cultivars of 12 species have been screened to date, including 23 cultivars of soybean [Teramura, 1986]. An evaluation of growth and yield responses found 41% of the soybean cultivars to be tolerant or unaffected; the rest were UV-B sensitive. In terms of plant height, leaf area and total dry weight, the cultivars Forrest and York were the most tolerant and even showed increases in vegetative responses. James, Bay and Essex were the

most sensitive cultivars showing reductions in vegetative growth between 26% and 38% when grown in a greenhouse where controls received no UV-B, and between 11% and 22% in the field [Teramura and Murali, 1980].

Differences in total biomass accumulation also were found in five cucumber cultivars in greenhouse studies [Murali and Teramura, 1986a]. The cultivar Marketmore was most tolerant, and XPH 1484 was the most sensitive to UV-B radiation simulating a 19% ozone depletion. The reasons for this diversity might be differential accumulation of UV-screening pigments or morphological alterations. Many UV-B irradiated plants respond to reduced leaf area with increased leaf thickness as shown previously in studies of cucumber [Tevini et al., 1983] and soybean leaves [Mirecki and Teramura, 1984].

Although only limited information exists, conifers also appear to be sensitive to UV-B radiation. Three out of ten conifer species — lodgepole pine (Pinus contorta), red pine (Pinus resinosa) and loblolly pine (Pinus taeda) — showed reduced seedling height in a UV-B dosedependent way in greenhouse studies where controls received no UV-B radiation [Sullivan and Teramura, 1988] (Figure 3.3). Trees have long life spans extending over decades. Therefore, trees planted now will spend their lives under increased levels of UV-B radiation. Since breeding new varieties is a slow and expensive process, increased UV-B may be of particular concern to forests.

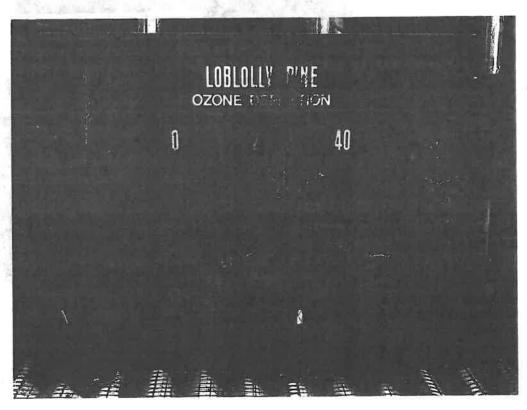


Figure 3.3
The effects of increased UV-B radiation on loblolly pine growth. The control plants received no UV-B radiation. Reductions in growth were found in seedlings receiving 7 months of UV simulating 25% and 40% ozone depletions.

UV-B induced growth reductions are associated with changes in cell division and/or cell elongation. A clear interaction with the growth regulator indole-3-acetic acid (IAA) was demonstrated in sunflower seedlings. IAA absorbs in the UV-B range and can be converted inside the plant to various other metabolic products [Tevini et al., 1989b]. One of these products inhibits hypocotyl growth when applied exogenously. UV-B effects resulting in growth reduction, obviously not associated with DNA damage was characterized in cress seedlings by action spectra. This growth inhibition would increase linearly with increasing solar UV-B dose [Steinmetz and Weldmann, 1986].

#### Competitive Balance

Many plants exhibit differential sensitivities to enhanced UV-B, which could govern competition between species. In a field study with seven competing pairs of agricultural crops and associated weeds (Table 3.2), it has been shown that enhanced UV-B increased the competitive advantage of wheat over the weeds [Gold and Caldwell, 1983].

Table 3.2 shows species pairs growing in natural ecosystems, such as montane forage species *Poa pratensis* and *Geum macrophylum*. Simulating an ozone depletion of 40%, Geum had a considerably greater advantage over Poa, compared to the competitive balance under ambient levels where both had crowding coefficients near

1.0 [Fox and Caldwell, 1978]. The reasons for the competitive shift are due mainly to morphological changes as shown for the competing crop/weed pair of wheat and wild oat [Barnes et al., 1988]. Wild oat showed less stem elongation and smaller leaf lengths under enhanced UV-B than did wheat. There was no direct effect on photosynthesis in either species and thus the competitive changes must have other causes [Beyschlag et al., 1988].

#### Pollination and Flowering

Pollen is well-protected against UV-B radiation because the anther walls filter out over 98% of incident UV-B [Flint and Caldwell, 1983]. The pollen wall, which contains UV-absorbing compounds, is also wellprotected during pollination. However, after transfer to the stigma, the pollen tube may be susceptible to UV-B, especially binucleate types with longer time courses for germination and penetration than trinucleate types [Flint and Caldwell, 1984a]. Indirect evidence from experiments on 10 species supports the notion that UV-B impacts pollen germination [Campbell et al., 1975; Chang and Campbell, 1976; Caldwell et al., 1979; Flint and Caldwell, 1984b]. Even moderate UV-B irradiances inhibited germination of Petunia hybrida and Vicia villosa by 65% within one hour [Campbell et al., 1975]; Tradescantia clone 4430, Brassica oleracea, Papaver rhoeas, or Cleome lutea were inhibited by 33% within three hours. In three of four species, the UV-B irradiation currently found at high elevations or low latitudes

Table 3.2 Relative crowding coefficients of competing species pairs grown under ambient and enhanced UV-B radiation. [Fox and Caldwell, 1978; Gold and Caldwell, 1983]

Competing	Relative Crowding Coefficient <sup>1</sup>			
Species 1	Species 2	O <sub>3</sub> Depletion <sup>2</sup>	_	Enhanced UV
Alyssum alyssoides Amaranthus retroflexus Amaranthus retroflexus Setaria glauca Triticum aestivum	Pisum sativum Medicago sativa Allium cepa Trifolium pratense Avena fatua	40% 40% 40% 40% 16%	0.34 3.56 1.89 2.06 1.08	0.25 0.73* 2.01 18.74 1.28
Triticum aestivum Triticum aestivum Poa pratensis Bromus tectorum Plantago patagonica	Avena fatua Aegilops cylindrica Geum macrophyllum Alyssum alyssoides Lepidum perfoliatum	40% 16% 40% 40% 40%	1.08 0.48 0.85 6.35 0.75	1.69* 1.57* 2.28* 1.63* 0.68

Relative crowding coefficient of 1.0 means that neither species has the competitive advantage; more than 1.0 means that Species 1 has a competitive advantage, and less than 1.0 means that Species 2 has the advantage.

<sup>&</sup>lt;sup>2</sup> Simulated ozone depletion based upon generalized plant action spectrum [Caldwell, 1971], calculated at 40°N.

<sup>\*</sup> Denotes a significant difference (P < 0.05) between control and enhanced UV treatment.

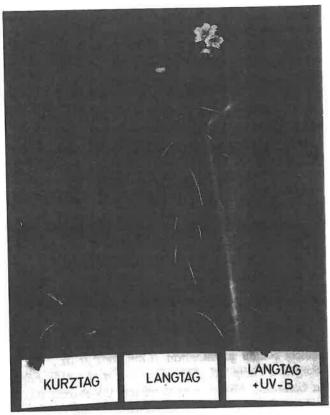


Figure 3.4

The long day plant Hyoscyomus niger flowers after induction by long days (and continuous illumination) but not in short days. However, when UVB is added to continuous illumination, flowering is inhibited.

is effective in partially inhibiting germination [Flint and Caldwell, 1984b]. Currently, it is not possible to assess the general UV impact on plant pollen because of the lack of experiments. Ovules are well hidden in the ovaries and therefore may be sufficiently protected against solar UV-B radiation.

Flowering responses of plants have been reported for about 10 species. Generally, flowering was increased when UV-B was excluded by Mylar plastic films or glass, as shown for Melilotus [Kasperbauer and Loomis, 1965], Trifolium dasyphyllum [Caldwell, 1968] and Tagetes [Klein et al., 1965]. In addition, a clear UV-B dose rate and dose-dependent inhibition of photoperiodic flower induction was observed in the long day plant Hyoscyamus niger [Rau et al., 1988] (Figure 3.4). Even 100 mW m<sup>-2</sup> UV-B led to a 20% decrease in photoperiodic flower induction compared to plants irradiated only with white light, whereas 300 mW m<sup>-2</sup> produced a 50% reduction. In contrast, Hart et al. [1975] did not find any significant effect on flowering of Petunia, tasseling of Zea mays, or heading of Sorghum bicolor. Besides

flower suppression by UV-B, its effect on photoperiodic induction may alter the timing of flower induction, although no experimental data are available. This could have far reaching consequences for natural ecosystems, if plants flowered earlier or later than their natural insect pollinators appear.

## Effects on Plant Function: Photosynthesis and Transpiration

When high UV-B irradiances were used in combination with low levels of white light, such as commonly found in growth chambers, effects on photosynthesis (measured as CO2-assimilation) were generally deleterious. However, even in the presence of higher levels of white light in greenhouses and in the field, reductions in photosynthesis of up to 17% were reported in the UV-B sensitive soybean cultivar Essex when supplied with UV-B equivalent to an 18% ozone depletion [Murali and Teramura, 1986b; 1987J. Solar UV-B also reduced net photosynthesis in sunflower seedlings by about 15 % when a 12% ozone depletion was simulated by using the new ozone filter technique [Tevini et al., 1988a]. It seems likely that the effect of enhanced solar UV radiation on photosynthesis increases during development in sunflower seedlings [Tevini et al., 1989b]. One reason for the reduction in photosynthesis might be due to stomatal closure by enhanced UV-B, as demonstrated earlier in cucumber seedlings [Teramura et al., 1983] and for Eragrostis leaves [Negash, 1987].

The action spectra for stomatal closure of Eragrostis tef peaks below 290 nm, whereas radiation longer than 313 nm is nearly ineffective [Negash and Björn, 1986]. Stomatal closure may be caused by a loss of turgor pressure mediated through ion leakage from the guard cells as demonstrated with \*6Rb +-ions in epidermal strips of bean leaves [Negash et al., 1987]. Transpiration was reduced in some UV-sensitive seedlings, such as cucumber [Teramura et al., 1983] grown under artificial UV-B in growth chambers, or in sunflower seedlings grown under ambient solar UV radiation in Portugal compared with those receiving a reduced UV dose [Tevini et al., 1989b]. The time course for stomatal closure was rapid at low UV-B doses and stomatal opening was slow at higher UV-B doses.

In addition to stomatal responses, photosystem II activity in chloroplasts also is reduced (Figure 3.5). This was demonstrated in isolated chloroplasts [Noorudeen and Kulandaivelu, 1982; Iwanzik et al., 1983; Tevini and Pfister, 1985], thylakoids [Bornman et al., 1984], and photosystem II membrane fragments [Renger et al., 1989].

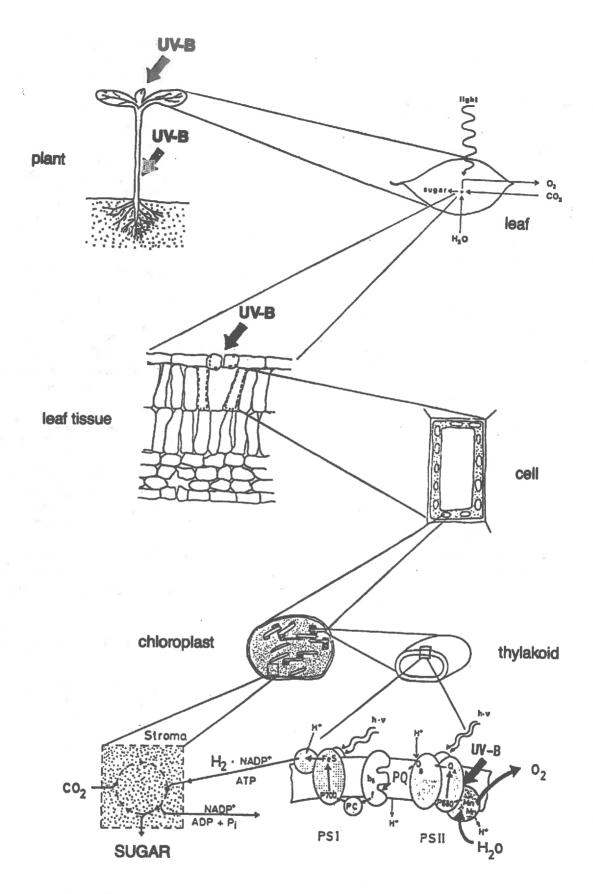


Figure 3.5
A generalized model for the effects of UV-B radiation on plants. Presumed targets of UV-B on growth, stomatal function and thylakoid structure are indicated by arrows.

#### **Effects on Plant Composition**

Photosynthetic Pigments, Other Lipids, and Proteins

The effects of UV-B radiation on chlorophylls were previously reviewed by Teramura [1983]. Chlorophylls are relatively stable except at very high white light illumination (see Chapter 4). Chlorophyll destruction was found to be a function of UV-B dose only in UV-sensitive plants such as bean and cucumber in growth chamber studies (Table 3.1) [Tevini et al., 1983]. Carotenoids are affected similarly in those sensitive species. Using ozone filters in a field study in Portugal, solar UV-B simulating a 12% ozone depletion reduced chlorophyll content when expressed on a per plant basis [Tevini et al., 1989b].

Effects of enhanced UV-B on surface waxes of cucumber seedlings grown in growth chambers were studied by Tevini and Steinmüller [1987]. They found that the distribution of the main wax compounds was shifted towards shorter chain lengths. This shift was due to a direct UV-B impact on wax biosynthesis.

In a six-year field study with Essex soybean, a 25% ozone depletion resulted in possible changes in food quality, appearing as reductions in the protein and oil content of seeds (*Table 3.3*).

#### **UV Protective Pigments**

Most higher plants accumulate UV-absorbing pigments in the epidermal portion of their leaves after exposure to UV-B [Wellmann, 1983; Tevini et al., 1983; Beggs et al., 1986]. Rumex patentia, a weedy plant that is relatively sensitive to UV-B, has a higher epidermal

UV transmittance than the more resistant species Rumex obtusifolius when exposed to solar radiation [Robberecht and Caldwell, 1986]. These UV-absorbing compounds are mainly phenylpropanoids, such as flavonoids. Anthocyanins, which also accumulate under enhanced UV-B in many plant species, have only weak absorption in the UV-B region and, therefore, may be regarded as UV-screens only at very high concentrations. In addition, other important secondary plant products also accumulate under increased UV-B radiation [Zangerl and Berenbaum, 1987; Lydon et al., 1987]. Because many of these compounds are toxic to organisms including insects, changes in their concentration might affect their resistance to herbivores.

It has been clearly shown that flavonol accumulation is specifically UV-induced and linearly dependent on UV-B dose [Wellmann, 1985]. This dose-response relationship also was observed in the field within four hours of solar radiation in dark-grown radish seedlings exposed to UV-B radiation simulating a 12% ozone depletion [Tevini et al., 1989a]. This increase in flavonoid concentration is due to a higher activity of the key enzyme PAL (phenylalanine ammonia lyase) and/or to higher rates of biosynthesis of this enzyme. In rye, PAL activity increased within minutes by decreasing the PAL inhibitor, trans-cinnamic acid, through its isomerization to the cis form. This trans-cis shift is wavelength dependent and may be responsible for regulation of genetic transcription as shown in potato tissue [Shirsat and Nair, 1986]. The isomerization of trans-cinnamoyl derivatives may protect seedlings within minutes of breaking through the soil surface; the absorption of isolated epidermal layers is clearly shifted to shorter wavelength by cis isomerization [Tevini et al., 1988b]. Schmelzer et al.,

Table 3.3 Summary of UV effects simulating a 25% ozone depletion on soybean yield and quality. [From Teramura and Sullivan, 1988]

Cultivar	Year	% Change in Yield	% Change in Seed Quality Protein Oils
Essex	1981	-25	
	1982	-23	-5 $-2$
	1983	+6	4 +1
	1984	<del></del> 7	0 -2
	1985	-20	0 0
	1986	-19	0 -1
Williams	1981	+22	
	1982	+9	0 +5
	1983	—11	<b>−2 −1</b>
	1984	+10	+3 -5
	1985	+4	<b>-1 0</b>
	1986	+6	-3 +1

[1988] showed that epidermal cells of parsley leaves accumulating flavonoids contain the whole sequence for the UV-induction of flavonols. Each individual cell synthesizes m-RNA, encoding the key enzyme of flavonoid synthesis, the enzymes themselves, and the end product. Further protective pigments may be carotenoids. It is a well-known phenomenon that carotenoids protect the photosynthetic apparatus against high intensities of visible light by quenching singlet oxygen or free radicals. In the fungus Fusarium aquaeductuum, it has been found that carotenoid pigments also protect the organism against UV-B [Rau et al., 1988]; however, to what extent this protection is effective has to be further elucidated.

A second important protecting mechanism in plants, as in organisms in general, is photoreactivation. UV radiation induces pyrimidine dimer production in DNA with increasing efficiency at shorter wavelength. However, this potential damage can be overcome by simultaneous irradiation with UV-A/blue light, which activates the enzyme DNA-photolyase, responsible for dimer repair (i.e., photoreactivation). UV-B induces stress phenomena as isoflavonoid formation in bean leaves [Beggs et al., 1985] or inhibition of light dependent anthocyanin synthesis in mustard cotyledons [Wellmann et al., 1984]. These effects occurred exclusively under experimental conditions that restricted photoreactivation. Limited knowledge exists about capacity, regulation or distribution of this repair mechanism in naturally grown plants [Wellmann, 1988].

#### Effects on Yield

Due to space limitations and the artificial nature of the environment in growth chambers, investigation of plant yield must be conducted outdoors in carefully designed field studies. Of particular concern in most growth chambers and greenhouses is the low level of visible radiation supplied to the plants. It is well-documented that the effectiveness of UV-B radiation is magnified when levels of white radiation are below the optimum for photosynthesis. The reasons for this phenomenon are not completely understood; however, it is thought that natural UV protective mechanisms do not become fully developed in low levels of visible light.

Since the last comprehensive review [Teramura, 1987], limited additional field studies have been performed, and most of those have been with soybean cultivars. Earlier results on about 25 plant species illustrated the degree of technical difficulty and uncertainty surrounding the estimates of UV-B effects on yield. Many of these studies were conducted with filtered UV-B sources simulating relatively high ozone reductions [Biggs and Kossuth, 1978; Biggs et al., 1984]. In a

German field study using filtered lamps and simulating 10% and 25% ozone reductions, no UV-B effects were demonstrated in three cabbage cultivars, lettuce, nor rape. Because flavonoid contents increased in most plants, there might have been a UV-B effect on food quality [Dumpert, 1983], but this was not tested specifically. Biggs and Kossuth [1978] and Biggs et al. [1984] grew 10 crop species in Gainesville, Florida (29°N) and found yield reductions between 5% and 90% in half of the species, including wheat (-5%), potato (-21%), and squash (-90%). Rice, peanut and corn were unaffected. The overall results indicate a high degree of variability among species complicated further by differences in artificial light sources, climate, soil quality, day length, etc.

In addition to this species level variability, there is a high degree of variability among different cultivars [Biggs et al., 1981; Teramura and Murali, 1980]. Twentythree soybean cultivars were grown in a greenhouse and, of these, six were selected for a comparative field study. Results from the greenhouse and the field indicated that the cultivar Forrest was the most tolerant, whereas Shore and York were the most susceptible to UV-B. The conclusions were based upon a combination of responses including plant height, leaf area, total dry weight and seed yield. Only York had a significant 25% reduction in yield when exposed to a simulated 16% ozone reduction. Although James, Forrest and Essex demonstrated a similar level of yield reduction, they were not statistically significant. During the next five years, only Essex and Williams were grown under a simulated 16% and 25% ozone depletion. These two cultivars were chosen because they are widely grown in the United States and had demonstrated contrasting UV-B sensitivities. Except for 1983 and 1984, yield in Essex was reduced by 19-25% while a 10-22% higher yield was found in Williams when simulating a 25% ozone reduction (Table 3.3). At a 16% ozone reduction, no consistently significant relationship could be found in Essex or Williams. The 1983 and 1984 field trials may not be representative of typical years because both years were abnormally dry and hot; yield in the controls were already reduced by up to 80%. UV-B effects might have been partially masked when growth is already impacted by other stresses.

Currently, limited information is available on the reasons for these large UV-B response differences among cultivars. The genetic bases (heritability) of UV tolerance and sensitivity need to be understood to estimate the possibility of using conventional breeding practices to minimize the potential impacts of UV damage. At present, plant breeders have not yet considered UV sensitivity as a selective factor. This has resulted in the

development of cultivar Essex which appears to be quite sensitive to UV-B radiation. Essex is a newer cultivar which is replacing the UV-tolerant cultivar Williams in many areas of the United States.

### Effects in Combination with Other Stresses

Among the most common stresses experienced by plants growing in the field are water and mineral deficiencies. Interactions of other environmental factors with UV-B radiation have been extensively reviewed by Teramura [1986]. Water stress in combination with enhanced UV-B (simulating a 12% ozone depletion) adversely affected water loss in cucumber seedlings. Stomata of water-stressed control plants receiving ambient levels of UV-B radiation displayed the normal daily pattern of opening and closing; plants irradiated with enhanced levels of UV-B lost their capacity to close stomata with increasing UV-B dose [Teramura et al., 1983]. Radish seedlings were much less sensitive to UV-B radiation under water stress than cucumber. Radish had higher leaf flavonoid contents, which could absorb UV in the leaf epidermis and thereby protect underlying tissues [Tevini et al., 1983]. Well-watered Essex soybean that was grown in the field under enhanced UV-B (simulating a 25% ozone depletion) showed reductions in growth, dry weight and net photosynthesis. But no significant UV-B effect could be detected in waterstressed plants [Murali and Teramura, 1986b]. Photosynthetic recovery after water stress was shown to be greater and more rapid in UV-B irradiated soybean plants [Teramura et al., 1984a] and to be associated with stomatal opening instead of with internal water relations [Teramura et al., 1984b]. Phosphorus deficiency was also examined in the Essex soybean cultivar under enhanced UV-B artificially supplied in a greenhouse and equivalent to a 16% ozone reduction [Murali and Teramura, 1987]. UV-B did not produce any additional damage to growth and photosynthesis in phosphorusdeficient plants. However, enhanced UV-B reduced net photosynthesis by about 20% in plants well-supplied with phosphorus. Information on the interactions between mineral deficiency and UV-B radiation are limited to small-scale experimental studies. Therefore, the applicability of these studies to natural field conditions is currently unknown.

### ASSESSMENT OF RESULTS

Because of technical difficulties in conducting realistic UV-B experiments, many of the earlier studies show quite conflicting responses. In addition, a number of greenhouse studies excluded UV-B entirely from the controls, which is unrealistic in nature. Therefore, one must be cautious when interpreting these results. The

use of an ozone filter to reduce solar radiation might solve this problem, but it is only applicable in small growth chambers placed in locations with high solar UV-B input. Refined plastic materials with absorption coefficients matching that of ozone might be developed to conduct more realistic greenhouse and field studies.

Plant responses to enhanced UV-B levels vary markedly within species and among species. Photorepair, accumulation of UV-absorbing pigments, and growth delay are potential adaptive mechanisms; however, only a few studies have demonstrated a direct relationship between these protective mechanisms and insensitivity to UV-B radiation.

The accumulation of UV-absorbing compounds and growth reduction have been shown to be dependent on wavelength, dose rate, and dose. However, growth reduction is not always correlated with reductions in photosynthesis, total biomass, or yield. Reductions in net photosynthesis on a whole plant basis also may be due to overall growth reductions rather than to direct effects on photosynthetic function, although inhibition of photosystem II activity by UV-B has been demonstrated. Conclusions from growth chamber studies using low levels of white light, which limit photosynthesis in most plant species, are not applicable to the field or the greenhouse where higher levels of visible radiation are present. Differential growth response also may be involved in shifts in competitive balance between plant species. From the few competition studies which have been performed, there is a potential risk for future changes in ecosystem composition. Global agricultural yield is also potentially at risk, but only a few studies have been made under realistic UV radiation conditions. Significant reductions in harvestable yield have been found in several soybean cultivars. Other species might also be impacted but they have not been properly tested. To date, it is not known whether other environmental variables such as drought, mineral deficiency, temperature and humidity mask the real impact of enhanced UV-B radiation.

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#### **CHAPTER 4**

## **AQUATIC ECOSYSTEMS**

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#### SUMMARY

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

Planktonic marine organisms account for over onehalf of the total, global amount of carbon fixed annual (10<sup>11</sup> 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 even current UV-B levels, and are potentially endangered by expected increases in UV-B radiation.

UV-B radiation 1) affects adaptive strategies (e.g., motility, orientation), 2) impairs important physiological functions, such as photosynthesis and enzymatic reations, 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, and elicits 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
- Reduced sink capacity for atmospheric carbon dioxide, thereby augmenting the greenhouse effect

Additional information is needed before more reliable assessments of the risks posed to the marine environment from increasing UV-B radiation will be possible.

#### INTRODUCTION AND BACKGROUND

Photosynthetic organisms on our planet are estimated to fix about 10<sup>11</sup> tons of carbon annually. This enormous mass can be visualized by a coal train that spans the distance from the earth to the moon and back five times. Less than one-half of this is due to photosynthesis in all higher plants (i.e., crops, forests, grassland, tundra, etc.). Planktonic organisms in the oceans fix the remaining amount of carbon dioxide.

Solar UV-B radiation penetrates deep into the zone where the organisms live. If increased UV-B impairs the productivity of the organisms, the effects may be dramatic both for the intricate marine ecosystem and for humans, who are affected by this system. More than 30% of the world's animal protein for human consumption comes from the sea; in many countries, this percentage is significantly larger. Any reduction of this productivity will undoubtedly affect global food supply.

In addition, a decrease in the size of the phytoplankton populations will result in a higher CO<sub>2</sub> concentration in the atmosphere, which will augment the CO<sub>2</sub> increase caused by fossil fuel burning. This consequence of stratospheric ozone depletion is not yet accounted for by the current climate change/greenhouse effect models.

Research on marine ecosystems is needed to improve our understanding of how stratospheric ozone depletion could influence the world food supply. Past efforts have addressed the physical variables that determine the exposure (or dose) to the systems, as well as the amount of UV-B radiation that produces biological effects. Studies also have addressed the direct effects on the sensitive life stages of ecologically important marine organisms, and the extent to which the additive effects might impact marine resources that are significant to man. The sum of past efforts suggests that the likelihood of a significant impact resulting from UV-B

exposure to marine environments is real, even if it cannot yet be fully quantified.

The different sensitivity of the primary producers (e.g., phytoplankton) and of the primary consumers (e.g., zooplankton) to UV-B radiation will result in altered species composition within these communities. Any increase in the radiation level is also likely to decrease the overall productivity. Both factors will introduce instabilities in ecosystems and will likely have an influence on higher levels within the food web. The biological food web in both freshwater and marine ecosystems starts with the primary producers — mainly the phytoplankton (Figure 4.1). Primary consumers utilize the biomass the phytoplankton produce, and are themselves food input for the next level in the food web.

Because of their need for the sun's energy, phytoplankton are restricted to the upper layers of their oceanic environment. Mutual shading, absorption, and light scattering prevent effective light penetration below a certain depth where phytoplankton cannot survive. The penetration of light into a body of water strongly depends

on the characteristics of the water. Water can range from turbid coastal waters to clear blue oceanic waters. In addition, light penetration depends on the wavelength of the radiation; shortwave violet and longwave red light are more strongly absorbed than blue-green light (Figure 4.2) [Jerlov, 1970]. Even though partially attenuated, a fair amount of solar UV-B radiation penetrates into the photic zone [Worrest, 1986]. This presents a potential hazard for the planktonic organisms, because they do not possess the protective epidermal UV-absorbing layers that are characteristic of higher plants and animals. For most of the observed effects in planktonic organisms studied to date, visible radiation and longer wavelength UV-A radiation (315-380 nm) may not be as effective.

Ambient or slightly increased doses of UV-B radiation can decrease phytoplankton primary production [Worrest, 1986; USEPA, 1987]. Currently, no quantitative assessment of the loss in biomass production in aquatic systems is available. However, even a small loss will have a noticeable adverse effect. The annual biomass

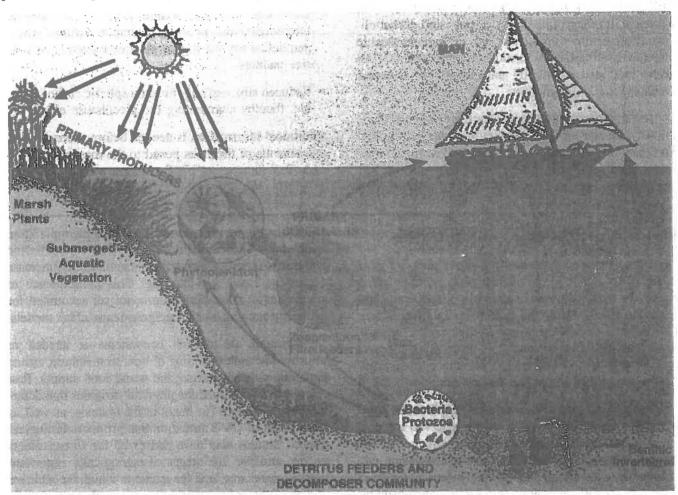


Figure 4.1

Example of the biological food web in a marine ecosystem, which starts with the primary producers; the biomass they produce is utilized by the primary consumers, which in turn serve as food input for the next level in the food web.

production by phytoplankton can be calculated as about  $6 \times 10^{14}$  kg. A loss of 10% would far exceed the gross national product of all countries in the world, assuming any reasonable price for biomass on the market.

#### STATE OF THE SCIENCE

#### **Primary Producers: Phytoplankton**

Ultraviolet radiation damage to the primary producers will have dramatic consequences because these organisms produce more than one-half of the earth's biomass. In addition, a large food web of dependent organisms relies upon the productivity of the phytoplankton. The first evaluations were performed on laboratory test systems, the physiology of which was well known and for which stress situations could easily be determined experimentally. Most initial studies used UV-B radiation from artificial sources producing a spectrum that deviated significantly from natural solar radiation both quantitatively and qualitatively. One important group of phytoplankton, the nanoplankton (defined by its extremely small size), has not yet been studied in any detail. Factors that control the adaptation of phytoplankton to constantly changing environmental conditions are the most important vital attributes for their survival.

Planktonic organisms are not equally distributed in the water column. They orient with respect to external factors such as light, gravity, chemical gradients, temperature and the earth's magnetic field [Nultsch and Hader, 1988]. Experiments in laboratory and natural situations have shown that solar UV-B radiation drastically affects orientation, motility and development in these organisms even after short exposure times. This reduces the chances for growth and survival of the populations. More recent experiments have shown that UV-B radiation affects the general metabolism, photosynthetic energy production, and nitrogen fixation and assimilation in many species.

#### Motility

Motility and orientation are vital prerequisites for adaptive defense mechanisms in phytoplankton and are. thus, the basis for survival and productivity. Recent studies have shown that UV-B radiation impairs motility in a number of motile microorganisms as diverse as prokaryotic (bacteria-like) blue-green algae, unicellular flagellates, and gliding green algae [Häder, 1988; Häder and Häder, 1988a,b, 19891. When exposed to unfiltered solar radiation, the percentage of motile flagellates decreases within a few hours. Likewise, the speed of movement is drastically reduced by the radiation. These responses are not due to overheating, because thermal effects have been excluded by irradiating the organisms in temperature-controlled growth chambers. Eliminating the exposure to UV-B radiation either by inserting suitable filters or by artificially introducing a thicker layer of ozone results in far better motility. This response indicates that the solar UV-B radiation is responsible.

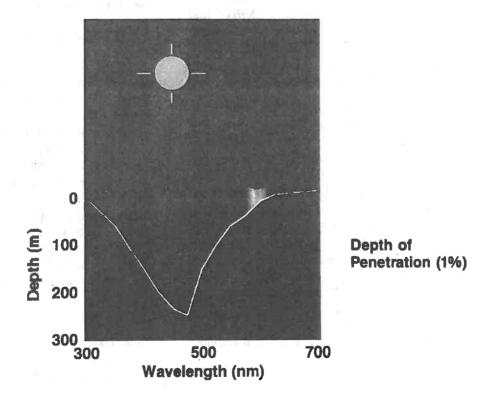


Figure 4.2
Penetration of radiation into oceanic waters relative to wavelength [data from Jerlov, 1970, and Baker and Smith, 1982].

Inhibition of the cellular locomotion apparatus prevents the organisms from escaping hazardous environments, e.g., bright white light and UV-B radiation [Hader, 1988a]. The results indicate that motility is affected even at ambient UV-B levels. In addition to temperature, nutrition, and other stress factors, solar UV-B radiation may be one of the factors that decreases algal growth during summer (algal blooms occur mostly in spring and in autumn).

#### Orientation

Most motile microorganisms do not possess a sensor for UV-B radiation, but rather use various bands in the visible and long-UV range for photoorientation [Foster and Smyth, 1980]. Studies have shown that their orientation mechanisms are affected by UV-B radiation, even after short exposure times. Any decrease in orientation of motile phytoplankton prevents the necessary constant adaptation to the changing environmental conditions and possibly hazardous situations.

The organisms have a repertoire of several responses to light, which are often antagonistic and allow a fine tuning of orientation [Häder, 1988]. Some flagellates move toward the light source at low light intensities. This brings the population toward the surface where they receive sufficient solar radiation for photosynthesis. At high light intensities, most organisms escape from the light source. This is ecologically important because excessively intense irradiation bleaches the photosynthetic pigments of many phytoplankton [Kamiya and Miyachi, 1984; Häder et al., 1988; Nultsch and Agel, 1986] and damages cellular structures [Spikes and Straight, 1981]. Another important strategy for orientation is the response to gravity [Häder, 1987b; Kessler, 1986], by which the organisms orient in space and move toward the surface even in the absence of light.

The various orientation strategies result in the movement of populations to specific, suitable horizons in their environment. These horizons fluctuate in a body of water as a result of changing environmental conditions, and many planktonic organisms are known to undergo daily vertical movements of up to 12 m [Burns and Rosa, 1980]. Researchers have studied the motility patterns of microorganisms by placing populations in vertical transparent plexiglas columns immersed in a pond or lake (Figure 4.3). The movements of the organisms in response to the external conditions were followed and the cell densities were determined [Häder and Griebenow, 1987, 1988]. Currently, even larger columns are being constructed to follow the movement patterns of phytoplankton in their environment and their response to UV-B exposure.

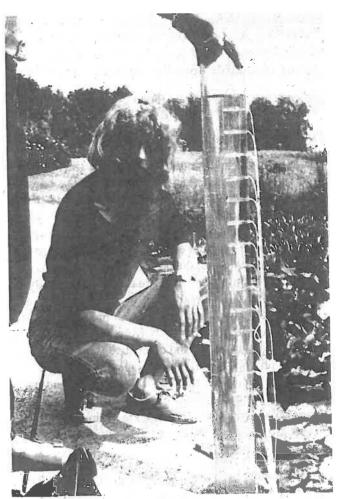


Figure 4.3
A plexiglas column is used to study the vertical movements of phytoplankton in response to changing light conditions. The column is immersed in a natural habitat.

#### Development and Physiology

Most microorganisms undergo a developmental cycle. During some stages of the cycle, the organisms are more vulnerable to solar UV-B radiation than during others. This can be due to a higher sensitivity or a more exposed position in the water column. Any inhibition of one of the developmental stages or physiological functions has long-lasting effects on productivity and reproductive capacity of the whole population. UV-B inhibition of development also can cause a drastic change in the species composition of phytoplankton, which in turn may affect energy transfer through the food web. Loss of certain algal species and predominance of toxic or non-palatable organisms may interfere with growth and multiplication in organisms higher in the food web.

• General Metabolism. At sublethal exposure levels, UV-B radiation causes intracellular damage and affects growth and the endogenous rhythms found in many microorganisms [Worrest, 1982]. This low level of UV radiation damages proteins, but the proteins can be

replaced by dark and light repair mechanisms. Higher doses affect the cellular membrane's permeability to important chemicals and induce irreversible damage to proteins, eventually causing death [Döhler, 1984].

- Photosynthesis. Enhanced UV-B radiation reduces the concentration of photosynthetic pigments and decreases the production of ATP and NADPH, which in turn affects the general CO<sub>2</sub> fixation. Specifically, the photosystem II reaction center is damaged, accompanied by a structural change in the membranes and a decrease in the lipid content. Any change in nucleic acids and protein composition affects enzyme activity and production [Döhler et al., 1986].
- Nitrogen Assimilation. Nitrogen assimilation is one of the key processes for growth because it determines the rate of protein synthesis. In addition, prokaryotic organisms such as cyanobacteria are capable of utilizing atmospheric nitrogen dissolved in water a metabolic mechanism that higher plants cannot perform. Thus, cyanobacteria have an important role in providing nitrogen for higher plants (e.g., in tropical rice paddies). The annual nitrogen assimilation by this group of organisms alone has been assumed to amount to 35 million tons, which exceeds the 30 million tons of artificial nitrogen fertilizer produced annually.

The key enzyme for nitrogen assimilation is nitrogenase. Light activates nitrogenase and UV-B radiation inactivates it [Döhler, 1985]. Subsequent enzyme activity incorporates nitrogen into precursors, and eventually into amino acids and proteins. Studies have found that UV-B radiation drastically affects these processes in a number of ecologically important phytoplanktonic species [Döhler et al., 1987].

#### Pigmentation and Fluorescence

Unlike land plants, most phytoplankton are not capable of tolerating excessive solar radiation. When exposed to full sunlight the photosynthetic pigments are bleached [Nultsch and Agel, 1986; Häder et al., 1988] and the organisms die within a few days. Some of the accessory pigments, which play a role in light harvesting for photosynthesis, are bleached within 15 minutes of exposure to full sunlight (Figure 4.4). The chlorophylls usually have a lifetime of several hours at constant exposure. Using UV-B radiation from artificial sources has shown that the photosynthetic pigments also are bleached by the UV-B component alone, indicating the detrimental effect of this radiation on photosynthesis.

Following a short exposure to UV-B radiation, a strong increase in fluorescence by the phytoplankton occurs. This reemission of light energy demonstrates



Figure 4.4
When exposed to strong sunlight, phytoplankton populations are bleached within a short time (right flask), which can be seen even visibly when compared with a population kept under dim light (left flask).

that the photosynthetic apparatus did not effectively use the photosynthetic light but rather wasted it in fluorescence. After longer exposure times, the fluorescence decreases again, indicating that radiation increasingly destroys the absorbing pigments. Pigment concentration can be determined in laboratory samples and also in natural plankton communities from satellite measurements using spectroscopic data [Jeffrey and Humphrey, 1975].

#### UV-B Targets

Most action spectra for biological damage measured suggest that short wavelength UV-B radiation below 300 nm is most effective. Thus, any long-term decrease in the ozone layer causing an increase in this radiation is likely to have adverse effects for biological systems. Several components of the system are sensitive to the UV-B radiation, as described in the following sections.

• DNA. DNA can be the primary UV target in some microorganisms [Yammamoto et al., 1983]. Some of these conclusions have been determined primarily from the similarity between action and absorption spectra. In a recent study of a green flagellate, however, DNA does not seem to be the major target for UV-B radiation [Häder and Häder, 1988a]. The conclusion is based on the very fast effect of the radiation on motility and the fact that no photorepair has been observed. This mechanism relies on the activity of an enzyme that

removes the lesions produced by high-energy UV radiation and is activated by long wavelength UV-A (315-380 nm) or visible radiation [Hirosawa and Miyachi, 1983]. After inducing UV-B damage, no recovery could be found in dim white light. These results argue against an involvement of DNA in these particular organisms. The same result was found in gliding cyanobacteria [Häder et al., 1986].

- Photodynamic Responses. One of the mechanisms by which high-energy radiation can damage cells and tissues is by photodynamic responses [Ito, 1983]. In this response, a photoreceptor molecule absorbs a high energy photon and uses the energy for the production of singlet oxygen [Maurette et al., 1983] or free radicals [Spikes, 1977]. These substances destroy membranes and other cellular components. In some studies, however, photodynamic reactions could be excluded as the main mechanism of UV-B radiation damage by using diagnostic reagents and quenchers for singlet oxygen and free radicals [Häder et al., 1986; Häder and Häder, 1988b].
- Other UV-B Targets. In those organisms for which neither DNA nor photodynamic responses are involved, specific targets that are responsible for UV-B inhibition need to be identified. The primary targets could be the

receptor molecules for photoorientation or specific components of the motor apparatus.

#### **Consumers: Marine Animals**

For the consumer components of marine ecosystems, various experiments have demonstrated that UV-B radiation causes direct damage to juvenile fish, shrimp larvae, crab larvae, and other small animals essential to the marine food web. These damaging effects include decreased reproductive capacity, growth, survival, and other reduced functions [Worrest, 1986]. Although not as important as light, temperature or nutrient levels, evidence indicates that ambient solar UV-B radiation is currently an important limiting ecological factor. Even small increases of UV-B exposure could result in significant ecosystem changes [Damkaer, 1982].

#### Effects on Zooplankton

Marine invertebrates differ greatly in their sensitivity to UV-B radiation. For example, one small crustacean suffers 50% mortality from UV-B radiation dose rates that are smaller than those currently present at the sea surface. By contrast, some shrimp larvae tolerate dose rates at the sea surface greater than those forecast for a 16% ozone depletion.

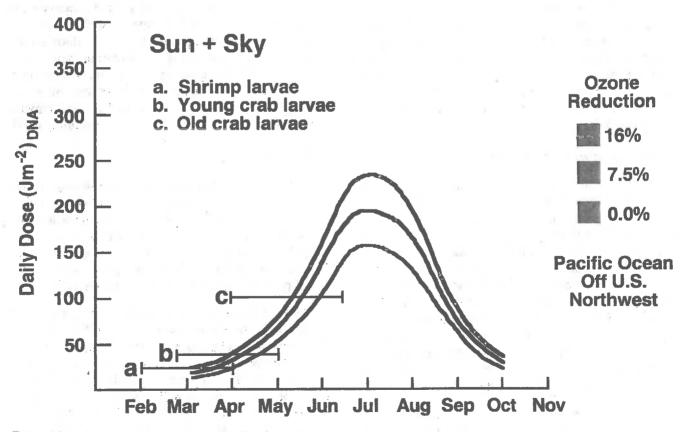


Figure 4.5
Estimated effective UV-B solar daily dose at various atmospheric ozone concentrations. Also shown are approximate thresholds of UV-B daily dose for shrimp and crab larvae, in natural seasonal position [adapted from Damkaer et al., 1981].

Larval shrimp exhibit a mortality threshold of 22 J m<sup>-2</sup> day<sup>-1</sup> (DNA weighted, 4-day exposure) /Dev et al., 19881. This threshold is close to the reported UV-B dose near the surface of the sea in spring, but is exceeded during the longer days of summer at midlatitudes (Figure 4.5). Larval crabs have a slightly higher threshold sensitivity to UV-B radiation (36-100 J m<sup>-2</sup> day - 1 for 6-20 day exposures) [Damkaer and Dey, 19831. These threshold levels are higher than those produced by existing and anticipated ozone levels for spring spawners, but they are well below the 150 J m $^{-2}$ day 1 possible at similar latitudes in mid-summer, even without ozone depletion. With a 16% ozone depletion over temperate pelagic waters, a lethal (50% mortality) cumulative radiation dose for about half the zooplankton species examined would be reached at a depth of 1 m in less than five days in summer.

Field investigations and laboratory experiments with freshwater crustaceans (*Daphnia sp.*) have shown big differences in UV-B sensitivity between different species probably due to different pigmentation and to various capacity for reactivation [Siebeck and Böhm, 1987].

#### Effects on Fisheries

UV-B stress is most likely to affect fisheries in two ways: through eggs and larvae, and through effects on the food chain upon which the juvenile fish depend. The bulk of the world's marine harvest of fish, shellfish, and crustaceans consists largely of species that have eggs and larvae at or near the sea surface where they would be exposed to increasing levels of UV-B radiation [Hardy, 1982].

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

Evidence indicates that increased UV-B irradiance could also result in fishery losses through indirect effects on the planktonic food web. Based on one assessment, a 5% decrease in primary production (estimated for a 16% ozone depletion) would reduce fish yield by approximately 6 to 9%. A 7% reduction in fish yield, if it occurred on a global basis, would then represent a loss of about 6 million tons of fish per year.

#### Risk of UV-B Damage

The biological effects of small changes in UV-B irradiance at the ocean surface will be very difficult to determine because marine ecosystems have an extremely large physical and biological "noise" level. Storms, clouds, and global currents cause dramatic changes in the status of marine life, and they are currently unpredictable. However, one should not conclude that changes that are lost in the noise of the system are insignificant simply because they cannot be measured or defined exactly. Changes that occur because of small systemic events (e.g., higher UV-B exposure) could accumulate in time to produce much more significant changes in marine organisms that appear very sensitive to current UV-B exposure.

The possibility exists that changes outside the historical range of UV-B exposure could have implications far greater than we are currently able to predict with confidence. At this time, conclusions about what could happen if levels of UV-B exposure increase cannot be drawn. An increase in UV-B exposure might have small effects or it might be much more significant.

#### Change in Species Composition

In marine plant communities, a major change in species composition - in addition to a global decrease in net production - might result from enhanced UV-B exposure [USEPA, 1987]. A change in community composition at the base of food webs may produce instabilities within ecosystems affecting organisms higher in the food web [Kelly, 1986]. The generation time of marine phytoplankton is in the range of hours to days; whereas the potential increase to ambient levels of solar UV-B irradiance resulting from stratospheric ozone depletion would occur in the range of decades. The question remains as to whether the gene pool within species is variable enough to adapt during this relatively gradual change in exposure to UV-B radiation (with respect to the generation time of the target organisms). Indirect effects also may occur in the form of altered patterns of predation, competition, diversity, and trophic dynamics if species resistant to UV-B radiation were to replace sensitive species. The combined effects of direct (larval mortality) and indirect (food web) losses cannot as yet be predicted, nor have assessments been made of adaptive strategies or genetic selections that could minimize population or ecosystem effects.

#### Loss in Nitrogen for Higher Plants

Cyanobacteria play a role in nitrogen fixation, especially in tropical rice paddies. Some of these organisms are extremely sensitive to current levels of UV-B exposure [Hader et al., 1986]. A significant decrease

in the nitrogen fixation by prokaryotic microorganisms will affect growth and productivity of higher plants. The amount of artificial nitrogen fertilizer necessary to compensate for a substantial loss will stress the capabilities of lesser developed countries.

## Atmospheric CO<sub>2</sub> Concentration and Global Climate Change

Another important consequence of a decrease in phytoplankton growth is the reduction in the important marine sink for carbon dioxide. The fluxes of carbon dioxide show that the oceans take up a major proportion of the carbon dioxide released annually. A 10% decrease in the carbon dioxide uptake by the oceans would leave about the same amount of carbon dioxide in the atmosphere as is produced by fossil fuel burning. This effect would have long-term consequences for the global climate and would enhance the predicted sea level rise.

In addition, if UV-B radiation inhibits dimethyl sulfide (DMS) production by marine phytoplankton, this could result in a reduction in the formation of atmospheric cloud condensation nuclei, decreased cloudiness, increased incident solar radiation including UV-B radiation — a positive destructive feedback loop. However, an alternative prediction argues that a substantial warming of the atmosphere would increase the evaporation from the oceans and thus cause a more massive cloud formation.

#### **ASSESSMENT OF RESULTS**

For components of marine ecosystems, various experiments have demonstrated that UV-B radiation causes damage to fish larvae and juveniles, shrimp larvae, crab larvae, other small animals, and plants essential to the marine food web. These damaging effects include decreases in reproductive capacity, growth, survival, and other reduced functions of the organisms. Although not nearly as important as light, temperature or nutrient levels, evidence indicates that ambient solar UV-B radiation is currently an important limiting ecological factor, and that even small increases of UV-B exposure could result in significant ecosystem changes.

In marine plant communities, a change in species composition, in addition to a global decrease in net production, would be a likely result of enhanced UV-B exposure. A change in community composition at the base of food webs may produce instabilities within ecosystems that likely would affect higher trophic levels. The generation time of marine phytoplankton is in the range of hours to days; whereas the potential increase in ambient levels of solar UV-B irradiance will occur

in the range of decades. The question remains as to whether the gene pool within species is variable enough to adapt during this relatively gradual (relative to the generation time of the target organisms) change in exposure to UV-B radiation.

There is evidence that a decrease in column ozone abundance could diminish the near-surface season of invertebrate zooplankton populations. For some zooplankton, the time spent at or near the surface is critical for food gathering and breeding. Whether the population could endure a significant shortening of the surface season is unknown.

The direct effect of UV-B radiation on food-fish larvae closely parallels the effect on invertebrate zooplankton. Before effects of exposure to solar UV-B radiation can be predicted, information is required on seasonal abundances and vertical distributions of fish larvae, vertical mixing, and penetration of UV-B radiation into appropriate water columns. However, in one study involving anchovy larvae, a 20% increase in UV-B radiation (which would accompany a 9% depletion of total column ozone) would result in the death of about 8% of the annual larval period. This highlights the need for caution when trying to extrapolate conclusions to natural conditions when those conclusions are based on results from laboratory studies.

In many countries, marine species supply more than 50% of the dietary protein. This percentage is larger in many developing countries. Research is needed to improve our understanding of how ozone depletion could influence the world food supply derived from marine systems.

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#### **CHAPTER 5**

# TROPOSPHERIC AIR QUALITY

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#### 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<sub>x</sub> 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<sub>x</sub> 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.

#### INTRODUCTION AND BACKGROUND

If stratospheric ozone levels decline, more UV-B radiation will penetrate deeper into the atmosphere, causing some tropospheric chemicals to react faster. The increased reactivity could adversely affect tropospheric air quality, since most undesirable compounds (e.g., ozone, peroxides, and acids) are not emitted, but formed through chemical reaction. This degradation of tropospheric air quality could create new pollution problems related to human health and welfare, and increase stress in the biosphere. This Chapter describes the physical and chemical processes linking tropospheric air quality with stratospheric ozone loss. The final section presents an assessment of relevant policy implications.

#### STATE OF THE SCIENCE

#### Mode of Chemical Response to Increased UV-B

The reaction rates of some chemical processes depend strongly on the amount of UV-B radiation [Marx et al., 1984; DeMore et al., 1987]. Measurements [Bahe et al., 1979; Dickerson et al., 1982] have shown that the rate of tropospheric ozone photo-dissociation:

$$O_3 + hv(UV-B) \rightarrow O(^1D) + O_2$$

is inversely related to the amount of overhead ozone, mostly stratospheric. Calculations indicate that this rate would increase between 20 and 25% for a 10% loss of stratospheric ozone at mid-latitude, sea-level locations [Gery et al., 1987]. Smaller rate increases also should occur for all tropospheric compounds that absorb UV-B and photodissociate, particularly oxygenated organics such as aldehydes and ketones.

A future increase in the tropospheric ozone photodissociation rate could be significant because the rapid reaction of O(<sup>1</sup>D) with water vapor is the major source of tropospheric hydroxyl radical (OH) [Crutzen and Fishman, 1977]. OH is a member of a chemically interlinked family of extremely reactive molecules known as odd-hydrogen radicals (OH, H, and HO<sub>2</sub>). It is the primary oxidizer of virtually every trace gas found near the earth's surface [Logan et al., 1981]. Increased UV-B should increase odd-hydrogen production rates, and therefore, the chemical reactivity or oxidizing potential of the troposphere [Liu and Trainer, 1988]. This increased reactivity has been demonstrated in smog chamber experiments [Winer et al., 1979], where increased UV-B radiation led to increased production of oxidized products.

Potential changes to tropospheric chemistry will vary depending on local concentrations of oxides of nitrogen (NO<sub>x</sub>), volatile organic compounds (VOC), and other trace gases [Liu and Trainer, 1988; Thompson et al., 1989]. The following discussion of potential air quality impacts is separated into sections describing remote, rural, and urban regions.

#### Effects on Remote and Rural (Non-urban) Areas

Remote regions receive little or no direct impact (emissions) from human activities. These areas occur over oceans or sparsely populated land areas, comprising over two-thirds of the earth's surface. Remote concentrations of VOC (except for methane, CH<sub>4</sub>) and NO<sub>x</sub> are extremely low, as are ozone concentrations because NO<sub>x</sub> is necessary for sustained ozone production. Rural regions record higher concentrations of NO<sub>x</sub> and VOC due to both local emissions and atmospheric transport from more densely populated areas. NOx levels are generally high enough to sustain low levels of ozone production. However, since most agricultural production occurs in rural areas, degraded rural air quality could still adversely affect food production, forest yield, and other components of the biosphere. In addition, regional aerosol formation and cloudwater acidification occur most often under rural conditions. These processes also can have an urban contribution, indicating that some rural pollution problems also can be influenced by longrange transport of urban air.

The effect of increased UV-B on the air quality of remote areas should be to decrease the already low surface ozone concentrations. This is because, with little NO<sub>x</sub> to sustain ozone production, increased UV-B will destroy ozone more rapidly through the above photodissociation reaction. Calculations [Liu and Trainer, 1988] indicate that a 20% loss of stratospheric ozone at northern mid-latitudes could induce a 10 to 35% decline in

remote tropospheric ozone for NO<sub>x</sub> levels between 0.10 to 0.01 ppb by volume (Figure 5.1). A similar decline in remote tropospheric ozone was calculated for a low-latitude future scenario combining increases of carbon monoxide (CO) and CH<sub>4</sub> emissions with a 15% loss of stratospheric ozone reached after 50 years [Thompson et al., 1989].

For rural areas the potential for ozone production is increased because NO<sub>x</sub> and VOC concentrations are higher. At some combination of higher (less remote/more rural) trace gas concentrations, an increase in UV-B will cause future surface ozone production to be greater than at present. For the mid- and lower-latitude calculations [Liu and Trainer, 1988] shown in Figure 5.1, this occurs where the lines cross into positive ozone response with increasing NO<sub>x</sub>, for NO<sub>x</sub> concentrations between 0.1 and 0.2 ppb. This NO<sub>x</sub> range, however, is somewhat scenario-dependent and should only be taken to indicate the order of magnitude.

Many rural regions and all urban areas have NO<sub>x</sub> concentrations that place them in the positive response region of Figure 5.1. This indicates that, except for relatively remote areas with very low NO<sub>x</sub> levels, increased UV-B should produce higher tropospheric ozone concentrations than occur presently. Based on calculations which led to Figure 5.1 [Liu and Trainer, 1988], this ozone increase is estimated to be about 10% for a 20% loss of stratospheric ozone at rural mid-latitudes (NO<sub>x</sub> centered around 1 ppb). Two other mid-latitude modelling studies [Thompson et al., 1989; Morris et al., 1989] also calculated increases in future rural ozone, but the specific impact of increased UV-B could not be determined because the scenarios combined future stratospheric ozone loss with global warming effects.

Another important indicator of the potential consequences of enhanced UV-B on air quality is the concentration of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). Along with nitric acid (HNO<sub>3</sub>), H<sub>2</sub>O<sub>2</sub> is a chemical reservoir for odd-hydrogen radicals and is a more direct indicator of changes to odd-hydrogen concentrations. Its effects are particularly significant in the formation of acidic precipitation because H<sub>2</sub>O<sub>2</sub> is believed to be the principal oxidizer of sulphur dioxide (to form sulphuric acid) in cloudwater/Calvert et al., 19851. Because enhanced UV-B is expected to increase odd-hydrogen production, H<sub>2</sub>O<sub>2</sub> levels are projected to increase globally [Thompson et al., 1989]. Even for the previously noted remote scenario calculations where UV-B increases were expected to diminish surface ozone concentrations, H<sub>2</sub>O<sub>2</sub> levels were projected to increase slightly. For scenarios with higher NO<sub>x</sub>, H<sub>2</sub>O<sub>2</sub> increases of approximately 30% were calculated for NO<sub>x</sub> concentrations of 0.2 and 1.4 ppb. These increases were beyond already significant

## Calculated Surface O<sub>3</sub> Changes

(as a function of NO<sub>x</sub> and latitude)

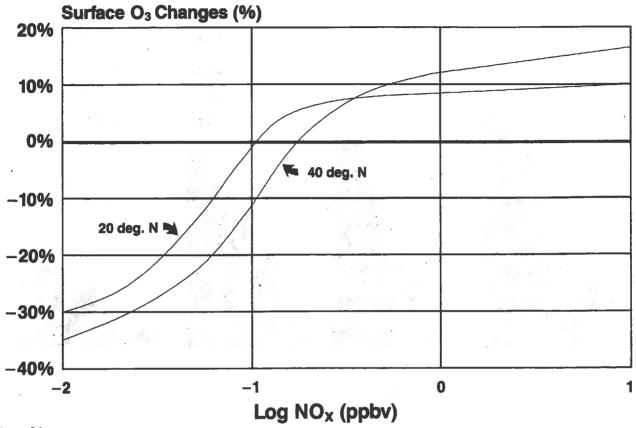


Figure 5.1

Model predicted surface ozone concentration changes as a function of  $NO_x$  due to 20% reduction in column ozone, calculations were for summer conditions at 20°N and 40°N [Liu and Trainer, 1988].

increases due to projected global climate changes [Thompson et al., 1989].

#### Effects of Increased UV-B on Urban Areas

Urban and surrounding areas record high NO<sub>x</sub> and VOC concentrations due to high man-made emissions. This leads to very reactive chemistry that generates high concentrations of ozone and other oxidized compounds through the process commonly known as photochemical smog formation. When such large amounts of VOC are oxidized, the chemistry of the oxidation products also becomes important. Formaldehyde and other oxidized organics are primary reaction products of many different VOCs and are formed at relatively high rates in the urban troposphere. Like tropospheric ozone, some of these oxidized organics can produce odd-hydrogen radicals upon absorption of UV-B [Marx et al., 1984; DeMore et al., 1987]. This provides additional chemical channels that could contribute to increased urban reactivity with future increases in UV-B [Gery et al., 1987; Whitten and Gery, 1986].

In urban areas with present conditions reactive enough to form significantly harmful levels of ozone without using all ozone precursors (NO<sub>x</sub> and VOC), the additional energy from increased UV-B radiation could produce even higher levels of urban ozone. In other urban regions, almost all precursors react away during an ozone episode. Because the amount of NO<sub>x</sub> and VOC limit ozone production, increased UV-B probably will not significantly alter those maximum ozone concentrations in the future. However, depending on the amount of UV-B increase, precursors could react faster and produce potentially harmful concentrations of ozone earlier in the day and nearer to emission sources and population centers [Gery et al., 1987].

Throughout the world, various emission control strategies are being planned and implemented to limit production of urban ozone. These strategies are based on the control of VOC and NO<sub>x</sub> emissions. Until recently, no change in stratospheric ozone was expected, and therefore, pollution control strategies do not address a future with increased UV-B. Unfortunately, because

## Additional NMOC Control vs. % Loss of Column Ozone

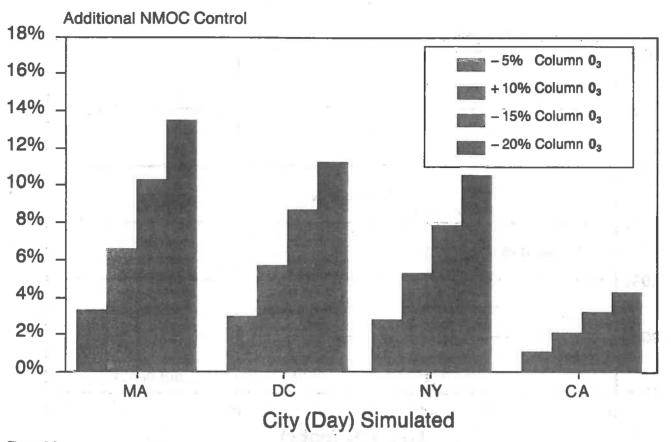


Figure 5.2
Model predicted VOC controls in addition to existing controls for test days in four cities in the United States (Springfield, Massachusetts; Washington, DC; New York, New York; Los Angeles, California). Each bar represents a 5% column ozone decrease up to -20% [Gery and Burton, 1989].

chemical reactivity in urban smog systems depends on the amount of UV-B, the ozone reductions anticipated in these strategies could be less than planned if significant stratospheric ozone destruction occurs. For test cases in four United States cities (with present maximum hourly ozone concentrations ranging between 0.380 and 0.135 ppm) calculations indicated that additional, unanticipated VOC emission controls, ranging linearly from 0.3% to 0.8% per percent stratospheric ozone loss, would be needed to maintain the present national ozone standard [Gery and Burton, 1989]. The extra VOC control is shown in Figure 5.2 for these cases, with the lower rates for cities which presently have the highest ozone levels and already require the most emission control. These results indicate that additional expenditures (for VOC control) may be needed to maintain the same measure of human health protection from air pollution if stratospheric ozone is destroyed.

In urban areas, H<sub>2</sub>O<sub>2</sub> and HNO<sub>3</sub> levels increase late in the day as odd-hydrogen radicals combine with each

other and  $NO_x$ . During this period, a loss of stratospheric ozone might increase  $H_2O_2$  concentrations significantly [Gery et al., 1987]. However, future control of urban VOC, an odd-hydrogen source, should have a strong effect at lowering  $H_2O_2$ . On the other hand, reductions in urban  $NO_x$  could have a different effect by eliminating a future odd-hydrogen sink.

#### Combined Effects with Changing Global Climate

It is possible that global climate changes could occur concurrently with stratospheric ozone loss. Temperature changes near the earth's surface will affect the rates of some chemical reactions and tropospheric chemistry would be influenced by changes in vertical mixing, weather patterns, biological and man-made emissions, and transported concentrations of reactive gases. In addition, the effects of UV-B-related processes already discussed in this Chapter could: 1) decrease with additional cloud cover, aerosol loading, or higher levels of UV-B absorbing gases including ozone, or 2) increase if higher

water vapor levels increased the production of OH after ozone photodissociation. Enhanced tropospheric ozone production might also modify radiative feedback levels because higher concentrations of ozone, also a greenhouse gas, would exist very near the surface. Finally, it is possible that UV-B enhanced chemical reactivity could generate higher concentrations of atmospheric aerosols, providing a surface upon which heterogeneous ozone destruction reaction could occur in the non-polar lower stratosphere, lowering stratospheric ozone levels even further.

#### **ASSESSMENT OF RESULTS**

Changes to atmospheric chemical processes due to stratospheric ozone destruction suggest the following future directions for tropospheric air quality:

#### **Urban Ozone**

- For urban areas where most precursor (NO<sub>x</sub> and VOC) emissions react away during an ozone episode, an increase in UV-B would probably not increase the maximum ozone levels for the most extreme cases. However, higher ozone levels could be reached earlier in the day, exposing more of the urban population to hazardous short-term levels and possibly increasing long-term human exposure.
- For urban cases where a significant amount of emitted NO<sub>x</sub> and VOC remains at the end of the day, the added UV-B energy could induce even higher ozone levels to occur throughout the day in the future.
- Increased UV-B should make the urban troposphere more reactive and less responsive to planned emission control measures. Presently planned emission controls may not be adequate to achieve air quality goals.
- Specific VOC and NO<sub>x</sub> emission control strategies, based on present conditions, may not be the most effective approaches if UV-B changes significantly in the future.

#### Rural and Continental Ozone

 Most rural areas have sufficient NO<sub>x</sub> levels such that increases in UV-B would increase ozone levels. In addition, air transported to rural areas from urban airsheds may be more polluted with increased UV-B. Such changes, perhaps combined with global climate changes, could affect plant stress, agricultural productivity, and increase long-term human exposure.

#### Hydrogen Peroxide

- A future increase in UV-B could significantly increase urban production of H<sub>2</sub>O<sub>2</sub>. However, a large percentage of this increase might be offset if pollution control measures to reduce ozone are implemented.
- Remote and rural H<sub>2</sub>O<sub>2</sub> concentrations are projected to increase globally if UV-B increases. This could exacerbate cloudwater acidification, since that process is often limited by the availability of H<sub>2</sub>O<sub>2</sub>.

#### Global Distribution of Polluted Areas

 Because increased UV-B would make the lower troposphere more reactive, the percentage of areas with remote tropospheric conditions may decline, and some rural regions may become more urban-like.

#### **Direct Influences of Changes to Global Climate**

- Added cloud cover could attenuate UV-B to the surface, diminishing the changes to tropospheric air quality. However, increased water vapor concentrations could counter this by providing more odd-hydrogen radicals from ozone photodissociation.
- Increased tropospheric reactivity could lead to increased global aerosol production, decreasing visibility and possibly providing additional condensation nuclei to the lower stratosphere where heterogenous ozone destruction processes could become more important in non-polar regions.

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#### CHAPTER 6

## MATERIALS DAMAGE

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#### 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 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 substantial increase in the rates of yellowing of 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 AND BACKGROUND

The weathering deterioration of outdoor materials depends on the nature and extent of their interaction with the environment. Light-induced degradation of plastics is a key factor that determines the useful lifetime of plastics routinely exposed outdoors. Chemical stabilizers generally are incorporated into plastic formulations to minimize the photodegradation of plastics and rubber intended for outdoor use. Depending on the type of plastic and the intended application, 0.1 to 2% light stabilizer is incorporated into the plastic material to control the light-induced degradation.

Any depletion of the stratospheric ozone layer will result in higher levels of short wavelength radiation (<295 nm). This will lead to a significant acceleration of light-induced degradation processes, and a subsequent decrease in the useful lifetimes of plastics used outdoors. The degree of increased damage will vary depending on the latitude; it is more likely to be severe at near-equator locations (see Chapter 1). Possible responses to such increased damage include: the use of higher

levels of stabilizers, the design and use of new stabilizer compounds, the use of more resistent types of plastics for outdoor applications, and the use of alternative non-plastic materials.

#### STATE OF THE SCIENCE

Polymeric materials (both plastics and rubber) are widely used in building, agriculture and other applications, involving routine outdoor exposure where they continue to replace the traditional materials such as wood, glass, and metal. Building and agricultural plastic materials are particularly important to the present discussion because they undergo long-term exposure to sunlight, and they are designed to have relatively long useful lifetimes, compared for instance to packaging plastics. Relevant plastic products include the following:

PE = polyethylene
PP = polypropylene
PU = polyurethane
PC = polycarbonate
PVC = poly(vinyl) chloride

EPDM = ethylene propylene diene monomer

rubber

CPE = chlorinated polyethylene PMMA= poly(methyl methacrylate)

ABS = acrylonitrile-butadiene-styrene

couple

#### **Building Applications**

- Rigid PVC siding, window/door frames, exposed pipes, gutters, trim, fascia
- Plasticized PVC, EPDM, CPE and PE single ply membrane roofing (used with membrane on exterior), cable coverings
- PC and Acrylics glazing, coatings
- Unsaturated Reinforced Polyester outdoor panels, water tanks, pipes

#### **Transportation Applications**

- PU and PP bumpers on automobiles, coatings
- High performance composites on aircraft construction

#### **Marine Applications**

- Nylon, PE and PP fishing nets, ropes, sacks
- Unsaturated Reinforced Polyester vessel hulls, etc.

#### **Agricultural Applications**

- PE, Polyester, Plasticized PVC greenhouse application
- PE agricultural mulch film

#### **Miscellaneous Applications**

- PE and PP outdoor furniture (e.g., stadium seats)
- Synthetic Elastomers tires and hoses, polymerbased coatings
- PE industrial packaging

The lifetimes of most of these products are determined by their light stability outdoors. Inadequately stabilized plastic materials suffer a variety of damages under extreme or prolonged exposure conditions such as: discoloration, chalking, blistering, warping, loss of strength, and cracking [Hawkins, 1984; Davis and Sims, 1983; Decker, 1984]. Poly(vinyl chloride), PVC, is the most widely used plastic material in building applications. In the case of white or lightly colored rigid PVC formulations widely used in building applications, initial damage is an uneven yellowing or discoloration, rendering it unacceptable for further use [Decker, 1984].

The extent of damage resulting from the exposure of a material to polychromatic light depends on a) the spectral distribution of the light, b) the sensitivity of the material to light of different wavelengths emitted by the source (i.e., activation spectrum), and c) the doseresponse curves for the particular type of damage. Information on the effect of these three factors requires reliable estimates of damage due to exposure of a plastic to a spectrally altered sunlight resulting from partial ozone depletion.

Early research on PVC and several other polymers attempting to identify the spectral sensitivities was based on pure polymer films [Martin and Tilley, 1971; Mullen and Searle, 1970]. Recent work [Andrady et al., 1989a; Andrady and Searle, 1989; Andrady et al., 1989b] has focused on extruded, rigid PVC formulations which closely resemble the materials used in relevant practical applications. The research was aimed at studying the light-induced yellowing phenomenon in these materials. On prolonged exposure to sunlight, plastic materials such as PVC, polycarbonate, polystyrene and polyesters undergo discoloration or uneven yellowing. Yellowing is often the first mode of damage to occur on exposure to light and makes the material unacceptable for further use. Similar studies have been conducted on commercially available polycarbonate sheets

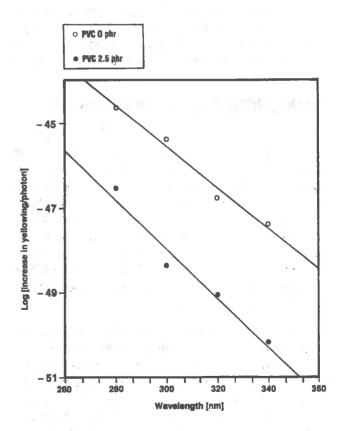


Figure 6.1
Efficiency of yellowing damage in PVC formulations at different wavelengths.

[Andrady et al., 1989c]. The recent findings pertinent to the present discussion can be summarized as follows:

- 1. Rigid PVC formulations containing 0, 2.5, and 5 parts per hundred (phr) of titanium dioxide, a pigment which also acts as a light stabilizer, showed wavelength-dependent yellowing or photobleaching in the range of 280 to 500 nm. Yellowing was obtained at 280 nm, 300 nm, 320 nm, and 340 nm, while longer wavelengths of 400 nm and 500 nm resulted in photobleaching [Andrady et al., 1989a; Andrady and Searle, 1989]. The same was true for yellowing of commercial unfilled UV-stabilized polycarbonate exposed to monochromatic light [Andrady et al., 1989c].
- 2. The spectral sensitivity of rigid PVC formulations to monochromatic light-induced yellowing can be expressed quantitatively as linear plots of Ln (yellowing/photon per sq. cm.) versus the wavelength [Andrady et al., 1989a] having the following intercept a and gradient b (Figure 6.1). The constants describe the action spectra for yellowing of these PVC formulations.

[phr = parts per hundred (parts by weight) of resin] Source: Andrady et al., 1989a

Similar studies [Andrady et al., 1989c] on polycarbonate yielded the following parameters:

$$a = -24.2$$
  $b = -0.082$   $r = 0.99$ 

ASTM D 1925 yellowness index was used [ASTM Standards, Vol. 8.021], and r is the correlation coefficient for the data.

3. In both cases (PVC and polycarbonate), sunlight-induced yellowing outdoors is the net result of a competing yellowing and bleaching reaction. The wavelength region which causes most damage will depend on the yellowing efficiency at a given wavelength and the intensity of light of that particular wavelength present in sunlight. Using polychromatic radiation (simulating the spectral irradiance distribution of sunlight), the wavelength region for maximum damage was determined for both rigid PVC and polycarbonate

using a filter technique. This approach yields activation spectra for specific types of damage resulting from exposure to sunlight. Recent results based on white light exposures are summarized below.

PVC (0 and 2.5 phr TiO <sub>2</sub> ) [Andrady et al., 1989a; Andrady and Searle, 1989]	310 - 325 nm
PC (unstabilized, stabilized) [Andrady et al., 1989c]	308 - 329 nm
PP (unstabilized, molded) [Andrady, unpubl.]	315 - 330 nm
ABS [Searle et al., 1989]	300 - 380 nm
PMMA (unstabilized) [Fueki et al., unpubl.]	260 - 300 nm

Action and activation spectra based on chemical measures of damage (e.g., increase in carbonyl absorption) have been reported, but are not relevant to the present discussion.

- 4. In the case of PVC and polycarbonate, the data from two types of experiments (using monochromatic and polychromatic light) have been compared and found to be consistent [Andrady and Searle, 1989].
- 5. Very limited data are available on dose-response curves relating to yellowing of PVC and other polymers. Both theoretical [Andrady and Shultz, 1987] and experimental studies [Weiler, 1984] on the effectiveness of titanium dioxide in controlling light-induced yellowing suggest such curves to be nonlinear. Results reported by Summers [1983] on rigid PVC under Arizona exposure are particularly useful and suggest a logarithmic dependence of stabilizer effectiveness on TiO<sub>2</sub> loading.

 $Ln \text{ (yellowness)} = 3.2 - 0.044 \text{ (phr of TiO<sub>2</sub>)} \quad r = 0.98$ 

6. In general, the effect of higher ambient temperatures in establishing faster rates of photodegradation of polymers is well known. The true temperature of the plastic material is much higher than the ambient temperature due to heat build up [Clark, 1952]. Thus, the darker colored surfaces degrade at a faster rate than white or light colored materials. Rigid PVC and

other relevant plastics mentioned above have not been studied to quantify the effects of temperature on yellowing and/or other modes of damage. The same is true of the effect of humidity on light-induced damage.

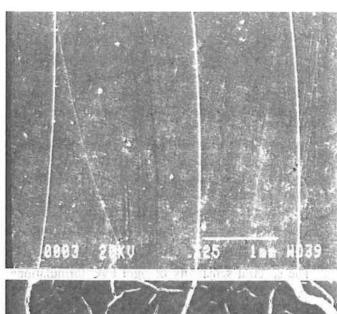
Unstabilized linear low density polyethylene films survived (i.e., maintained up to 50% of initial strength) for less than three months in Dhahran, Saudi Arabia [Qureschi et al., 1989]. The annual total sunshine at this near-equator location is about 250 kW cm<sup>-2</sup> [Hamid et al., 1988], or about 40% higher than that in Florida [Pouncy, 1985]. Consequently, the outdoor lifetime of the plastic film is reduced by about 40% in Saudi Arabia [Hamid et al., 1989a]. The relationship between total sunshine levels and useful lifetimes of plastics, however, may vary widely depending on the type of plastic formulation and the climatic conditions

7. Researchers in Saudi Arabia found that exposure to light affected surface characteristics of rigid PVC pipes. Microscopic surface cracking, discoloration, and loss of desirable mechanical properties were observed [Hamid et al., 1988] (Figure 6.2). Further studies are needed to establish dose-response relationships for photodegradation of the material.

#### **ASSESSMENT OF RESULTS**

The data presented above suggest that, at least in the case of yellowing (the first observed mode of damage for rigid PVC and plastic glazing), any increase in the content of UV-B light will result in a logarithmic increase in the amount of damage. A partial depletion of the stratospheric ozone layer will increase the fractional content of ultraviolet light in the solar spectrum. Low levels of light of short wavelength UV radiation (<295 nm) not presently found in sunlight also might occur.

As the UV range of the spectrum is particularly damaging, any increase in UV-B radiation will accelerate the light-induced damage outdoors. Logarithmic dependence of yellowing on wavelength UV radiation will have a deleterious effect on these plastics. In addition to yellowing damage, other processes will be accelerated under these conditions, such as loss of impact strength, reductions in tensile strength, etc. Although no data are available on the subject, it is conceivable that the relative rates of chemical reactions contributing to different modes of damage will change under different sunlight conditions. This may lead to other damages appearing in a shorter time scale than the development of unacceptable levels of yellowing.



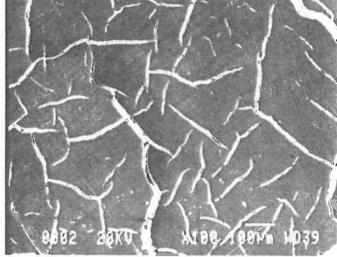


Figure 6.2

A photomicrograph comparing the surface of a PVC extrudate before (top) and after (bottom) outdoor exposure.

Given that the solar spectral changes accompanying partial depletion of ozone will be latitude dependent, it is important to determine the regions that will be most affected in terms of materials damage. The severity of the effects will depend upon 1) the extent to which plastics are used in outdoor applications at a given location, 2) the ambient temperature at the location, and 3) the anticipated level of increase in ultraviolet light in that region.

While the northern latitudes will experience the largest net changes in ozone levels, the relatively smaller changes at near-equator locations are likely to be more significant. These regions undergo severe insolation (296 kW cm<sup>-2</sup> annually in Saudi Arabia) [Hamid et al., 1989b] compared to, for instance, 104 kW cm<sup>-2</sup> in Basel, Switzerland [Ghani, pers. comm.]. Near-equator locations also have high ambient temperatures with

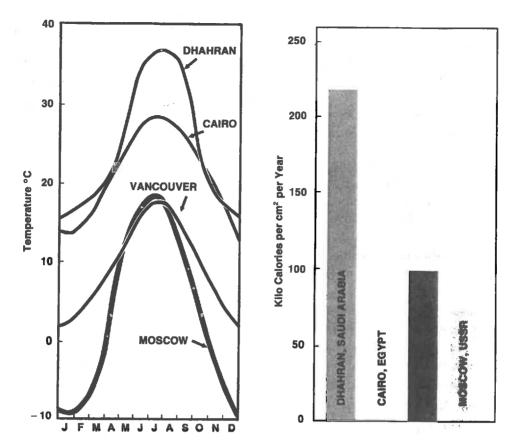


Figure 6.3
Typical mean monthly temperature (left) and total solar radiation (right).

summer air temperatures reaching 50°C [Hamid et al., 1989a] (Figure 6.3). The effect of UV radiation might be synergistically enhanced by the high ambient temperatures, humidity, and drastic thermal cycling. These regions are subjected to the short wavelength UV radiation filtering through a thinner layer of stratospheric ozone, not a significant component of sunlight received in higher latitudes. The deleterious effects of short wavelength UV light on materials has already been described. The most affected areas are developing countries where the use of plastics in building is popular and growing because of their economies.

Industry response to the anticipated decrease in service life of outdoor plastics is likely to be to resort, at least initially, to higher levels of stabilization [Shultz et al., 1975]. The strategy assumes that the chemical mechanisms of damage under altered solar spectral conditions will be the same as those under present conditions. In view of the studies cited previously, the assumption is not unreasonable. It also assumes that the increase in the level of stabilizers will be able to mitigate the effect of higher light levels. Because the effectiveness of at least the light shielding TiO<sub>2</sub> pigment changes logarithmically with concentration [Summers,

1983], the approach might not be the most cost effective. In any event, processing of plastics containing high levels of pigment presents certain technical difficulties, which can further increase the cost or even rule out this approach. Processing innovations, as well as new stabilizer systems, might be developed in response to the needs of the market.

An alternative strategy might be to use a more expensive but light-resistant grade of thermoplastic material to maintain the outdoor lifetimes of the products at their current levels. The use of such approaches has been discussed in the literature for some properties, regardless of increased UV radiation in spectrally altered sunlight. In the absence of an immediate need, the new materials and processes have not replaced the existing products. The lack of a data base concerning the effect of enhanced UV radiation on plastics is unfortunate. As opposed to effects of extended periods of exposure to moderate or severe sunlight (e.g., Miami, Florida or Phoenix, Arizona), exposure to sunlight enriched with UV radiation has hardly been investigated. The resulting lack of data hinders a full appreciation of the consequences of ozone depletion on plastics used in outdoor applications.

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#### CHAPTER 7

## RESEARCH NEEDS

Additional research is needed to gain a more complete understanding of the effects of increased solar UV-B radiation on man and the environment. The work should focus on susceptible systems and geographic regions, such as the tropics and subtropics, where the potential for damage is significant. The investigators should incorporate a range of possible UV-B increases in their studies, recognizing the provisions of the Montreal Protocol. The goal for effects research is to provide high-quality, relevant information that can be used in developing quantitative estimations of damage.

The primary focus of additional research should be on problems in tropical and sub-tropical regions, where most developing countries are located. To date, very little work has been done to measure the atmospheric ozone structure and ultraviolet radiation in the equatorial-tropical region. Based on a series of studies, it has been possible to estimate the average ultraviolet radiation increase at different latitudes for a given ozone depletion. These estimations include the effect of clouds on the radiation penetration. The results show a sharp increase in the surface level radiation flux as one moves toward the equator. Also, the relative increase in the UV-B flux due to a 10% global ozone decrease leads to substantially more radiation at the equatorial-tropical region. In absolute terms, the resultant increase alone would be more than the total radiation flux received at mid-latitude, or at around 50°.

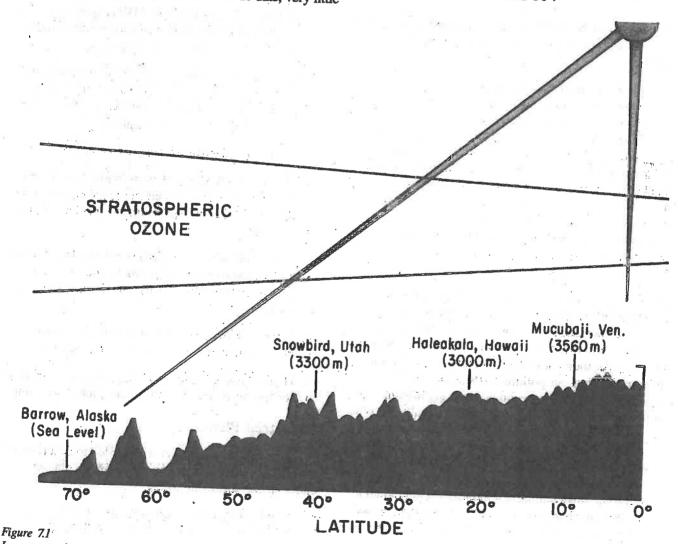


Figure 7.1

Low stratospheric ozone content and high incoming UV flux at the lower latitudes versus low UV flux at mid and high latitudes.

The high ultraviolet flux condition prevails at the lower latitudes (due to low ozone content and high incoming UV flux) in comparison to the low UV flux at mid and high latitudes (Figure 7.1). In addition, high air temperature and humidity occur in the tropics throughout the year. These conditions, together with the high UV radiation flux, may produce severe biological and physiological effects including serious human health problems. However, increased UV radiation has not been given serious attention in the context of adverse health and environmental effects that might be occurring in these regions. It is generally presumed that people living in the tropical belt have darker skin. Darker skin is thought to provide greater protection against ultraviolet radiation penetration and damage to the skin. Actually, the human skin colouration is not dark in a substantial part of the tropics.

In tropical countries, there are large populations with little education, insufficient awareness, a lack of proper understanding of UV-induced damages, a false sense of the protection due to skin colour, and increased outdoor activities. The seriousness of the situation cannot be over emphasized. Lack of meaningful scientific research in these regions further complicates this situation.

It is important to assess the potential effects of any ozone layer depletion on the surface-level UV flux at the equatorial-tropical latitudes and how this increase may enhance the adverse biomedical and other effects. Skin cancer and other skin related problems — the prime concern in Western populations with regard to ozone depletion — may not be of immediate importance in the tropics. More serious health effects on people living in the tropics and sub-tropics may include: increased incidence of viral infections, eye damage (cataracts), damage to the immune system, and reduced life expectancy.

The effects of any increases in UV radiation as a result of ozone layer modification on the tropical problems previously discussed in this report would be serious. The increased UV dosages also may affect the threshold limit to which the tropical system has become adapted. As more developing countries move toward industrialization, air pollution effects due to UV radiation would gradually become more significant. The enhanced UV radiation also would gradually become more significant and would have adverse effects on marine systems, vegetation and natural ecosystems. Developing countries in the tropics will have difficulties with these effects. It is important that these countries become involved in the global effort to counteract the inadvertant changes to the earth's atmosphere as well as in relevant research work to better understand the situation.

Based on an assessment of the current state of science in the major effects areas, the authors recommend the research initiatives outlined below.

#### **Human Health**

There are still many questions to be answered with regard to the impacts of UV-B on human health. Identified below are a number of areas that require further research. These have been compiled from a variety of sources and discussions with individuals working in the field of photobiology.

- 1. Studies of animal models of infectious diseases with UV-B radiation to determine which diseases might be affected by increased UV-B and what the extent of an effect may be further.
- 2. Studies of the effects of UV-B on human skin of all skin types, including immune function, to determine if all skin types show the same quality and quantity of effects.
- Studies of vaccination processes in animals and humans in conjunction with UV-B exposure to evaluate whether stratospheric ozone depletion could have an impact on vaccination programs.
- 4. Detailed exposure studies of people at various stages of life (0-1, 1-3, 4-6, 7-12, 13-18, 19-21, >21 years) and in various activities to determine when and how great a dose of UV-B is acquired.
- 5. An action spectrum for cataracts in primates.
- Detailed studies of melanoma induction in animal and in vitro models to determine the dose-response relationship action spectrum mechanism of transformation.
- Studies of infectious disease epidemiology, including diseases shared by animals and man, in conjunction with UV monitoring especially in tropical areas.
- 8. Further characterization of geographic distribution of important diseases, vectors and agents.
- Health effects of increased degradation of air quality due to ozone depletion and global warming.

#### **Terrestrial Plants**

Substantial research is still needed to describe and evaluate the effects of enhanced UV-B on plants, especially in the following areas:

1. Field validations on crop plants must be expanded to determine whether UV-B affects yield in other agriculturally important plants.

- Studies must be initiated to determine the impacts to natural ecosystems. Little is known of the effects of UV in other natural ecosystems such as natural forests, where 80% of net primary production is currently stored.
- 3. It is important to study natural plants because they serve in supplying new drugs, medicines and other natural products. They also act as a reservoir of genetic diversity for modern crop breeding programs. Therefore, despite the fact that they currently have limited economic value, natural plants could become quite important in the future.
- 4. It is necessary to know whether the generally deleterious UV-B effects may be compensated by changes in CO<sub>2</sub> and/or temperature. Temperature increases cause regional and global climate changes that may impact plant growth through altered water supply.
- Another area of worldwide interest is tropical rice growing regions, where information is limited on how rice will be affected either under enhanced UV-B or under increased temperature and CO<sub>2</sub>.
- 6. Of increasing interest are man-made air pollutants such as ozone, sulphur dioxide and nitrogen oxides, which are known to have damaging effects on crops and forests. Attention must be focused on whether the negative effects of these air pollutants may be aggravated by UV-B radiation.

#### **Aquatic Ecosystems**

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Current data suggest that predicted increases in UV-B radiation could have important negative effects in the marine environment. However, uncertainties regarding the magnitude of these effects remain large, including problems of extrapolating laboratory findings to the open sea, and the nearly complete absence of data on long-term effects and ecosystem responses. Additional information is needed in several areas before more reliable assessments of risk are possible. Needed research includes:

- Determine accurate and appropriate biological action spectra for select endpoints of key marine species.
- Produce dose-response data on a greater variety of ecologically important primary producers than is now available, as well as data for key higher organisms within the food web.
- 3. Determine long-term effects for embryos or larvae exposed to UV-B radiation. Is the survival of the adult population (or their offspring) affected?

- 4. Obtain results from field studies that will lead to better understanding and application of laboratory findings.
- Obtain detailed temporal and spatial distribution data for early life stages to determine natural exposure levels.
- 6. Determine effects on ecosystems, including the Antarctic ecosystems.
- Obtain data on the mechanisms of damage and ranges of possible adaptation or genetic selection in response to increased UV-B radiation.
- Determine effects on important marine biogeochemical cycles involving compounds such as methane, nitrous oxide, carbon monoxide, and organosulfides.
- Determine effects of the sea surface microlayer in mediating air/sea exchange, and microbial and neuston interaction.
- Determine the effects on complicated ecosystems with many mutually influencing factors (e.g., naturally fluctuating radiation).
- 11. Develop predictive 3-dimensional model for loss in biomass production and CO<sub>2</sub> increase, including the enhancing effect of temperature increase.

Only when the results of such studies are available will an accurate assessment of the risks posed to the marine environment from increasing UV-B radiation be possible.

#### Tropospheric Air Quality

- 1. Much of the existing emission and air quality information is estimated. To define the current conditions and assess future changes to air quality, better emissions inventories and tropospheric measurements are needed. These include VOCs, NO<sub>x</sub>, and greenhouse gases of both biological and human origin.
- 2. Basic chemical research is needed to decrease uncertainty in future atmospheric model calculations. For the ozone depletion problem, the main research areas are: a) peroxides (including peroxy radical reactions and photodissociation and oxidation of H<sub>2</sub>O<sub>2</sub> and organic peroxides), b) photodissociation reactions of compounds that absorb UV-B (including oxidized organics, particularly the absorption cross-section of formaldehyde), and c) aerosol formation.

- 3. Expanded modelling is needed to understand the effects of increased UV-B on tropospheric air quality, particularly for areas of the earth not yet studied because of limited data. Following this, a more comprehensive effort to address feedback processes, including possible global climate changes, should be performed to assess future impacts to human health and welfare, the biosphere, and materials damage.
- 4. For areas where human health is at high risk from air pollution, methods to analyze human exposure statistics could be coupled with analysis of existing and alternate emissions control strategies to determine the effect of future increases in UV-B.
- 5. As much as possible, model predictions of future changes based on increased UV-B should be verified experimentally.

#### Materials Damage

- 1. Relatively little information is available on the lifetimes of plastics in near-equator exposure. A comparative study of environmental photodegradation of relevant plastic materials under near-equator and far-equator conditions. The study will involve exposures to under a) natural sunlight, b) filtered sunlight, c) UV excluded sunlight, and d) natural sunlight under controlled temperature conditions. Several near-equator sites should be included in the study.
- 2. 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
  - d. Textiles

The deleterious effect of UV radiation on these materials is generally known. But little quantitative data on their weathering behaviour are available, making it impossible to produce meaningful economic projections.

3. Action spectra for degradation of polyolefins (polyzethylenes and polypropylene), as well as the doseresponse information for most commercially relevant plastic formulations, are presently unavailable.

- Even in the case of poly(vinyl chloride), PVC, where action spectra 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.
- 4. Temperature and humidity are important factors in controlling the rate of weathering. It is likely to play a crucial role in determining light-induced damage under exposure to UV-rich sunlight resulting from a partial depletion of the ozone layer. Studies on the temperature and humidity dependence of photodegradation of common plastic formulations under UV-enhanced sunlight are needed to quantify this effect.
- 5. The most likely initial response to increased UV-B content in sunlight, and consequent shorting 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.

#### Monitoring Needs

- Better ground- and satellite-based measurements of surface UV radiation are needed to document the impact of stratospheric ozone depletion on ambient UV, and to assess the effects of enhanced UV-B radiation on exposed populations. A long-term data record is important.
- 2. Monitoring data are needed as input to models and for model validation. Current models need to be modified to account for cloud cover and aerosols.
- Common calibration and audit procedures should be developed and implemented for national and international monitoring programs.
- 4. Monitoring activities should be coordinated with the efforts of other groups on a national and international scale. Close coordination is needed for intercomparison studies and quality control/quality assurance efforts.

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## MONTREAL PROTOCOL ON SUBSTANCES THAT DEPLETE THE OZONE LAYER

FINAL ACT

1987

Na. 87-6106

1. The Conference of Plenipotentiaries on the Protocol on Chlorofluorocarbons to the Vienna Convention for the Protection of the Ozone Layer was convened by the Executive Director of the United Nations Environment Programme (UNEP) pursuant to decision 13/18 adopted by the Governing Council of UNEP on 23 May 1985.

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- 2. The Conference met at the Headquarters of the International Civil Aviation Organization, Montreal, with the kind support of the Government of Canada, from 14 to 16 September 1987.
- 3. All States were invited to participate in the Conference. The following States accepted the invitation and participated in the Conference:

Algeria, Argentina, Australia, Austria, Belgium, Brazil, Burkina Faso, Byelorussian Soviet Socialist Republic, Canada, Chile, China, Colombia, Congo, Costa Rica, Czechoslovakia, Denmark, Democratic Yemen, Egypt, Finland, France, Germany, Federal Republic of, Ghana, Greece, Indonesia, Israel, Italy, Japan, Kenya, Korea, Republic of, Luxembourg, Malaysia, Mauritius, Mexico, Morocco, Netherlands, New Zealand, Nigeria, Norway, Panama, Peru, Philippines, Portugal, Senegal, Spain, Sweden, Switzerland, Thailand, Togo, Tunisia, Uganda, Ukrainian Soviet Socialist Republic, Union of Soviet Socialist Republics, United Kingdom of Great Britain and Northern Ireland, United States of America, Venezuela.

- 4. The European Economic Community also participated and the state of the state of
- 5. Observers from the following States attended the proceedings of the Conference:

Dominican Republic, Ecuador, Hungary, India, Kuwait, Poland.

6. Observers from the following United Nations bodies, specialized agencies, intergovernmental and non-governmental organizations also attended the Conference:

World Meteorological Organization (WMO), General Agreement on Tariffs and Trade (GATT), International Civil Aviation (ICAO), Organization of African Unity (OAU), Council of the European Communities (CEC), Organization for Economic Co-operation and Development (OECD), International Chamber of Commerce (ICC), Federation of European Aerosol Associations, European

Chemical Industry Federation, Chemical Manufacturers Association, Natural Resources Defense Council, World Resources Institute, Environmental Defense Fund, Greenpeace, Friends of the Earth. Seattle Foundation (Canada), Mammouth International Humanitarian Societies Square Project Inc. (Canada), Watto Laboratories International (Canada), Dr. F.A. Homonnay and Associates (Canada), International Organization of Automobile Manufacturers, Alliance for Responsible CFC Policy, Air-Conditioning and Refrigeration Institute (USA), Environmental Protection Agency (USA), Institute for European Environment Policy. National Fire Protection Association, Dupont Canada, The Beloff Group (Canada), Produits Chimiques Allied Canada Inc., United States Air Force.

- 7. The Conference was formally opened by Dr. Mostafa K. Tolba, the Executive Director of UNEP. In the course of the inaugural ceremony, the Conference heard a welcoming address by the Honorable Tom McMillan, P.C., M.P., Minister of the Environment, on behalf of the Government of Canada.
- 8. Dr. Mostafa K. Tolba served as Secretary-General of the Conference and Dr. Iwona Rummel-Bulska (UNEP) served as Executive Secretary.
- 9. The Conference unanimously elected Ambassador W. Lang (Austria) as its President.
  - 10. The conference also elected the following officers:

Vice-Presidents: Ambassador E. Hawas (Egypt)
Dr. V. Zakharov (Union of Soviet Socialist Republics)

Rapporteur: Mr. C.R. Roque (Philippines)

- 11. The Conference adopted the following agenda:
  - 1. Opening of the Conference.
  - 2. Organizational matters:
    - (a) Adoption of the rules of procedures;
    - (b) Election of the President:
    - (c) Election of the Vice-President and Rapporteur;
    - (d) Adoption of the agenda;
    - (e) Appointment of the members of the Credentials Committee;
    - (f) Appointment of the members of the Drafting Committee;
    - (g) Organization of the work of the Conference.

- 3. Consideration of the draft Protocol to the Vienna Convention for the Protection of the Ozone Layer.
- 4. Report of the Credentials Committee.
- 5. Adoption of the Protocol to the Vienna Convention for the Protection of the Ozone Layer.
- 6. Adoption of the Final Act of the Conference.
- 7. Signature of final instruments.
- 8. Closure of the Conference.
- 12. The Conference adopted as its rules of procedure document UNEP/IG./9/2 proposed by the secretariat.
- 13. In conformity with the rules of procedure, the Conference established the following Committees:

Committee of the Whole:

Chairman: The President of the Conference

General Committee:

Chairman: The President of the Conference

Members: The Vice-President of the Confer-

ence, the Rapporteur and the Chairman of the Drafting Committee

Drafting Committee:

Chairman: Mr. Jon J. Allen (Canada)

Members Argentina

Australia France Japan

United Kingdom
United States

Credentials Committee:

Chairman: Ambassador Jose M. Bustani

(Brazil)

Members: Finland

Germany, Federal Republic of

Indonesia Kenya Mexico Norway

- 14. The main documents which served as the basis for the deliberations of the Conference were:
  - Seventh Revised Draft Protocol on [Chlorofluorocarbons] [and Other Ozone Depleting Substances], UNEP/IG.93/3 and Rev. 1;

- Reports of the Ad Hoc Working Group of Legal and Technical Experts for the Elaboration of a Protocol on Chlorofluorocarbons to the Vienna Convention for the Protection of the Ozone Layer (Vienna Group), UNEP/WG.151/L.4, UNEP/WG.167/2 and UNEP/WG.171/2.
- 15. In addition, the Conference had before it a number of other documents that were made available to it by the Secretariat of UNEP.
- 16. The Conference approved the recommendation of its Credentials Committee that the credentials of the representatives of the participating States as listed in paragraph 3 should be recognized as being in order.
- 17. On the basis of the deliberations of the Committee of the Whole, the Conference, on 16 September 1987, adopted the Montreal Protocol on Substances that Deplete the Ozone Layer. The Protocol, which is appended to the Final Act, will be open for signature at the Ministry for External Affairs of Canada in Ottawa from 17 September 1987 to 16 January 1988 and at the United Nations Headquarters in New York from 17 January 1988 to 15 September 1988.
- 18. The Conference also adopted the following resolutions which are appended to the Final Act:
  - 1. Resolution on the Montreal Protocol.
  - 2. Resolution on the exchange of technical information.
  - 3. Resolution on the reporting of data.
  - 4. Tribute to the Government of Canada.
- 19. At the time of the adoption of the Final Act, some delegations made declarations which are recorded in this document.

IN WITNESS WHEREOF the representatives have signed this Final Act.

DONE at Montreal, this sixteenth day of September one thousand nine hundred and eighty seven in one original in the Arabic, Chinese, English, French, Russian and Spanish languages, each language version being equally authentic. The original text will be deposited with the Secretary-General of the United Nations.

## 1. RESOLUTION ON THE MONTREAL PROTOCOL

The Conference,

Having adopted the Montreal Protocol on Substances that Deplete the Ozone Layer,

Noting with appreciation that the Protocol was opened for signature in Montreal on 16 September 1987,

Recalling the Vienna Convention for the Protection of the Ozone Layer, adopted on 22 March 1985,

Bearing in mind the Resolution of the Conference of Plenipotentiaries on the Protection of the Ozone Layer adopted on the same day which urged in the sixth operative paragraph "all States and regional economic integration organizations, pending entry into force of a protocol, to control their emissions of CFC's, inter alia in aerosols, by any means at their disposal, including controls on production or use, to the maximum extent practicable",

- 1. Calls upon all States and regional economic integration organizations that have not yet done so to implement the sixth paragraph, bearing in mind the special situation of the developing countries;
- 2. <u>Appeals</u> to all States to become Parties to the Vienna Convention for the Protection of the Ozone Layer;
- 3. <u>Urges</u> all States and regional economic integration organizations, including those that have not participated in this Conference, to sign and become Parties to the Montreal Protocol on Substances that Deplete the Ozone Layer;
- 4. <u>Requests</u> the Executive Director of the United Nations Environment Programme to forward this Resolution to the Secretary-General of the United Nations and to circulate it to all States and regional economic integration organizations.

## 2. RESOLUTION ON THE EXCHANGE OF TECHNICAL INFORMATION

The Conference,

Having adopted the Montreal Protocol on Substances that Deplete the Ozone Layer,

**Realizing** the importance of reducing as quickly as possible the emissions of these substances,

Recognizing the need for an early exchange of information on technologies and strategies to achieve this,

- 1. <u>Requests</u> the Executive Director of the United Nations Environment Programme (UNEP), pending the first meeting of the Parties, to make appropriate arrangements to facilitate the exchange of information on technology referred to in Articles 9 and 10 of the Protocol;
- 2. Appeals to interested States and regional economic integration organizations to sponsor, at the earliest opportunity, in co-operation with UNEP, a workshop with the aim of:
- (a) Exchange information on technologies and administrative strategies for reducing emissions of the substances listed in Annex A to the Protocol and for developing alternatives, taking into account paragraph 2 of Annex II to the Vienna Convention for the Protection of the Ozone Layer; and
- (b) Identifying areas in which further research and technical development are required,
- 3. <u>Urges</u> all interested parties to participate in and contribute to such a workshop and to make expeditious use of the information so gained in order to reduce the emissions of those substances and to develop alternatives.

#### 3. RESOLUTION ON REPORTING OF DATA

The Conference,

Having adopted the Montreal Protocol on Substances that Deplete the Ozone Layer,

<u>Convinced</u> that the timely reporting of complete and accurate data on the production and consumption of controlled substances is critical to the effective and efficient implementation of this Protocol,

- 1. <u>Calls upon</u> all Signatories to take, expeditiously, all steps necessary to acquire data and report on the production, import and export of controlled substances in a complete and timely fashion in accordance with Article 7 of the Protocol and taking into account paragraph 1 of Article 4 of the Vienna Convention for the Protection of the Ozone Layer;
- 2. <u>Invites</u> Signatories to consult with other Signatories, and to seek advice and assistance from the United Nations Environment Programme (UNEP) and other relevant international organizations, as necessary, in designing and implementing data reporting systems;
- 3. <u>Calls upon</u> the Executive Director of UNEP to convene, within six months of the adoption of this Resolution, a meeting of governmental experts with the assistance of experts from relevant international organizations to make recommendations for the harmonization of data on production, imports and exports to ensure

consistency and comparability of data on controlled substances.

## 4. TRIBUTE TO THE GOVERNMENT OF CANADA

The Conference,

Having met in Montreal from 14 to 16 September 1987 at the gracious invitation of the Government of Canada,

Convinced that the efforts made by the Government of Canada and by the civic authorities of Montreal in providing facilites, premises and other resources contributed significantly to the smooth conduct of its proceedings,

<u>Deeply appreciative</u> of the courtesy and hospitality extended by the Government of Canada and the City of Montreal to the members of the delegations, observers and the secretariat attending the Conference,

Expresses its sincere gratitude to the Government of Canada, to the authorities of Montreal and, through them, to the Canadian people and in particular to the population of Montreal for the cordial welcome which they accorded to the Conference and to those associated with its work and for their contribution to the success of the Conference.

#### **DECLARATIONS**

made at the time of adoption of the Final Act of the Conference of Plenipotentiaries on the Montreal Protocol on Substances that Deplete the Ozone Layer.

- 1. Speaking on behalf of the developing countries, the delegate from Egypt stated that the developing countries' understanding on Article 2 of the Montreal Protocol on Substances that Deplete the Ozone Layer is that any of its provisions will in no way affect the agreement reached on subparagraph (c) of Article 3 and on Articles 4 and 5.
- 2. Speaking on behalf of the European Economic Community, the delegate from Denmark stated that all Member States of the European Economic Community and EEC will sign the Montreal Protocol on Substances that Depelete the Ozone Layer and that all Member States and EEC will ratifiy the Vienna Convention for the Protection of the Ozone Layer as soon as possible to allow the Montreal Protocol to enter into force on 1 January 1989.

3. The delegate from the Soviet Union stated that while fully sharing the idea that the trade in CFCs should be controlled, the Soviet Union finds it necessary to include into a corresponding Article a provision allowing Parties to fulfill their earlier commitments. That would be consistent with the letter and spirit of all international agreements. At the first meeting of the Parties an effort should be made to introduce amendments and corrections into a number of Articles to make the Protocol more flexible and responsive to the needs of different countries, in particular, those with a low level of consumption of ozone depleting substances. At the first meeting of the Parties, among other things, they should consider, besides the ozone depleting substances, the scientific data on the effect of the use of alternative substances on human health and environment as well as ecological consequences. Scientific experts, to this end, should prepare a review of alternatives. In reiterating the will of our country to develop international cooperation in the field of environmental protection and that of the ozone layer, the delegation of the Soviet Union considers, in general, that the present Protocol seems to be ready for signing and that after having considered the legal basis of the provisions contained in certain Articles formulated in the last few days of the Conference, the question can be solved.

## MONTREAL PROTOCOL ON SUBSTANCES THAT DEPLETE THE OZONE LAYER

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,

<u>Conscious</u> 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.

<u>Determined</u> 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,

Acknowledging that special provision is required to meet the needs of developing countries for these substances,

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 the research and development of science and technology relating to the control and reduction of emisions 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 to this Protocol, whether existing alone or in a mixture. It excludes, however, any such substance or mixture which is in a manufactured product other than a container used for the transportation or storage of the substance listed.
- 5. "Production" means production plus imports minus exports of controlled substances.
- 6. "Consumption levels" of production, imports, exports and consumption means levels determined in accordance with Article 3.
- 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 or another, for the purpose of achieving economic efficiencies or responding to anticipated shortfalls in supply as a result of plant closures.

#### **ARTICLE 2: CONTROL MEASURES**

- 1. Each Party shall ensure that for the twelve-month period commencing on the first day of the seventh month following the date of the 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 twelve-month period commencing on the first day of the thirty-seventh month following the date of the entry into force of this Protocol, and each twelve-month period thereafter, its calculated level of consumption of the controlled substances listed in Group II of Annex A does not exceed its calculated level of consumption in 1986. 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. The mechanisms for implementing these measures shall be decided by the Parties at their first meeting following the first scientific review.
- 3. Each Party shall ensure that for the period 1 July 1993 to 30 June 1994 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, eighty 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, eighty per cent of its calculated level of production in 1986. However, in order to satisfy the basic domestic needs of the Parties operating under Article 5 and for the purposes of industrial rationalization between Parties, 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 period 1 July 1998 to 30 June 1999, 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 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 Article 5 and for the purposes of industrial rationalization between Parties, 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 unless the Parties decide otherwise at a meeting by a two-thirds majority of Parties present and voting, representing at least two-thirds of the total calculated level of consumption of these substances of the Parties. This decision shall be considered and made in the light of the assessments referred to in Article 6.

- 5. Any Party whose calculated level of production in 1986 of the controlled substances in Group I of Annex A was less than twenty-five kilotonnes may, for the purposes of industrial rationalization, transfer to or receive from any other Party, production in excess of the limits set out in paragraphs 1 2 and 4 provided that the total combined calculated levels of production of the Parties concerned does not exceed production limits set out in this Article. Any transfer of such production shall be notified to the secretariat, no later than the time of the transfer.
- 6. Any Party not operating under Article 5, that has facilities for the production of 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 fulfill their obligations respecting consumption under this Article provided that their total combined

calculated level of consumption does not exceed the levels required by this Article.

- (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 Member 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 decided whether:
  - (i) Adjustments to the ozone depleting potentials specified in Annex A should be made and, if so, what the adjustments should be; and
  - (ii) Further adjustments and reductions of production or consumption of the controlled substance 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 making 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 percent of the total consumption of the controlled substances of the Parties;
- (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 communications 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 decision shall become effective, provided that it has been accepted by a two-thirds majority vote of the Parties present and voting.
- 11. Nothwithstanding the provisions contained in this Article, Parties may take more stringent measures than those required by this Article.

## ARTICLE 3: CALCULATION OF CONTROL LEVELS

For the purposes of Articles 2 and 5, each Party shall, for each Group of substances in Annex A, 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; and
  - (ii) Adding together, for each such Group, the resulting figures;
- (b) Imports and exports, respectively, by following, *mutandis mutatis*, 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 substances to any State not party to this Protocol.
- 3. With three years of the date of the entry into force of this Protocol, the Parties shall, following the procedures 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.
- 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. Nothwithstanding the provisions of this Article, imports referred to in paragraphs 1, 3 and 4 may be permitted from 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 and this Article, and has submitted data to that effect as specified in Article 7.

## 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 is less than 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 shall, in order to meet its basic domestic needs, be entitled to delay its compliance with the control measures set out in 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 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 subsidies, aid, credits, guarantees or insurance programmes to Parties that are developing countries for the use of alternative technology and for substitute products.

## 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 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 for the year 1986, or the best possible estimates 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.

#### **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 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. With 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, cooperate in promoting technical assistance to facilitate participation in an implementation of this Protocol.
- 2. Any Party of Signatory to 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 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 the 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 or 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 1;
- (f) Review reports prepared by the secretariat pursuant to subparagraph (c) of Article 12;
- (g) Assess, in accordance with Article 6, the control measures 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 nongovernmental, 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 maybe 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 provisions 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 requests 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 bee 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 fulfill forthwith the sum of the obligations under Article 2, as well as under 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 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	Substance	Ozone Depleting Potential*/
Group I		
CFCl <sub>3</sub>	(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
$C_2F_5C1$	(CFC-115)	0.6
Group II		
CF <sub>2</sub> BrCl	(halon-1211)	3.0
CF₃Br	(halon-1301)	10.0
$C_2F_4Br_2$	(halon-2402)	(to be determined)

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