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Environmental Effects of Ozone Depletion and its Interactions with Climate Change

Progress Report, 2009

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United Nations Environment Programme, Environmental Effects Assessment Panel*

The Parties to the Montreal Protocol are informed by three panels of experts. One of these is the Environmental Effects Assessment Panel (EEAP), which deals with the increased UV radiation and its effects on human health, animals, plants, biogeochemistry, air quality and materials. Since 2000, the analyses and interpretation of these effects have included interactions between UV radiation and global climate change.

When considering the effects of climate change, it has become clear that processes resulting in changes in stratospheric ozone are more complex than believed previously. As a result of this, human health and environmental problems will be longer-lasting and more regionally variable.

Like the other Panels, the EEAP produces a detailed report every four years; the most recent was published in 2006. In the years in between, the EEAP produces a less detailed and shorter Progress Report. The present report is for 2009 and a full Quadrennial Report will be published in 2010.

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Ozone and changes in biologically active UV radiation reaching the Earth's surface

- **Long-term changes in surface UV irradiance vary geographically. In some cases, the response of surface UV radiation[1] to the beginning of an ozone recovery is apparent, but in others UV radiation is still increasing.** Since the mid 1990s, irradiance changes within the United States Department of Agriculture's UV Network ranged from −5% to +2% per decade,[4] although, in most cases, the trends for individual months were not statistically significant. Over the ~1 decade measurement period, there was a general increase in ozone, suggesting that changing cloud, aerosol, air pollution, and snow conditions were responsible for driving surface radiation variability in addition to ozone trends. At Belsk, Poland, an increase in column ozone and levelling off of UV irradiance since 1995 has been identified from observations spanning the period 1976 to 2006.[5] Analysis of satellite data[6] revealed significant increases in UV irradiance from 1979 to 1998 at all latitudes, except the equatorial zone, which were caused by decreases in total ozone. For clear skies, the largest increases in UV since 1979 were found in the Southern Hemisphere (~8% increase in erythemal irradiance (UV_{Ery}) at 50°S compared with ~5% at 50°N). At southern mid to high latitudes, the annual average increase in UV due to ozone depletion has been partially offset by increases in cloud and aerosols (hemispherical dimming). After 1998, ozone and UV irradiance have been approximately constant. However, compared with ground-based measurements, the satellite estimates of UV_{Ery} are 25% and 14% lower for all-weather and clear-sky cases respectively. In the Northern Hemisphere, apart from some regions in Asia,[7] there has been widespread brightening over this period. Long-term changes in extinctions by aerosols (from man-made pollution),[8, 9] volcanic eruptions,[10] and cloud cover[11, 12] (which may be related to climate change – see below) may also influence UV irradiances at regional or even global scales.

- **Large differences in surface UV irradiance between polluted and pristine locations have been observed, caused by differences in clouds and aerosols in the boundary layer, by differences in the profile of ozone, and by interactions between ozone and aerosols in the lower atmosphere.[13-15]** Measurements and model calculations show that in polluted environments, harmful

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[1] For ease of reading we will sometimes abbreviate the term "UV radiation" to "UV". The term "UV irradiance" means the measured quantity of UV radiation (usually in units of Wm^{-2}).

UV-B irradiances can be reduced to less than 50% of their values under pristine conditions.[16] Naturally-occurring aerosols (e.g., Saharan dust) can also have substantial effects on UV-B radiation far from their source regions.[17] These reductions in radiation as it passes through the troposphere (i.e., tropospheric extinctions) seriously compromise the accuracy of satellite sensors, which tend to overestimate the UV irradiance at the surface in polluted locations.

- **Using information about season, sun angle, and daily sunshine duration alone, daily totals of solar UV radiation back to 1893 were reconstructed for Central Europe.**[18] Extrapolation prior to the period when ozone column measurements became available was based on the fact that UV changes since 1979 were not highly correlated with ozone. The estimated annually averaged erythemal irradiances were found to be relatively constant prior to the 1980s. This new information extends our knowledge of historical changes in UV irradiance. However the uncertainty in the reconstruction is greater than 20%.

- **Stratospheric ozone is no longer decreasing, and is possibly increasing as a result of reductions in ozone depleting substances (ODSs), supporting the success of the Montreal Protocol. However, the continuance of this may be influenced by other factors as noted below.** The long-term globally averaged trends derived from 50–60 total-ozone stations range from ~-2% per decade in the late 1980s to ~+1% per decade by the start of the 21st century.[19] In the northern temperate zone, analysis of height-resolved data showed that nearly half of the increase in total-ozone trend is due to increases in the lower stratosphere, with the troposphere contributing only about 5%. It has recently been demonstrated using ground-based data that the beginnings of an ozone recovery detected at higher regions in the stratosphere (> 40 km) - where chemical effects outweigh dynamical effects - are indeed attributable to reductions in ODSs resulting from the Montreal Protocol.[20] Similar conclusions were reported in another study of ozone changes in the Antarctic vortex region, where ozone is affected by both chemical and dynamical processes.[21] Decreases in stratospheric halogen loading are the primary cause of the recent levelling of ozone in this region.

- **In a study of the "world avoided" by the success of the Montreal Protocol, it has been shown that decreases in stratospheric ozone due to increasing chlorofluorocarbons (CFCs) would have led to a marked increase in ultraviolet**

radiation, with the UV index (UVI) more than doubling in the northern summer mid-latitudes by 2060.[22] In view of what is known about effects of excess UV radiation this would have had very serious consequences. A future "world avoided" scenario where ODSs were never regulated and ODS production grew at an annual rate of 3% was simulated in the model. By 2020, 17% of the globally-averaged column ozone in 1980 would have been destroyed, increasing to more than 60% by 2060. In polar regions, large ozone depletion would have become year-round rather than just seasonal. Very large temperature decreases would have occurred in response to circulation changes and decreased shortwave radiation absorption by ozone. In the tropical lower stratosphere, ozone would have remained constant until about 2053 and then collapsed to near zero by 2058. However, the calculations excluded the troposphere, and self-healing in that part of the atmosphere could have ameliorated some of these predicted decreases.

- **There has been an increased focus on interactions between ozone depletion and climate change, which can work in both directions: ozone changes can induce changes in climate, and climate change can induce changes in ozone. Thus, a return of ozone to its value at any particular date should not necessarily be interpreted as a recovery of ozone from the effects of ozone depleting substances alone.**[23] For example, it has been suggested that ozone depletion in Antarctica can influence tropospheric wind patterns in the Northern Hemisphere, both at high latitudes and mid-latitudes.[24] Furthermore, in the 2060s when the stratospheric halogen loading is projected to return to its 1980 values, it has been predicted[25] that, outside tropical regions, column ozone will be significantly higher than in 1975–1984, due to changes in circulation resulting from increases in greenhouse gases.

- **New model calculations predict that surface erythemal irradiance will decrease over mid-latitudes by 5 to 15% over the 21st century, while at southern high latitudes the decrease will be twice as much.**[26] These simulations were from 11 coupled Chemistry-Climate Models (CCMs) incorporating projected changes in total ozone columns and vertical profiles of ozone and temperature with projected stratospheric ozone recovery.[26] Starting from the first decade of the 21st century, the projected surface erythemal irradiance decreases globally at somewhat higher rates in the first half of the 21st century and more slowly later on. This decreasing tendency will be more pronounced over latitudes where stratospheric ozone depletion was largest. However, the study ignores the potentially important changes in cloudiness, surface reflectivity, and tropospheric aerosol loading due to climate change.

- **A recent modelling study suggests that, in response to climate change, cloud cover will increase at high latitudes but will decrease at low latitudes.[27] If this prediction is correct, then there could be important implications for human health, since UV radiation would increase at low latitudes, places where it is already high, but decrease at high latitudes, where it is already low.** The already large latitudinal gradients in UV radiation will become even larger. However, the modelled cloud effects have not been verified against measurements and large uncertainties remain. Even the direction of future changes in forcing agents for UV radiation, such as aerosol and clouds, is not well established.

- **New studies have examined the relationship between erythemally-weighted and vitamin D-weighted UV radiation. There appears to be an inconsistency in our understanding of the production of vitamin D by sunlight.** For high UV levels (UVI > 6), the ratio of vitamin D-weighted to erythemally-weighted radiation (see Figure 1 for these weighting functions) is approximately 2. However, for lower UV levels the proportionality breaks down and vitamin D-weighted UV decreases more rapidly. For UVI < 1, the ratio is less than 1.[28] Empirical relationships, and direct spectral measurements have been used to investigate geographical and seasonal distributions of the ratio of vitamin D-weighted to erythemally-weighted irradiance over the USA and Canada.[28, 29] The ratio ranges from ~2 at low latitudes to ~0.5 at high latitudes in the winter. The effective daily dose of

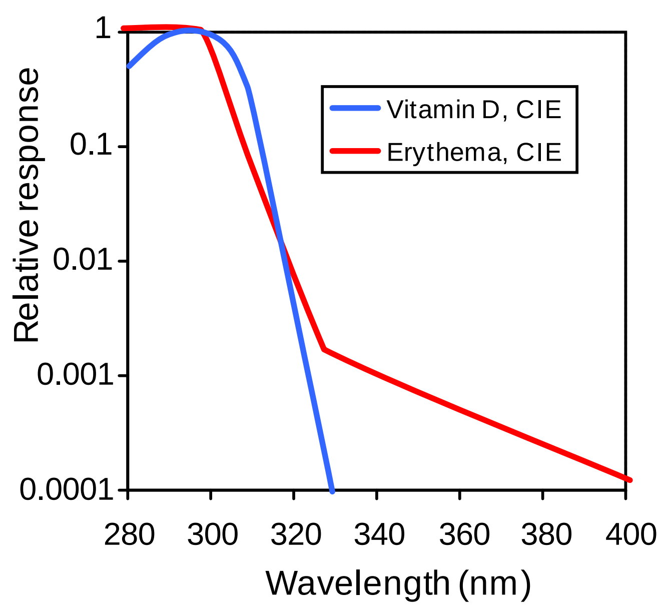

Figure 1. Weighting functions (or action spectra) for erythema [1] and pre-vitamin D production[3] as published by the International Commission on Illumination (CIE)

vitamin D-weighted UV has been calculated from spectral measurements at three European stations.[30]

Daily doses of UV are much lower at the high latitude sites, particularly during the winter months. For the highest latitude sites in this study the recommended daily vitamin D dose cannot easily be attained for several of the winter months.

Spectral irradiance measurements have been used to calculate the exposure times to optimize beneficial effects of UV while minimizing risks.[31] For the intensities of UV present at mid-latitudes in the winter, sufficient vitamin D should be produced in less than 1 hour of full body exposure. However, this result is inconsistent with earlier findings that no vitamin D is produced at mid-latitudes in winter, and therefore suggests that there may be a problem with the currently assumed action spectrum for the production of vitamin D.

- **The UV radiation dose which is received by the population is usually only a very small fraction of the available ambient dose, depending on lifestyle.[32] These small exposure ratios (ER) may be beneficial for preventing skin damage, but may be detrimental for maintaining vitamin D status.** A recent study among sunbathers in Italy found ERs of 20% or more,[33] which were much larger than in the general population at other mid-latitude sites studied previously using similar polysulfone badges. For example, in Germany, the ER was found to vary greatly between anatomical body sites, but was typically ~2%.[34] In two studies in New Zealand using electronic dosimeters, designed to measure erythemal UV irradiance, the ER was found to be ~5% for primary school children,[35] and only reached ~20% for the population subset of outdoor workers.[36]

Human health: Effects of solar UV radiation and interactions with climate change

- **Worldwide incidence rates for cutaneous melanoma, for which solar UV exposure is the major environmental risk factor, have risen faster than those of any other malignancy in the Caucasian population over the last 30 years. Mortality rates also continue to increase.** In central Europe and the USA, the incidence rate of cutaneous melanoma has tripled between the early 1970s and 2000 to 18-30/100,000 in fair-skinned populations.[37] In men aged 65 and older in the USA, the incidence is currently more than 125 cases per 100,000.[38] In the UK, melanoma has risen to be the third most commonly reported cancer after breast and cervix for women in their thirties, with a predicted doubling in incidence in both men and women over all ages by the year 2024.[39] Although melanomas develop less frequently in individuals with dark skin than in those with fair skin, a study in New Zealand has revealed a rapidly increasing incidence rate over the period 1996-2006 in subjects with darker-skinned ethnicities (ethnicity is self-identified in New Zealand); for example, the increase was 90% in Maori people.[40] A recent pooled analysis of 15 case-control studies involving subjects living at various latitudes demonstrated that recreational (intermittent) sun exposure and sunburn are strong predictors of melanoma at all latitudes, while occupational and total sun exposure predict melanoma at low latitudes.[41] Another meta-analysis showed an increasing risk of melanoma with increasing numbers of sunburns throughout all ages of life (childhood, adolescence, adulthood and lifetime),[42] strengthening the view that sunburn as a risk factor for melanoma is not confined to overexposure episodes in childhood.[43, 44] In the Swedish population, melanoma on the trunk represented an increasing proportion of all melanomas over the period 1960-2004, a situation attributed to behavioural and societal changes leading to intentional high sun exposure on the body.[45] Any reduction in mortality in the next few years is likely to be due to early detection and treatment, and not to primary prevention.[46] Targeted public health campaigns that encourage personal behaviour resulting in a reduced incidence of this malignancy are currently being developed and evaluated and need to include messages relevant to both those with dark and fair skins.[40, 47, 48]

- **Analyses of trends in the incidence of non-melanoma skin cancer (basal cell and squamous cell carcinomas) in several countries have confirmed the critical role of sun exposure.** Basal cell carcinoma (BCC) is the most common cancer in fair-skinned populations. The relationship between UV exposure and risk may be complex as some tumours occur on less exposed parts of the body such as the trunk, although the distribution of BCCs is broadly consistent with the sun exposure expected under normal circumstances at the various body sites.[49] A study of fair skinned subjects in subtropical Australia revealed that risk of BCC on the head is particularly increased in sun sensitive individuals, whereas BCC of the trunk appears to be more related to number of reported sunburns rather than to sun sensitivity in general.[50] In this population the incidence rate in people affected multiple times by primary BCCs was almost the same as those affected on a single occasion, thus the BCC burden may be higher than is apparent from the normal incidence rates.[49] The association of BCC incidence with socio-economic status

(SES) was examined in a large Dutch population over the period 1988-2005; the proportion with BCC of high SES increased while the proportion with BCC of low SES decreased. Thus BCC may be changing to become a disease of the wealthy rather than of those with less income (who once tended to work outdoors) perhaps due to more recreational sun exposure and better recognition of skin lesions in the affluent population.[51] A registry-based study in Bavaria confirmed several earlier reports that outdoor workers have an increased risk of BCC and SCC compared with indoor workers, thus substantiating the view that chronic sun exposure is an important risk factor for both types of non-melanoma skin cancer.[52]

In Sweden the incidence of SCC in both men and women increased four-fold from 1960 to 2004. During this time a decrease of SCC on the face was apparent in all age groups, apart from the most elderly, with an increase on the trunk and upper arms, a change attributed to the growing fashion for intentional body tanning.[53] In women living in regions of the US with low (5 or less), medium (6) and high (7 or more) UV indices (defined on the basis of August UV levels), the risk of developing SCC when assessed at birth, or at 15 or 30 years of age was highest in states in the high category.[54] This emphasises the role of cumulative sun exposure in the aetiology of SCC. A lower risk of further cutaneous SCCs could result if guidance was given regarding preventative behaviour in patients recently treated for cutaneous SCCs.[55]

- **Recent work involving a large population has confirmed a relationship between melanomas of the internal eye and personal factors linked to sun sensitivity and solar UV exposure.** Intraocular melanoma can occur in the iris, cilary body and choroid layer (collectively known as the uvea) of the eye, all structures generally thought protected from ambient UV-B radiation. Recently a large scale study has confirmed and added to two earlier epidemiologic studies[56, 57] by revealing that the risk of uveal melanoma in subjects with light-coloured irides increased with increasing episodes of photokeratitis (due to welding or snow blindness), regular exposure to sunlamps, working more than 4 hours per day outdoors, and wearing sunglasses or hats (indicating photosensitivity).[58] The association of uveal melanoma with photokeratitis suggests that UV-B radiation may be involved, although a contribution from the longer-wavelength UV-A radiation cannot be ruled out.

- **Efforts to inform the public about the risk of skin cancers continue in several countries where these diseases present a major social and economic burden.** Simple, yet high impact, messages that emphasise sun protection for fair-skinned populations are required in countries where solar UV-B radiation is high.[59] One difficulty is that they need to be adapted according to place, season and skin phototype.[60] Understanding by the general public as to what the UV Index represents remains low, and greater efforts are required in order for it to become a useful tool in the management of sun exposure.[61] Schools represent the prime setting for the education of adolescents regarding excessive sun exposure, and data are now becoming available about the effectiveness of measures being adopted in Australia to change behaviour, such as by creating shade in playgrounds with purpose-built sails.[62] Particular care with personal sun exposure is required in any area of the world with increased solar UV-B radiation as a result of ozone depletion.

- **Patients with skin cancer may have an altered risk of developing other malignancies.** As solar UV-B exposure is the most common environmental risk factor in the induction of skin cancers, several studies have examined whether subjects with skin cancer have a higher or lower subsequent risk of various internal cancers, the latter possibly mediated through the protective effects of vitamin D. The results are not consistent to date: three of the most recent reports indicate a higher risk[63-65] and one a lower risk.[66] Thus this topic remains controversial and requires detailed information about individual UV exposure, vitamin D status and other risk factors to reach a firm conclusion.

- **The association between sunlight exposure and protection from some internal cancers, possibly due to the production of vitamin D, remains uncertain.** The International Agency for Research on Cancer (IARC) Working Group on "Vitamin D and Cancer" found limited evidence for a link between sun exposure and reduced risk of breast, colon and prostate cancer.[67] The published studies may have been affected by improper measurements of personal sun exposures and design issues specific to the epidemiological approach. Latitude or ambient UV exposures at the place of residence or season of diagnosis were often used as crude surrogates for personal solar UV exposure, and the lack of more individualized data may have resulted in confounding by uncontrolled correlations with different, and as yet unidentified, risk factors. Other investigators disagree with the cautious conclusion of the IARC and believe that there is strong and increasing evidence for solar UV radiation preventing cancer through vitamin D production.[68, 69]

- **The suggested association between increased levels of vitamin D, produced by solar UV-B exposure, and protection from several autoimmune diseases is strengthened.** Many previous studies have linked reduced sun exposure, and therefore suboptimal vitamin D status, with an increased risk of the autoimmune disease, multiple sclerosis (MS). Patients with relapsing-remitting MS in Tasmania were followed for more than 2 years: relapse rates were inversely correlated with erythemal UV radiation and vitamin D serum levels.[70] In addition, genetic analysis of the vitamin D receptor in MS patients has provided further support for the involvement of vitamin D in this disease.[71, 72] Small scale studies using vitamin D in MS therapy are promising although extensive clinical trials have not been undertaken as yet [reviewed in[73]].

  Type 1 diabetes mellitus (T1DM), like MS, is a T-cell mediated autoimmune disease with environmental and genetic risk factors. The incidence of T1DM roughly follows a latitudinal gradient, increasing at higher latitudes in both the southern and northern hemisphere, a situation suggested to be due to vitamin D insufficiency in the winter months at these latitudes. A study based in Newfoundland has revealed a geographical and temporal association between solar UV radiation and incidence of T1DM.[74, 75] The risk of T1DM correlated inversely with the average daily erythemal UV and this factor accounted for more of the variation in T1DM incidence than latitude.[74] There was also a significant temporal correlation, with a higher monthly incidence of T1DM in the winter months that had the lowest erythemal UV.[75]

- **The common assumption that vitamin D levels increase with decreasing latitude is not found in all studies; therefore the explanation that vitamin D status accounts for the latitudinal gradient in the incidence of several diseases requires corroboration.** Many past studies have revealed an increase in various diseases, such as certain internal cancers and autoimmune diseases, with increasing latitude, a situation commonly attributed to a decrease in vitamin D owing to diminishing solar UV-B exposure as the latitude increases. However, such surveys did not include actual measurement of vitamin D levels. A recent meta-analysis of some 400 studies revealed no overall latitudinal gradient in vitamin D levels (as measured by blood levels of 25-hydroxyvitamin D), and only a very small gradient if the analysis was limited to those with fair skin (-0.7±0.3 nmol/L/degree).[76] Moreover, in Europe vitamin D levels in post-menopausal women showed the opposite gradient – low levels in the South and high levels in the North.[77] In a multicentre global study of post-menopausal women, vitamin D levels were assessed in a single laboratory, thus eliminating the considerable variability in measurements between centres.[78] A small, although statistically significant, overall negative gradient was found for vitamin D concentration and latitude between 15° and 65°; the gradient was 3-fold steeper for readings in the winter than in the summer (about -0.6 vs -0.2 nmol/L/degree). Adaptation of the skin (pigmentation and thickening of the horny layer) and diets may dampen the gradient in vitamin D in comparison with the gradient in solar UV-B radiation that drives the synthesis of vitamin D. Hence ecological and epidemiological studies that attribute gradients in disease incidence or death to differences in vitamin D levels need to provide data for significantly strong matching gradients in vitamin D levels.

- **A variety of substances applied topically or taken orally show promise in protection against UV-induced skin damage in human subjects.** For example, both topical[79] and oral[80] nicotinamide protected against UV-induced immunosuppression of the tuberculosis skin test (Mantoux reaction), while a topical antioxidant mixture of vitamin C, ferulic acid and alpha-tocopherol provided substantial photoprotection.[81] Those subjects taking oral angiotension converting enzyme (ACE) inhibitors and angiotensin receptor blockers had a lower incidence of skin cancer than non-users over a 3 year study period.[82] Sunscreens filter UV radiation from entering the skin but are not beneficial after DNA damage has occurred. Now a moisturiser has been developed containing DNA repair enzymes which prevents the immunosuppression that normally follows UV exposure, and thus may help to protect the skin against cancer and photoageing.[83]

- **Recent evidence suggests an association between sunlight exposure and one form of age-related macular degeneration.** Age-related macular degeneration (AMD), also called age-related maculopathy, is a retinal disease that is the most frequent cause of loss of vision in older people in developed countries. AMD occurs in one of two forms: the more common non-exudative (dry/atrophic) form, and the less common but more severe exudative (wet/neovascular) form. The aetiology of AMD is unclear but is thought to involve both genetic and external factors, such as solar UV radiation. The development of AMD in about 2000 subjects, living in the

Blue Mountains, Australia, and aged over 49 years at the start of the study, was monitored over a 10 year period, and evaluated for any correlation with iris, skin and hair colour and with sun-related skin damage.[84] No associations were found except that the incidence of exudative AMD was lower in subjects with very fair skin, an effect attributed to sun-avoidance behaviour by this group. In contrast, a case-control study of Japanese male farmers revealed that lifetime exposure to sunlight, as assessed by facial wrinkling, was an important risk factor in the progression of late exudative AMD.[85] In addition, in the European Eye Study, an association was demonstrated between adult lifetime sunlight exposure and exudative AMD in individuals with low blood antioxidant levels.[86] This link was considered sufficiently strong for the authors to advocate ocular protection for the general population as well as a diet that contains the recommended amounts of key antioxidants.[86] As the wavelength dependence of the sunlight that is important as a risk factor for AMD is currently unknown, any effect of ozone depletion leading to an increase in terrestrial UV-B radiation is also unknown.

Terrestrial ecosystems: Effects of solar UV radiation and interactions with climate change

- **The large increases in UV-B radiation over the last four decades resulting from ozone depletion above the Antarctic, and to a lesser extent over Arctic regions, may have consequences for ecosystems in these areas.** Preliminary data on genetic diversity in Antarctic mosses suggest that some species may have a lower capacity to adapt to environmental change than those from temperate regions.[87] A meta-analysis of data from 34 field studies that investigated the effects of UV-B radiation on Arctic and Antarctic plants showed that they responded similarly to an increase in UV-B radiation as plants at lower latitudes.[88] This response was characterized by reduced aboveground biomass and plant height, increased DNA damage, and increased accumulation of UV-screening compounds. Compared to plants in Arctic regions, those investigated in Antarctica displayed larger decreases in leaf area and specific leaf area, i.e., the ratio between leaf area and leaf weight. These and earlier results[89] suggest that plants respond differently in Arctic and Antarctic regions, with larger impacts from the higher levels of UV-B in Antarctic areas. Caution is needed in the interpretation of some of the results, since at least part of the variability may be caused by differences in the experimental approach used to impose the UV-B treatments (e.g., filters vs. lamps).[88]

- **In temperate regions, the effects of realistic enhancements of UV-B radiation on photosynthesis and growth of terrestrial plants are generally small.** A field study with wheat conducted in southern Chile showed that a moderate enhancement of UV-B radiation did not affect crop yield, yield components or grain quality.[90] Detailed studies with silver birch (*Betula pendula*) carried out in Finland evaluated several parameters connected with photosynthetic function, including CO_2-assimilation rate, and found no significant effects of UV-B radiation.[91] Thus significant damage to photosynthesis of silver birch seedlings will likely not occur in natural settings under current and projected solar UV-B irradiances. These findings are consistent with the body of literature reviewed in earlier reports.[92] However, new studies continue to show that the effects of UV-B on plant growth can be modified by other environmental factors, including temperature[93] and water stress.[94, 95]

- **Sensitivity of DNA in plants from polar regions to UV-B may be modified by prevailing conditions such as low temperatures and water stress.** Accumulation of UV-induced DNA damage in plant species from polar regions can impair plant vitality. Such damage has been measured in a few terrestrial polar organisms including some mosses and higher plants, with studies showing large variability in tolerance among different species and strong temperature effects, with higher temperatures increasing the rates of DNA repair.[96-98] A recent study with two Antarctic moss species[99] found that DNA photo-repair decreased with decreasing temperatures in one species, but not in the other. Desiccation, a condition often experienced by mosses when the Antarctic surface is frozen, reduced the damaging effects of solar UV-B on DNA integrity.[95] This protective effect of desiccation may have been caused by the concentration of UV-screening compounds, whereas a previous study with a lichen,[98] had shown increased DNA sensitivity in the desiccated state due to decreased DNA repair. Of potential significance in the studies on moss is the tendency for the endemic Antarctic species (*Schistidium antarctici*) to show higher levels of DNA damage compared with two species that are widely-distributed (cosmopolitan species) (*Bryum pseudotriquetrum* and *Ceratodon purpureus*).[99]

- **Induction of UV-screening compounds in plants from polar regions leading to an increased UV-B tolerance may have costs in terms of reduced growth.** The UV-screening response (accumulation of protective UV-absorbing compounds) is highly variable in studies from Arctic and sub-Arctic regions, and it is affected by species differences and variation in environmental conditions.[100-102] This has been further corroborated by work in the Antarctic, which showed variation in UV screening capacity among moss species.[103] In the case of the Antarctic mosses, effective screening was achieved by phenolic compounds bound to cell walls. The metabolic cost of accumulating increased levels of UV-absorbing pigments in response to abrupt increases in UV-B radiation was calculated for an Antarctic leafy liverwort (a primitive plant belonging to the same class as mosses).[104] This cost represented a small fraction of the carbon fixed in photosynthesis, but could have cumulative effects on plants growing in polar regions constrained by season.[104]

- **Field studies of peat bogs and fens continue to indicate that UV-B radiation and its interaction with warming exerts small, but potentially important effects.** Globally, these systems store a considerable fraction of the world's belowground organic carbon. Although earlier studies show small, but inhibitory effects of solar UV-B radiation on growth of peats bogs,[105] a recent study in Finland using substantial UV-B radiation supplementation indicated a small increase in net ecosystem CO_2 uptake, due to an apparent reduction in respiration of the peat.[106] However, this result did not occur in a dry year (*see Biogeochemical Cycles*). Interactions of UV-B radiation reduction and a small degree of warming in a Tierra del Fuego fen[107] indicated generally small or no detectable effects of the treatments; however, there was a large effect of the mild warming in greatly decreasing earthworm populations in the fen. Earthworms have highly important regulatory functions in soils and other substrates.

- **Significant progress has been made in the understanding of molecular mechanisms that control plant responses to UV-B radiation.** Since our last full report,[92] various studies have demonstrated that a specific cellular signaling pathway (UVR8-COP1) controls several adaptive responses of terrestrial plants to UV-B radiation, including regulation of genes involved in the accumulation of phenolic sunscreens and DNA repair.[108, 109] These studies are also paving the way to the discovery of specific UV-B photoreceptors,[110, 111] which will greatly facilitate future research on plant responses to solar UV-B and biotechnological attempts to enhance UV-B tolerance in sensitive species. Recent work shows that it is possible to increase the capacity to repair UV-B induced DNA damage in plants by means of biotechnology.[112]

- **UV-B induces changes in plant tissue chemistry that can modify biotic interactions.** New studies with the reference plant *Arabidopsis thaliana* (a member of the mustard family) indicate that UV-induced DNA damage can activate cellular responses that increase resistance of plants to microbial pathogens.[113] Field studies in grapevine suggest that flavonoids, a group of phenolic compounds typically induced by UV-B radiation, also can reduce susceptibility of plants to leaf pathogens.[114] Phenolic compounds can also play a role affecting insect herbivory in plants exposed to UV-B radiation,[115] although the interactions between plant defense induction, developmental stage, and insect feeding mode can be complex,[116] and difficult to predict.[117] The potential impacts of UV-B induced changes in plant secondary chemistry on competitive interactions between plants,[118] and food quality and human health[119] are beginning to receive some attention.

- **The activity of insect herbivores can influence the UV radiation microenvironment under leaves and affect other animal species.** Two species of snail feed on biological films and various very small organisms on the undersides of floating lily leaves. They also use these leaf surfaces for egg laying. Their behaviour is strongly influenced by the leaf boring activity of a beetle which consumes some of the leaf tissue of the lilies allowing solar UV radiation to penetrate and this proves lethal to one species of snail, but not the other. Thus, with leaf boring by the beetle, there is a decided shift in snail species inhabiting the leaves and this is attributed to solar UV radiation, though not specifically the UV-B component.[120]

- **Solar UV radiation perceived by insects and birds influences behaviour.** Insect mating behaviour responded to solar UV radiation in different shade patches in a crop field.[121] Shade is relatively enriched in UV relative to visible radiation. Overhead filters were used to manipulate the UV component of shadelight to attain different levels of UV radiation. It was shown that, with more UV radiation in the shade, males detected females more readily and copulated more frequently. Thus, the behaviour was specifically in response to UV radiation, rather than just the low visible radiation in the shady areas. A new study confirmed that certain insects can detect the UV-B component of solar radiation, presumably by using dedicated parts of their visual systems specialized in UV-B perception.[122]

Nest parasitism occurs when an invading bird species lays eggs in nests of other birds (hosts) fooling the recipient host bird species to incubate and raise the chicks of the intruder. Honza and Polacikova[123] manipulated egg reflectance in different spectral regions and showed that blocking UV reflectance of eggs in nests allowed eggs laid by parasitic species to be left in the nests and accepted by host bird species. The host species apparently could not differentiate eggs of the intruder from their own if the UV signal was blocked. This study did not deal specifically with UV-B, and the reported effects are most likely attributable to the UV-A component.

- **Progress continues to be made in the search for a biological indicator for ozone column history before modern measurements were possible.** The concentrations of selected flavonoid compounds in dried moss tissues found in dated herbarium samples have been used as a biological indicator for ozone column levels. The rationale for this indicator is that UV often stimulates flavonoid production in plant tissues, and, thus, this accumulation is expected to correlate with the level of solar UV radiation, and by implication ozone levels. There is a general statistically significant relationship between flavonoid levels in moss tissues and daily ozone column, and a recent study[124] found that this relationship was somewhat better for ratios of selected flavonoids, which represents a small advance. Development of such a biological indicator would be very useful in assessing the history of ozone column variation prior to modern measurements (*see also the section above on 'Ozone and changes in biologically active UV radiation reaching the Earth's surface'*).

- **Experiments achieving different UV intensities by placing racks of UV-B lamps at different heights above plants can produce inaccurate results.** Many greenhouse and field studies have used racks of UV-B lamps placed at different heights above the plants to simulate different ozone depletion scenarios. Such studies have shown, for example, that intermediate UV fluxes can have a greater apparent effect on plant growth than higher or lower UV fluxes. The reason appears to be the patterns of shade cast by the bulbs. A recent analysis[125] showed that lamp racks at different heights produce different durations of shade whose distributions are concentrated at different times of day. Plants grown under unlit lamps suspended at two different heights showed significantly different growth characteristics. These differences in growth could, depending on the species and experimental conditions, either exacerbate or obscure UV-B effects. Other techniques for achieving different UV intensities are suggested.[125]

Aquatic ecosystems: Effects of solar UV radiation and interactions with climate change

- **One of the major phytoplankton groups, coccolithophores, affects the global carbon cycle through photosynthetic carbon fixation and calcification; growth of the cells is sensitive to UV-B radiation.** *Emiliania huxleyi* (Figure 2), the most abundant coccolithophore, is found in both near-shore and open oceans and from temperate to subpolar regions. Increased stratification of surface waters in the oceans due to global warming will expose these phytoplankton to higher solar UV irradiances. The cells produce UV-absorbing, protective coccoliths (Figure 2) which can reduce the penetration of UV radiation (300 – 400 nm) by 20 – 25 %. As an adaptation to UV-B, cells grow larger and have more coccoliths (enhanced calcification) indicating that they divert metabolic energy into UV protection. This was corroborated by studies showing that cells grow 25 % more slowly,[126] potentially resulting in lower biomass production in the water.

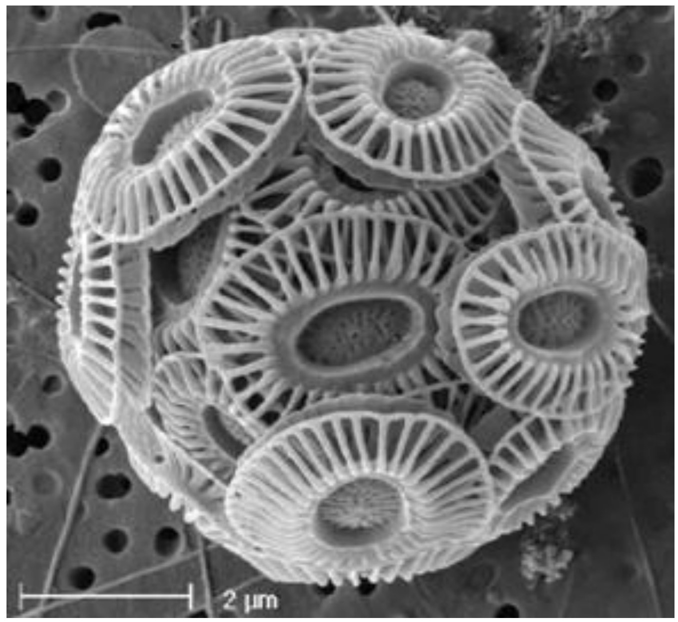

Figure 2. Scanning electron micrograph of the phytoplankton coccolithophore *Emiliania huxleyi* covered with coccoliths. Courtesy, Kunshan Gao, Xiamen, China

- **The rapid warming of surface waters around the Antarctic Peninsula over the past 50 years of 5-6°C has resulted in a shift in species composition attributed to deeper migration in the water column and thus further from the surface UV radiation.** These higher surface temperatures have led to later advance and earlier retreat of sea-ice and, consequently shorter sea-ice season.[127, 128] The resulting potentially higher phytoplankton productivity in the Antarctic Peninsula could augment carbon sequestering from the atmosphere through the shift from the invertebrates, such as krill, to an increased population of salps (tunicates).[129] Besides krill and copepods (crustaceans), salps are the most important metazoans in the Antarctic Peninsula [130, 131] involved in sequestering carbon from the atmosphere in one of the world's most important carbon sinks. Phytoplankton absorb carbon dioxide from the atmosphere via photosynthesis. Zooplankton graze on the phytoplankton and the organic material is packaged into large faecal pellets. These pellets sink to the deep sea floor and the embedded carbon is removed from circulation for tens of thousands of years. In addition, due to the deep migration of the salps in the water column they are less affected by surface UV radiation.

- **Decreases in the pH of marine waters resulting from increased concentrations of CO_2 in the atmosphere compromise the ability for protection of calcified marine organisms from solar UV-B radiation.** At 270 ppm CO_2 in the atmosphere, the average pH in the oceans was about 8.1 (late 19th century). At the current concentration of 380 ppm, a decrease in pH of 0.1 has been measured which corresponds to 30% more protons in the water. By the year 2100, a pH decrease of 0.3 – 0.4 units is expected. Acidification of the oceans reduces the amount of calcification in mollusks, phytoplankton (coccolithophoridae) and calcified macroalgae (e.g., *Corallina* and the *Conchocelis* stage of the abundant red alga *Porphyra* (used as nori)). Calcium encrustations are generally efficient absorbers of UV radiation, but an increased transmission has been measured at lowered pH values. The reduced protection by calcium due to the lower pH in the water column may expose the cells to higher levels of solar UV-B radiation.[132] In *Corallina*, UV radiation inhibited growth, photosynthetic oxygen evolution and calcification rates significantly at high CO_2 concentrations (1000 ppm). This is in contrast to a much lower inhibition at 380 ppm, reflecting a synergistic effect of CO_2 enrichment with UV radiation. Both UV-A and UV-B inhibited photosynthesis and calcification, but the inhibition caused by UV-B was much higher than that induced by solar UV-A radiation. These results show that UV-B can cause greater damage in coralline algae as progressively increasing acidification of the ocean affects their calcification. Also in the coccolithophore, *E. huxleyi*, calcification rates decrease at lowered pH levels resulting in thinned coccoliths. Acidification of seawater (of 0.1 pH units) significantly enhanced the transmission of harmful UV radiation in enclosure experiments (mesocosms). Photosynthetic carbon fixation is not affected by the visible range, 400 – 700 nm (photosynthetically active radiation, PAR).

- **Recent studies have demonstrated that some UV-B irradiated fish develop significant changes in blood chemistry and social interactions.** These experiments indicated that long-term exposure to low levels of UV-B radiation modified the immune system in carp and rainbow trout. There are also species-specific differences in sensitivity to the UV-B radiation.[133] In another experiment, exposure of Atlantic salmon to UV-B radiation retarded growth and had a negative effect on blood cell and plasma protein concentrations at exposures simulating a 20% loss of stratospheric ozone, but not for conditions simulating an 8% loss of stratospheric ozone.[134] The results demonstrate that juvenile Atlantic salmon may not be able to fully adapt to large, long-term increases in UV-B exposure. The interference with immune system function in Atlantic salmon suggests a negative effect of UV-B radiation on disease resistance. Other researchers[135] quantified several different behavioural activities among juvenile coho salmon located within acrylic mesocosms. Under higher PAR (400-700 nm), a greater proportion of juvenile coho salmon tended to take cover under rocks. Shade-seeking behaviour increased significantly in the presence of UV radiation. Feeding and combative interactions were partially inhibited at higher PAR and were significantly inhibited by UV radiation. UV radiation effects on behaviour could have ecological consequences through influencing summer population densities, density-dependent growth, and size-dependent winter survival.

- **Studies continue to show adverse effects of UV-B radiation on amphibians, sea urchins, mollusks, corals, and zooplankton.** UV-B-exposed amphibian larvae and adults may display decreased growth and increased prevalence of deformities.[136-141] The UV-B radiation may also cause increased susceptibility to predation[141, 142] and this increased susceptibility has implications for amphibian survival.[143-146] Other studies have demonstrated effects of UV-B radiation on sea urchins with respect to impaired viability of gametes and embryonic development.[147] UV-radiation and elevated temperature may have a synergistic negative effect on the survival of soft corals in their early life stages. Also, UV screening mycosporine-like amino acids may play a role in the survival of the different juvenile stages of two coral species.[148] Higher UV exposure accompanying ocean warming during low-wind doldrums conditions may significantly contribute to coral bleaching.[149] Modeling results indicate that decreasing attenuation of underwater sunlight over the coral reefs enhances UV-induced DNA damage and inhibition of photosynthesis in corals much more strongly than changes in the stratospheric ozone layer. In one experiment on zooplankton, exposure to high levels of UV radiation caused copepods to retain pigments in the absence of a predation threat. When exposed to predation threat, they reduced their pigmentation, regardless of UV level. This may indicate that the predation threat is more severe than UV radiation. Reducing the level of protective pigments in response to predation in a situation in which UV radiation is high, may, however, lead to higher mortality.[150] Also, in transparent lakes, UV radiation may constrain some zooplankton to cooler, suboptimal temperatures, which may compromise fitness[151]. In addition, solar UV radiation (measured at 320 nm and 380 nm) may be more important than fish predation in controlling the vertical distribution of zooplankton in relatively transparent lakes.[152]

Biogeochemical cycles: Effects of solar UV radiation and interactions with climate change

- **The combined effects of climate change and changes in solar UV radiation, due in part to changes in stratospheric ozone concentrations, could greatly affect carbon cycling in terrestrial and aquatic ecosystems, and cause feedback to atmospheric CO_2 concentrations.** Current models of sinks and sources of CO_2 do not generally include UV-induced effects [153-157], but doing so would improve climate predictions. For example, a recent modeling study has demonstrated the importance of including considerations of stratospheric ozone depletion in modeling carbon cycling in the Southern Ocean.[158] In terrestrial ecosystems a recent experimental study of a high latitude wetland showed that elevated UV-B slightly increased net CO_2 uptake, due to reduced soil respiration, but that the effect was small in terms of overall CO_2 budget of this community[159] (see Terrestrial ecosystems, above). The effects of other elements of climate change, such as warming and drying of terrestrial ecosystems, may well interact with UV-induced changes in carbon cycling.

- **Projected future shifts to warmer and dryer conditions in terrestrial ecosystems indicate that UV-induced CO_2 production from plant litter could become a major pathway for decomposition.** Current models project major changes in global ecosystems in response to climatic and social changes.[156, 160-165] Among the projected changes are warmer, dryer conditions and more open vegetation in many parts of the Earth[2] (Figure 3). These projections suggest that UV-induced photodegradation of above-ground plant litter, a process which is important in arid terrestrial ecosystems[166-171], will likely become a much more significant global pathway for terrestrial organic matter decomposition in the future. The role of UV-induced photodegradation in litter decomposition may also be increased by future changes in land use and management that allow increased penetration of sunlight to the ground. These changes include increased grazing[172] and felling of woodland.[173]

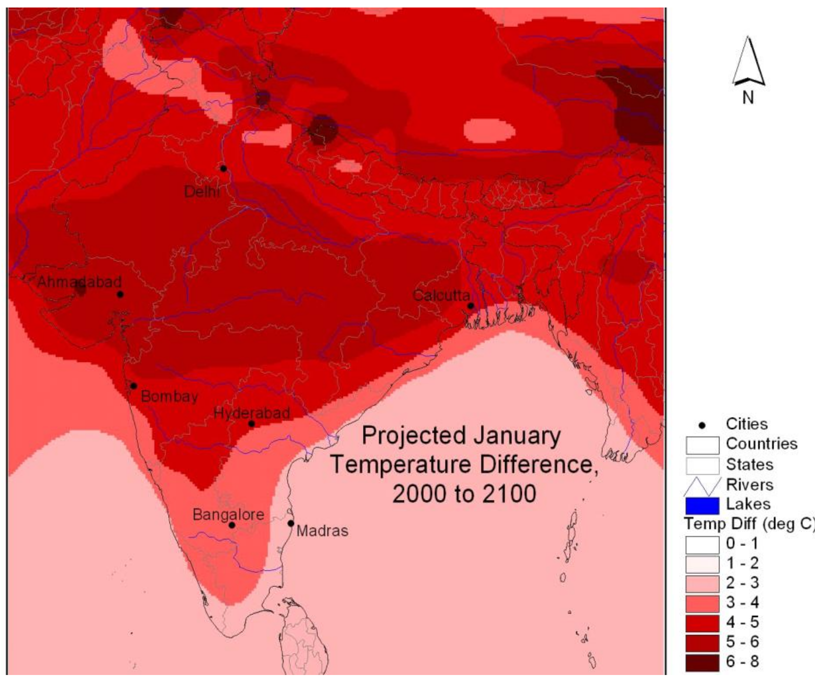

Figure 3. Projected temperature difference over India from the present to 2100 based on the A1FI scenario\\Ten-year average from 2000-2010 as subtracted from the 10 year average simulate for 2090-2100.[2]

- **Interactions between climate change and changes in solar UV radiation have pronounced effects on carbon cycling in the oceans.** In aquatic systems, the penetration depth of solar UV-B radiation is mainly controlled by the concentration and the optical properties of coloured dissolved organic matter (CDOM).[149, 174] However, CDOM is subject to UV-induced bleaching[149, 175-179], a process that occurs particularly efficiently in stratified systems.[149, 171] As a consequence of UV-induced CDOM bleaching, the penetration depth of UV-B increases and this enhances the exposure of organisms to UV-B. This may increase damage to aquatic organisms that play important roles in carbon cycling (see Aquatic ecosystems, above).[149, 180-182] Climate change causes regional increases in thermal stratification of marine systems which also reduces delivery of CDOM and nutrients from deeper water layers into the surface layer where photosynthesis occurs.[183] In addition, ocean acidification caused by increases in fossil-fuel CO_2[184] and regional decreases in mid-water O_2 (200 to 800 m deep)[183], caused in part by increased thermal stratification, interact to damage marine life that is a significant sink for atmospheric CO_2 (see Aquatic ecosystems, above).[183] These responses to solar UV-B radiation and climate change inhibit photosynthesis, and thus CO_2 uptake by the ocean.

- **Interactions between ozone depletion and climate change affecting biogeochemical cycles are particularly pronounced in the Southern Ocean.** Prevailing westerly winds in the mid-latitudes have strengthened in the past fifty years, possibly in response to warming caused by rising levels of atmospheric $CO_{2.}$[185] These changes in winds have resulted in enhanced water upwelling and thus enhanced ventilation of mid-depth CO_2 to the atmosphere.[154, 158, 185] The increased ventilation, accompanied by transport towards the equator of carbon-rich water[154] has resulted in a weakening carbon sink in the Southern Ocean. A recent modeling study[158] has further shown that the weakening carbon sink at latitudes south of 40˚S has been reinforced by increases in UV-B irradiance caused by stratospheric ozone depletion.[186] Increased UV-B has been shown to inhibit photosynthesis in this region.[180]

- **Enhanced input of dissolved organic matter (DOM) from land into aquatic systems due to climate change, coupled with UV-induced mineralization of DOM could result in enhanced release of CO_2 from aquatic systems.** Climate-related changes in continental hydrological cycles, for example, amplification of precipitation extremes[187], as well as land-use changes,[149] are likely to increase the input of organic carbon (OC) into streams and rivers[154, 188-194] and thus enhance export of OC from terrestrial to marine systems.[194-197] DOM from terrestrial systems is often recalcitrant but can be broken-down by UV-induced processes [190, 198, 199] which increases its bioavailability. Photoreactions driven by solar UV also release DOM from sediment[200] and from dead algal material.[201] The net effect of these UV-induced processes is to increase release of CO_2 from aquatic systems[198, 202] and, thus, contribute to climate change.

- **UV-B induced emission of methane from plants has been confirmed but the process appears to be of minor importance compared to other sources.** Methane is an important greenhouse gas, second only to CO_2 in greenhouse warming (excluding water vapour). Methane can be produced by plants under aerobic conditions and UV-B radiation partly drives the emissions,[203, 204] although some measurements suggest that emissions may also be the result of methane transport from the soil as water moves through the plant.[205] Current research indicates that UV-B induced methane is derived from pectic methyl groups in cell walls.[206] Processes that lead to reactive oxygen species production in plants, such as physical injury, also can lead to methane production.[207] Although methane can be produced by non-microbial light-induced pathways from plants, the quantitative role of aerobic plant methane emissions in the global methane budget is likely to be small.[205, 208]

- **UV-B radiation can influence the natural sources of aerosols involved in the Earth climate system.** Atmospheric aerosols play a major role in local air quality and the global radiation budget. Volatile organic compounds (VOCs) produced by terrestrial plants can contribute to aerosol production.[209] The effects of UV-B on these emissions appear to vary between different types of plant VOC,[210-212] but new evidence has shown that compounds produced by plants in response to UV exposure can form a major element of VOC emission and aerosol production from a desert ecosystem.[213] In marine systems, dimethylsulfide (DMS) is a major precursor of aerosols. UV-B radiation plays a major role in the cycling of DMS and related compounds both in polar[214] and temperate oceans.[215]

- **Climate-related increases emissions of halocarbons from terrestrial and aquatic ecosystems and UV-B-induced transformations of halocarbons can negatively affect atmospheric ozone concentrations.** Forests in South America are the major global source of methyl chloride (CH_3Cl) but not methyl bromide (CH_3Br),[216] while temperate woodland ecosystems are a net source of CH_3Br.[217] The Arctic tundra is a regional sink for both CH_3Br and CH_3Cl.[218] Climate change may affect halocarbon budgets from terrestrial systems through warming and decreasing soil moisture.[218, 219] Bromocarbons are ubiquitous in surface ocean waters, particularly in the tropical oceans[220], because of their release from phytoplankton.[221] Increased stratification (see above) may reduce outgassing of bromoform by limiting mixing between the surface and the subsurface layer where maximum concentrations are located.[222] Bromocarbons undergo UV-induced reactions yielding reactive radicals, e.g. bromine oxide (BrO), that participate in ozone depletion[223, 224] (see Atmospheric chemistry below). BrO has been shown to oxidize gaseous elemental mercury[225] (see bullet point below). UV radiation is also involved in iodine cycling and iodine-containing compounds are involved in ozone-depleting reactions.[226]

- **UV-B-induced processes are responsible for the formation of biologically available mercury that accumulates in the aquatic food web.** Mercury is known as a global pollutant, which is widespread in the environment, e.g. in the North Pacific Ocean.[227] In the troposphere, mercury in its elemental form (i.e., Gaseous Elemental Mercury, GEM) is transported over long distances and eventually is deposited, e.g., in Antarctic snow.[228] BrO and Br produced by UV-induced chemistry (see above) rapidly remove GEM from the atmosphere by oxidizing it.[225] In aquatic systems this oxidized mercury undergoes methylation[227] yielding methyl mercury (MeHg), which is the biologically available, and thus harmful, form of mercury that accumulates in the aquatic food web.[229, 230] Fish and other seafood are important sources of mercury in the human diet.[231]

- **UV-B plays a major role in the environmental fate of organic pollutants.** Many man-made organic chemicals accumulate in organisms and hence in food chains, including the human food chain. The environmental fate of these organic pollutants depends on many factors, and will be subject to the effects of various elements of climate change.[232] UV radiation also affects the environmental chemistry of organic pollutants such as pesticides, accelerating the rate of degradation in water, ice and snow,[233-235] both through direct and indirect photodegradation mediated by reactive oxygen species.[236] These processes may remove the original pollutant, but the degradation products may also be toxic to organisms and damaging to human health.

Tropospheric air quality, composition, and processes: Effects of solar UV radiation and interactions with climate change

- **Significant changes in the concentrations and the effects of tropospheric and stratospheric ozone are occurring in some locations and are predicted to occur in the future as a result of global climate change.** Tropospheric ozone (O_3) is the most important regional-scale air pollutant and causative agent for effects on health of humans[237] and crop production.[238] Since the mid-1980s, concentrations of tropospheric O_3 in a number of locations have increased at rates of 0.3 to 0.5 ppb/year, mostly as a result of anthropogenic activity.[238] Based on projections to 2100, concentrations of O_3 are expected to further increase in the mid-latitudes because of climate change and interactions of climate change with atmospheric chemistry. The drivers for this are a doubling of CO_2, a 50% increase in release of emissions of isoprene from plant-cover, and a doubling of emissions of soil-derived oxides of nitrogen (NOx) in conjunction with releases from human activity[239] and from the ocean.[240] Total tropospheric O_3 is projected to increase from 314 Tg in 2000 to 546 Tg in 2100. However, regional concentrations will vary. For example, climatic factors resulting in greater humidity will lead to greater rates of destruction of O_3 in the tropics but not in the mid-latitudes, which will be drier.[238] In another example, model predictions in the US have suggested that summertime ozone will decrease by up to 2 ppb with the change of climate predicted from 2000 to 2050, except over the Great Plains, where O_3 is predicted to increase slightly as a result of increasing emission of NOx from soil.[241] Climate change is predicted to negate the effect of rising global anthropogenic emissions on summertime tropospheric ozone in the eastern United States, but a 2-5 ppb increase is predicted in the western US from 2000 to 2050.[241] The effects of tropospheric O_3 will be exacerbated by an increase in the length of time that O_3 is present at concentrations that cause adverse effects and also as a result of climate change in regions such as the Mediterranean and central Europe. While this will have adverse direct effects on human health, because physiological responses to future climate change (increased dryness) will decrease uptake of O_3 by plants, effects of increases in O_3 on crop production in these regions will be mitigated. In areas with rapid warming and less drying, such as in northern latitudes, risks of ozone damage to crops have been projected to grow because of increasing hemispheric transport of pollution, leading to greater concentrations of ozone when plants are more sensitive.[238] These factors will have to be considered in future regulation of air pollutants (volatile organic compounds (VOCs), releases of natural VOCs,[242, 243] carbon monoxide (CO), and nitrogen oxides (NOx)), which, in conjunction with UV-radiation, lead to the production of O_3. Crop varieties that are tolerant to O_3 also will be increasingly needed.

The effects of climate-driven mixing of the atmosphere on concentrations of ozone in the troposphere (above) are also projected to have significant effects on stratospheric ozone and UV radiation. A model based on climate scenarios[244] suggests that the global ozone flux from the stratosphere to the troposphere will increase by 23% between 1965 and 2095 and this will have effects on UV radiation.[245] Responses will be different in the northern and southern hemispheres. The UV Index is predicted to decrease by 9% in northern high latitudes, a change that is much larger than that due to recovery of stratospheric ozone. However, the UV Index is predicted to increase by 4% in the tropics and by up to 20% in southern high latitudes in late spring and early summer. This increase at southern high latitudes is equivalent to about 50% of that caused by depletion of ozone due to the release of anthropogenic ODSs.[245] Clearly, climate change is likely to cause significant increases in UV-radiation in the southern hemisphere with implications for human health and the environment.

- **Halogens (Cl and Br) have a significant role in changing local ground-level atmospheric chemistry and concentration of ozone in the troposphere and stratosphere**. Bromoform ($CHBr_3$) is a well known source of reactive halogen with relevance to both tropospheric and stratospheric ozone, and recent studies have further highlighted the significance of oceanic sources (see the section on Biogeochemical Cycles, above).[246, 247] Studies of the atmosphere around the Dead-Sea have reported unexpectedly large ozone depleting events (up to 93% loss). The co-occurrence of significant amounts (176 pmol/mol) of bromine oxide (BrO) in the surface boundary layer are barely sufficient to explain the ozone loss.[248] A partial explanation may be provided by newly identified reaction mechanisms of halogen-containing compounds and aerosols.[249 and see below] While these studies have focused on polluted atmospheres, the particle-based reactions may also explain observations of reactive halogen species in the upper troposphere.[250] In the future, rising surface temperatures of tropical seas are expected to increase the movement of these reactive species from the troposphere to the stratosphere[251] and contribute to depletion of stratospheric ozone. Furthermore, anthropogenic emissions of halocarbons, e.g., methyl chloroform ($C_2H_3Cl_3$),[252] continue and are likely to contribute to depletion of stratospheric ozone.

- **New sources of ozone in the lower troposphere have been identified that are important for assessing human and environmental health risks.** Studies on the surface chemistry of hydrochloric acid (HCl) and oxides of nitrogen (NOx) have shown that when HCl and NOx are adsorbed on surfaces (formerly thought of as a removal mechanism), they react to generate gaseous nitrosyl chloride (ClNO) and nitryl chloride ($ClNO_2$).[249] When these absorb UV-radiation and visible radiation, they break down to form highly reactive chlorine atoms and this results in increases in the concentrations of ozone (O_3) in the troposphere. This effect is enhanced in the presence of sea salt and this route of ozone formation is more prevalent in coastal areas or in the air-shed of salt lakes. In modeling this process in the South Coast Air Basin of California, the addition of the interaction between HCl from sea salt, NOx, and solar radiation increased concentrations of O_3 by 40 ppb (20%) at peak periods. Knowledge of this new mechanism of formation of O_3 and how it interacts with changes in UV-B radiation will be important for more accurately predicting health risks to humans and the environment from tropospheric ozone in the future.

- **New studies have better characterized global transport of the precursors for tropospheric ozone that can enable mitigation of these pollutants.** Several studies based on models and/or measurements suggest that local sources of precursors are the major contributors to concentrations of O_3 in the troposphere[253-255] and that transport from distant locations over oceans contribute only small amounts to local regional concentrations. Because of regulation of pollutants, reductions in the local concentrations of precursors to O_3 of 20% are predicted to result in decreased tropospheric O_3 by about 1.5 ppb in the summer months. In contrast, the contribution of the same reduction in transoceanic releases of precursors to O_3 results in local reductions in concentrations of O_3 of only 0.3 to 0.4 ppb. These observations emphasize the importance of local regulation of air pollutants for the protection of humans and environmental health from the effects of O_3. In the Mediterranean, there is some contribution of O_3 from downward transport of stratospheric air masses, via stratospheric-tropospheric exchange (STE) and from removal processes “catalyzed” by mineral dust, for example, from the Sahara.[253] These changes may be widespread at latitudes where folding of the tropopause occurs but have only been observed in the Mediterranean so far.

- **Substitutes for ozone-depleting fumigants may contribute to global climate change.** Sulfuryl fluoride (SO_2F_2) is an industrial chemical released into the atmosphere in significant quantities (kilotonne(kt)/year). Sulfuryl fluoride has been suggested as a substitute for methyl bromide in fumigation of crops and soils.[256] Global production in 2006 and 2007 was 3.5 and 2.3 kt, respectively, but has increased steadily since 1960 when it was 57 t and will likely increase into the future, especially if used more widely. Estimates of atmospheric lifetimes are >300, >5000, and >10^7 years for removal processes driven by OH, Cl, and O_3, respectively.[256] However, the large uncertainty in the atmospheric lifetime of SO_2F_2 leads to significant doubt as to its final contribution to global warming potential (GWP). Based on uncertain data, the GWP for SO_2F_2 (i.e., its warming potential relative to CO_2) is estimated to range from 120-7600 for a 100 year time horizon.[256] Although SO_2F_2 is relatively soluble in water,[257] the significance of other potential removal processes such as partitioning to cloud water (followed by deposition) is not known. The rate of hydrolysis in water with pH similar to cloud water (5.9) is small (2.6×10^{-6} s^{-1})[257] which is consistent with lack of observed hydrolysis in the atmosphere.[258] However, the rate under alkaline conditions (pH 8.3) is 100 times faster, suggesting that it will not accumulate in surface waters, except in areas where pH is low and there is no loss of water, except through evaporation.

- **Interactions between climate-change, increases in the velocity of winds over the ocean, and aerosol formation can lead to reductions in transfer of solar energy to the oceans. A better understanding of this process will improve predictions of the effects of climate change on the oceans.** Measurements at Mace Head in Ireland have demonstrated a strong relationship between wind speed and aerosol optical depth (AOD) of the atmosphere with implications for future climate change. [259] The AOD was dependent on velocity of wind at four wavelengths from IR-A to UV-A (862 to 368 nm). The authors point out that, under moderate-to-high wind velocities (up to 18 m/s) the AOD from sea-spray (0.3-0.4) can equal or exceed that associated with pollution plumes over oceanic regions. This will reduce inputs of energy from solar absorption into the ocean and can potentially influence the radiative (including UV), dynamical, and biogeochemical feedback processes[260] associated with future climate change when greater wind velocities are predicted. The increase in AOD above the oceans will reduce the impacts of UV-B radiation in those regions where wind velocities are increased, thus mitigating the effects of ozone depletion in the stratosphere.

- **Increases in the release of nitrogen oxides from anthropogenic activity will slow the recovery of stratospheric ozone.** Nitrous oxide (N_2O), which is increasingly released into the atmosphere from human activities such as agriculture and industry, has significant potential for depletion of stratospheric ozone (ODP).[261] Of the total annual emission of N_2O (17.7 Tg as nitrogen) during the 1990s, 6.7 Tg N (6.7 million metric tonnes) is estimated to be anthropogenic. If these emissions continue to increase, by 2050 they are predicted to represent an ODP-weighted emission in excess of 30% of the peak ODP-weighted emissions of CFC of 1987. N_2O could become the major single substance contributing to ozone depletion, with this depletion occurring primarily in tropical and mid-latitude regions.[261] The effect of N_2O on ozone depletion means that the impacts of the latter could be present for much longer than previously predicted. As N_2O is a greenhouse gas, reductions of emissions will have a double benefit for protection of stratospheric ozone as well as mitigating global climate change.

- **There is no new evidence to suggest that trifluoroacetic acid (TFA), a breakdown product of HCFCs and HFCs, will have adverse effects on humans or the environment.** As has been discussed previously,[262] several of the HCFCs and HFCs, used as substitutes for ozone-depleting CFCs, can break down into TFA. The final environmental sink for TFA is in the oceans and landlocked lakes. Concentrations of TFA in rainwater range from <0.5 to 350 ng/L, depending on location and proximity to human activity[263] and this source is predominantly anthropogenic. As TFA is very stable and very water soluble, it accumulates in the oceans where concentrations, largely from natural sources are ≈ 200 ng/L.[264] Based on historical production of HFCs and HCFCs as potential sources of TFA as well as projections of future uses, a worst-case estimate of release of TFA from complete conversion of HFCs and HCFCs yielded a global increase of 22,000 kt of TFA by the time of planned phase-out of the HFCs and HCFCs. Eventually, this would result in an increase in concentration of TFA in the oceans by about 0.016 ng/L, a *de minimis* increase above the background concentration.[262]

  Because of high water solubility, low octanol-water (K_{OW}), and octanol-air (K_{OA}) partition coefficients, TFA does not accumulate in aquatic or terrestrial organisms and does not bioaccumulate in food chains. No adverse effects of TFA in mammals or humans were revealed in a recent search of the literature (August, 2009). Concentrations causing measurable effects in organisms in the environment are large (222,000 to 10,000,000 ng/L)[265, 266] and provide a more than 1000-fold margin of safety for worst-case scenarios. Projected future increased loadings to land-locked lakes and to the oceans (via fresh water) due to climate change and continued use of HCFCs and HFCs,[262] are still judged to present negligible risks for aquatic organisms and humans.

Materials: Effects of solar UV radiation and interactions with climate change

- **Penetration of solar radiation into wood is wavelength-dependent and correlates with the degradation depth profile.** A positive correlation between the depth of penetration of radiation into wood and the wavelength of the incident radiation in the range 246-496 nm was reported. While UV-B is more damaging than the longer wavelengths it is also attenuated more by the surface layers of wood. Because of this tradeoff, wavelengths around 400 nm that penetrate further into the bulk of the wood were found to be the most effective in causing photodamage in the wood.[267]Results suggest that penetration profiles need to be taken into account when quantifying the photodegradation of wood in laboratory studies[268] and especially where lasers are used as the light source to accelerate the degradation process.

- **The effectiveness of clear polyurethane coatings in controlling the UV-B-induced yellowing discoloration of wood has been demonstrated.** The lignin component in wood absorbs UV-B causing light-induced damage to the surface of wood exposed to solar radiation, as confirmed by recent studies.[269, 270] Using protective polyurethane (PU), clear coats based on either an aliphatic or an aromatic chemical structure can reduce such damage. Discoloration of clear-coated wood may be caused by the yellowing of both clear coating itself and underlying wood. While the aliphatic PU coatings increased UV-B transmission upon aging of the coating, allowing damage of the wood, the aromatic PU coatings were demonstrated to be much more effective in protecting the wood from UV-B damage.[271]

- **Estimates of light-induced damage deduced from accelerated photodegradation techniques in the laboratory may not be applicable to all types of plastics.** Using higher intensities of simulated solar radiation in damage assessment is a common strategy in accelerated laboratory studies on photodegradation of materials. Studies of photodamage on polycarbonate plastic and its blends with several other plastics showed that they obeyed the reciprocity rule, while others such as acrylonitrile butadiene styrene (ABS) and styrene acrylonitrile (SAN) plastics did not.[272] The reported action spectra and damage estimates for the latter plastics generated using accelerated techniques may therefore need to be reassessed.

- **Surface modification with appropriate coating chemistry shows promise in controlling photodegradation of plastic materials.** Novel approaches and improvements in existing surface treatments show promise in reducing damage from solar UV-B to several common polymers. The use of hybrid organic-inorganic polymers (ceramers) as a surface coating was shown to impart light stability as well as enhance surface hardness in polycarbonates.[273] Titanium dioxide (TiO_2) can similarly be used as a photostabilizer. However, depending on its crystalline structure, TiO_2 can either enhance or retard the photoxidation of polymers.[274] The surface treatment of polyethylene with TiO_2 nanoparticles was reported to enhance the photodegradation of polyethylene.[275]

- **New techniques for quantifying surface damage to materials that have undergone light-induced degradation have been developed.** Atomic force microscopy (AFM) has been used for the first time to characterize the photodamaged surface of wood.[276] This technique, used for studying surface deterioration at nanometer (nm) scale resolution, also has been recently employed to assess polymer photodamage.[277, 278] A novel, very low-angle slicing technique was used for the first time in depth profiling of photoxidation in polyethylene and polypropylene,[279] allowing better quantification of depth-dependent degradation. The use of these novel techniques contribute to a better understanding of photodamage and its quantification[280] and can help in the design of UV-B stabilizers.

- **Mixing existing light stabilizers with azo-type pigments was shown to improve the effectiveness of the stabilizers.** Synergism in light stabilization by mixtures of monoazo pigments with commonly used hindered amine type light stabilizers (HALS) was reported for polypropylene (PP) films exposed to UV-B radiation in the laboratory.[281] Based on retention of mechanical integrity, improvements in lifetimes in excess of 600% were reported when using the synergistic mixture compared to the HALS alone. Better light-stabilizers allow the service lifetimes of materials to be maintained or improved, despite increased solar UV-B levels.

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