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Environmental Effects of Ozone Depletion and its Interactions with Climate Change

Progress Report, 2015

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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 two focal issues. The first focus is the effects of increased UV radiation on human health, animals, plants, biogeochemistry, air quality, and materials. The second focus is on interactions between UV radiation and global climate change and how these may affect humans and the environment.

When considering the effects of climate change, it has become clear that processes resulting in changes in stratospheric ozone are more complex than previously believed. 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 as a series of seven papers in 2015 (*Photochem. Photobiol. Sci.*, 2015, **14**, 1-184). In the years in between, the EEAP produces less detailed and shorter Progress Reports, which highlight and assess the significance of developments in key areas of importance to the Parties. The present Progress Report for 2015 is a short report. A full Quadrennial Assessment, more detailed in terms of technical information, will be made available in 2018.

The 2015 Progress Report highlights the interactive nature of the effects of UV radiation, atmospheric processes, and climate change.

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Dedication

This report is dedicated to the memory of Dr David J. Erickson III (May 20, 1960 to November 16, 2015) member of the EEAP Panel since 1994 and contributor to Chapter 5 (Biogeochemical cycles). He was a scientist, a colleague, and a friend to all the members of the Panel. His expertise and knowledge of issues related to climate change and the effects of UV radiation on chemical processes in the environment will be sorely missed.

We will remember Dave for his colourful, larger than life, and humorous character - full of spirit and courage.

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

1.1

By 2013, the implementation of the Montreal Protocol had already achieved significant benefits for the ozone layer and, consequently, for surface UV-B radiation. Model calculations have shown that, without the Montreal Protocol, a deep Arctic "ozone hole", with total ozone values below 120 DU, would have occurred in 2011 given the meteorological conditions in that year (Figure 1). The decline of stratospheric ozone over the Northern Hemisphere mid-latitudes would have continued, more than doubling to about 15% by 2013 relative to the onset of ozone-depletion.

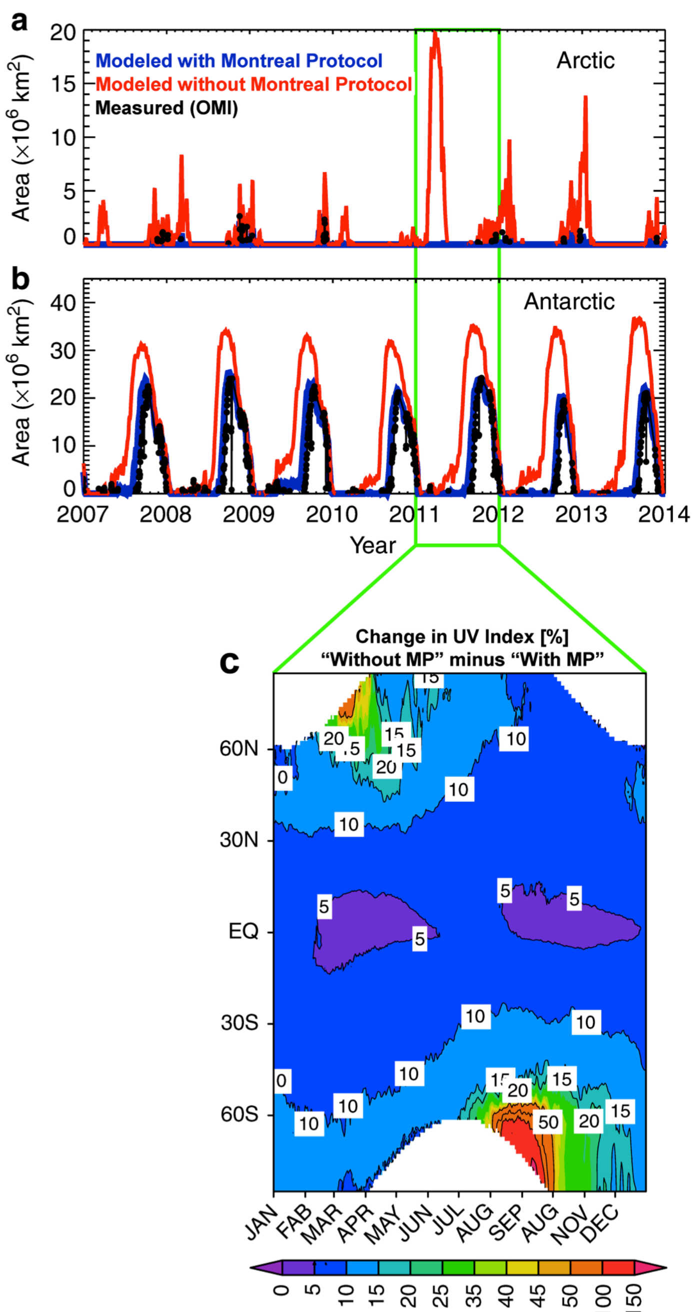

Figure 1. **(a)** Without the Montreal Protocol (MP), there would have been a deep ozone 'hole' (with calculated ozone less than 120 Dobson Units (DU) in the Arctic in 2011, of comparable area to that in Antarctica in recent years. These Arctic ozone depletions would have recurred in future years. The area of the Antarctic ozone hole would also have continued to increase. The area of the ozone hole is defined as the area with column ozone of 220 DU.
(b) The observed area of the Antarctic ozone hole from 2007 to 2014 estimated from Ozone Monitoring Instrument (OMI) data (black symbols), and calculated from model runs including the MP (blue) and without the MP (red). For the Arctic, no ozone hole has been observed during this period.
(c) The percentage difference in daily zonal mean ultraviolet index at local noon between model runs without and including the MP. (Adapted from Chipperfield et al., Nature Communications, 6 (2015)).

In addition, the Antarctic ozone hole would have been 40% larger in 2013 relative to what was observed, with enhanced loss of ozone also at sub-polar latitudes of the Southern Hemisphere.[68] These large reductions in ozone would have resulted in springtime increases in UV-B radiation at the Earth's surface of about 10% at mid-latitudes and over 20% at high latitudes of both hemispheres. For the implications of these changes for human health, see section 2 below.

1.2 **Measurements at several sites over the last decade have shown decreases in surface UV-B radiation that are consistent with observed increases in total ozone.** However, at some sites, changes in aerosols, clouds and, at high latitudes, sea ice were the main drivers of changes in UV-B radiation. Between 1990 and 2011, changes in UV-B irradiance ranging between +0.4 and -8% per decade were found at four northern high-latitude locations (59°–71° N) in agreement with opposite trends in total ozone.[103] In contrast, UV irradiance at 325 nm, aerosol optical depth and cloud fraction did not have significant long-term trends. No significant trends in UV irradiance were found for the three southern high-latitude locations considered in this study.

Particularly in urban areas, effects of aerosols can mask changes in UV-B radiation that arise from changes in ozone. Despite increasing total ozone over the 1991 to 2013 period, erythemally weighted irradiance at Uccle, Belgium, had increased by 7% per decade due to a combination of decreasing amounts of aerosol and cloud, which more than counteracted the effect of ozone.[87] Statistical analysis showed that trends in UV-B irradiance and total ozone changed in the late 1990s, consistent with the recovery of stratospheric ozone starting at about the same time.

UV radiation for the period 1950–2011 was reconstructed from a variety of proxy data for nine locations in Spain. Erythemal irradiance increased between 1950 and 2011 by about 13%, of which half was due to decreases in ozone. Between 1985 and 2011, an increase of about 6% was calculated, mostly due to decreasing amounts of aerosols and clouds.[285] The day-to-day variability of noon-time clear-sky UV Index at Thessaloniki, Greece, was found to be influenced more by aerosols than total ozone, even for extreme total ozone events.[117]

Reflectivity data from several satellites between 1979 and 2012 suggest that decreases in sea-ice and small increases in the amount of clouds over the region of the Southern Ocean around the Antarctic Peninsula have resulted in decreases in UV-B radiation at the surface.[40, 84]

1.3 **New measurements have confirmed high levels of UV radiation at low-latitude and high-altitude locations.** Extreme large values of the UV Index (peaking at >20) have been measured at four sites of the Tibetan Plateau. These large values are due to high elevation (3,600–4,500 m), low latitude (29–31°N) resulting in small solar zenith angles, and low total ozone.[246] In Kampala, Uganda (0.3°N, elevation 1,200 m), UV Index values of more than 17 were measured on several occasions between 2005 and 2015,[243] while in La Paz, Bolivia (6.5°S, elevation 3420 m), up to 70% of the measurements in 2008-2012 exceeded UV Index values of 10.[381]

1.4 **New studies have improved understanding of the effects of clouds on UV radiation and the physical mechanisms of the processes involved.** The weak wavelength-dependence of the cloud optical depth predicted through theoretical calculations was confirmed with measurements. Data of erythemal and total solar irradiance recorded at Valencia, Spain, indicate that the difference in the cloud optical depth derived from these measurements is smaller than 2%.[300] The effective albedo caused by clouds below a mountain summit was quantified using measured and modeled UV irradiance data from the Izaña observatory (28°N, 2,400 m above sea level).[129] The largest observed effective albedo value in the UV was 0.58 (i.e., 58% of incident radiation is reflected upwards). More typical values range between 0.2 and 0.5 and are about 10 times larger than the local surface albedo (0.02–0.05). Measurements combined with radiative transfer modeling confirmed theoretical predictions that clouds composed of small water droplets attenuate UV radiation more efficiently than clouds composed of large droplets, for the same liquid water content.[228] The magnitude of this effect depends on solar zenith angle and liquid water content.

1.5 **Surface UV radiation may have been affected by changes in the amount and optical properties of anthropogenic aerosols, which have been observed at multiple sites worldwide since the year 2000.** However, at most sites, no UV radiation data are available to assess these effects quantitatively. Aerosol data from the AERONET network revealed decreases in the amount and absorption efficiency of aerosols (quantified by the single scattering albedo) at most stations since 2000.[13, 203, 227, 264] These changes were caused by decreases in air-pollution and should have led to increases in surface UV radiation. In contrast, aerosol amounts at many locations in China remain high (aerosol optical depth at 440 nm ranged between 0.3 and 1.0 and have exceeded 5 during extreme events in some locations) with no significant trend since 2002.[65] Measurements at six stations in the USA in 1995-2010 indicated no trend in direct irradiance but a positive trend in diffuse irradiance. This was attributed to an increase in the size of aerosols, possibly due to increased aircraft traffic.[125]

1.6 **Increasing frequency and extent of wildfires due to climate change become important sources of aerosols with significant effects on surface UV radiation.** Wildfires across the globe emit black carbon (BC) and organic carbon (OC) smoke particles that can persist in the atmosphere for days to weeks. Inclusion of emissions from fires in climate models increased the predicted global mean annual aerosol optical depth at visible wavelengths by 10%.[336] Modeling studies[320, 380] projected that climate change will increase summertime concentrations of OC aerosol over the western USA by 40-70% and concentrations of BC aerosol by 20-27% in 2050, relative to the present. Most of this increase (75% for OC and 95% for BC) is caused by larger emissions from wildfires with the remainder by changes in meteorological conditions. Such increases in carbonaceous aerosols would lead to significant reductions in UV radiation at the Earth's surface. A recent study has shown that wildfires in Russia in 2010 caused reductions of up to 50% in the daytime averaged photolysis rates of NO_2 and O_3, (driven by UV radiation) along the aerosol plume transport.[258]

1.7 **Over the Arctic and northern high latitudes, surface UV-B radiation is projected to decrease during the 21st century due to the recovery of total ozone, increases in cloud cover, and reduction of surface reflectivity caused by the shrinking of sea-ice and snow cover.** Relative to the present, the greatest reductions in surface UV-B radiation (280-315 nm) over land are projected for April under all skies, locally reaching about 30% for the noon UV Index and about 50% for the noon effective dose for the production of vitamin D.[75, 115] For mid latitudes, the UV Index is projected to show a decrease from 1975 to 2100 by about 5% in the Northern Hemisphere and by about 10% in the Southern Hemisphere, with about equal contribution from projected increases in stratospheric ozone, and cloud cover.[100]

1.8 **In the Arctic region, the processes that led to the sporadic large losses of stratospheric ozone observed in recent years are still unclear.** A recent study[278] suggests that these losses have not been caused by increasing greenhouse gases. This was concluded from the analysis of long-term changes in the volume of polar stratospheric clouds derived from measurements in 1979–2011 and model simulations for the 21st century. However, loss of Arctic sea ice may lead to changes in the circulation patterns over the polar region, which could ultimately lead to substantial reductions of polar ozone in March and April, delaying the ozone recovery by up to 12 years.[324]

1.9 **Depletion of Antarctic ozone has influenced the climate in the Southern Hemisphere but there is still no consensus that the ozone hole has caused the recently-observed increasing extent of Antarctic sea ice.** Ozone depletion in the late 20th century has likely driven the observed changes in circulation, temperature and salinity of the Southern Ocean.[316] Long-term records of data show that changes in circulation due to the ozone hole are contributing to a decrease in summer temperatures over southeast and south-central Australia, and inland areas of the southern tip of Africa.[29] In the decades since the appearance of the ozone hole, anomalously high and low total ozone in the spring have been significantly correlated with hotter and colder than normal summers, respectively, over large regions of the Southern Hemisphere, and in particular over Australia.

Increases in extent of sea ice leads to increased UV-B radiation above the surface, but to decreased radiation penetrating the water under the ice. Potential influences of the Antarctic ozone depletion on sea ice are complex and not well understood. Two processes of different time scales have been proposed:[111] In the short-term (a few years to a few decades depending on the model), changes in ocean circulation cool the sea surface around Antarctica leading to seasonal expansion of the sea ice, but also to upwelling of warm waters in the region of the seasonal sea ice. This leads to an annual expansion and retreat of sea ice. In the long-term (multiple decades), the effect resulting from upwelling of warm water will dominate, slowly leading to warming of the ocean and ultimately to an overall reduction of sea ice. Based on results of an improved model it has been argued[316] that the cooling due to ozone depletion is weak, does not occur in the month of maximum sea ice extent, and is overwhelmed by the warming due to increases in greenhouse gases.

1.10 **El Niño may indirectly influence UV-B radiation.** Measurements and model simulations for China suggest that decreases in total ozone during El Niño events lead to increases in clear-sky erythemal irradiance.[385] Increases due to El Niño events of up to 6% have been calculated for the middle and lower reaches of the Yangtze River in winter and up to 10% for the northwestern Tibetan Plateau during spring. Changes in cloud patterns associated with these events could also be important for modulation of UV radiation.

1.11 **High quality measurements are necessary to detect and quantify changes in surface UV radiation caused by ozone depletion and, eventually, by ozone recovery.** Array spectrographs are increasingly being used for monitoring spectral UV irradiance; however, their accuracy is limited by their inherent instrumental characteristics. A recent study confirmed that measurement errors caused by stray light limit the useful spectral range of these instruments to wavelengths longer than about 305 nm, in particular for small solar elevations.[134] Bearing in mind these limitations and the increased uncertainty of data in the UV-B range due to stray light, the usefulness of these instruments is mainly in monitoring the spectrum of radiation in situations when the radiation field changes rapidly (e.g., in partly cloudy conditions or under tree canopies).

1.12 **Instruments on satellites can provide reliable estimates of surface UV doses under low-aerosol and clear-sky conditions, but these estimates may be affected by large systematic biases over polluted areas, overcast skies, or snow-covered surfaces.** UV Index data of the Ozone Monitoring Instrument (OMI) were validated with ground-based measurements with a NILU-UV multifilter radiometer near New York.[107] For clear-sky conditions, data agree well (within 2%), while the OMI bias increases greatly with optical depth of clouds, reaching -24% on average for overcast conditions.

OMI UV data were also compared with ground-based measurements at 13 stations located in the Arctic and Scandinavia from 60° to 83° N.[43] When the surface albedo is known, OMI data typically exceed ground-based measurements by 0–11 %. Otherwise biases are much larger; ranging between +55%, when the albedo assumed by OMI is too high, to -59% when it is too low. These large negative biases are observed when reflections from snow and ice, which ultimately increase downwelling UV irradiance, are misinterpreted as reflections from clouds.

By combining satellite data on ozone from GOME-2 and clouds from AVHRR/3, an improved algorithm was developed to estimate surface UV radiation.[197] New global datasets of erythemal dose were constructed from OMI measurements for large-scale ecological studies. These data are provided at 0.25° spatial resolution (about 25 km at the equator).[40]

1.13 **Personal UV dosimeters are useful to estimate exposure to UV radiation and to quantify related effects, such as status of vitamin D and damage from UV radiation to skin.** While electronic UV dosimeters are more expensive and can be more difficult to use than traditional dosimeters (e.g., spore-[302] or polysulfone-dosimeters,[307]) they have several advantages: firstly, electronic dosimeters can be tuned to more closely match the biological weighting of interest than is the case for polysulfone dosimeters, for which differences between their response function and action spectrum of interest are large.[63] Secondly, even if there are differences between the instrument response and the target weighting, the latter can still be derived from the measurements using radiative transfer models that include ozone and solar zenith angle (SZA) as inputs. This is generally not possible for the older dosimeters because of their long integration periods that include a wide range of SZA.[301] Thirdly, the time series of data from the electronic dosimeters can assist in quality assurance and in verifying compliance of the users to the measurement protocols. For example, if the dosimeter is not actually worn, but left stationary, that will be obvious from the data record. Finally, because of their more linear response, calibration accuracy will generally be better in the reusable electronic devices, compared with polysulfone dosimeters, which have variable non-linear responses (e.g.[63]).

Further research has confirmed that UV irradiance on a horizontal surface (e.g., the UV Index) is not a good indicator of personal exposure. To more realistically model personal exposure, information on the directional distribution of radiation (radiance) would be preferable instead of the more commonly available irradiance data. However, such measurements are not widely available.[299]

UV dosimeters have recently been used to measure exposure to UV radiation of members of an Antarctic expedition,[288] high school students in Switzerland,[142] seafarers working on decks of vessels,[109] skiers,[64] tennis players,[301] hikers,[301] and runners.[248, 301] Amongst others, it was found that the Swiss students were exposed to 1.7% of the ambient UV irradiance during school days, while 85% of the cumulative UV dose was obtained on weekends and holidays. Skiers in Italy received 65% of the ambient dose on average, as measured by polysulphone detectors. Median daily UV exposure of hikers and tennis players typically exceeded 5 standard erythemal doses (SED), according to one study, but maximum exposures can be much higher.

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

2.1 Risky behaviour regarding sun exposure remains very common among fair-skinned populations, putting them at increased risk of skin cancer and other adverse effects of sun exposure.

Risky behaviour regarding sun exposure remains very common among fair-skinned populations, putting them at increased risk of skin cancer and other adverse effects of sun exposure. In the 2010 US National Health Interview Survey, 37% of adults reported sunburn on at least one occasion in the previous year.[163] Sunburn was particularly common in young adults (18-29 years, 52%), and in individuals with fair skin (44%). Amongst those reporting sunburn in the previous year, 12% had 4 or more sunburns. In a nationally representative sample of adolescents in the USA, self-reported use of sunscreen declined from 68% in 2001 to 56% in 2011.[34] In France, 78% of respondents in a telephone interview reported deliberate sun exposure and 38% did not use sufficient sun protection.[295] In one study, the eyes were the least likely part of the body to be protected from sun exposure.[127] East Asian immigrants to western countries typically have comparatively low sun exposure, but this increases as they become integrated into the culture of the host country.[144] This change in behaviour is beneficial for vitamin D status, but may be associated with an increased risk of skin cancers. In a cross-sectional study of 386 university students in north China, over 90% were aware that exposure to UV radiation caused skin cancer and sunburn, while only 28% were aware of effects on the risk of developing cataract and 3% on risk of pterygium (a growth on the surface of the eye, usually on the side closest to the nose, that may cover the cornea and impair vision).[127]

2.2 The incidence of cutaneous melanoma continues to increase globally, but, in many countries, mortality may have peaked. Exposure to solar UV radiation is the most important cause. A personal or family history of cutaneous melanoma (CM) does not reduce risky sun behaviour. Ongoing exposure of CMs to UV radiation may promote metastasis. The incidence of CM is highest in fair-skinned populations and has risen considerably in recent decades. For example, the age-standardised incidence rate of CM per 100,000 persons in the UK was 17.4 for 2009-2011, an increase of 57% in men and 39% in women respectively, compared to 2000-2002.[60] The age-standardised incidence rate increased from 26.7 in 1982 to 48.8 in 2010 in Australia[17] and doubled from 1982 to 2011 in the USA.[145] A further doubling in incidence by 2030 is predicted for the USA.[145] The incidence of CM increases with increasing age.[60, 145] The incidence rates in children and young adults have decreased over the last ten years in countries, such as Australia, which have had several decades of strong public health programs promoting sun protection, but rates continue to increase in other countries.[11, 105, 145, 173, 314, 349] High-dose sun exposure at any time during life increases the risk of CM, but exposure occurring in childhood years, and associated with the development of nevi, may be particularly important.[141]

Age-standardised mortality rates due to CM have stabilised in some countries, probably due to a combination of earlier detection, improvements in treatment and reductions in risky behaviour regarding the sun in younger cohorts who have grown up with strong sun protection programs. For example, in the USA the mortality rate was 2.7 per 100,000 persons in 2011, the same as in 1982.[145] In Australia, mortality has been stable at around 6.0 per 100,000 from 2004 to 2012.[17] In fair-skinned individuals globally, time trends in annual mortality rates for CM from 1955 to 2010 were closely related to the year of birth (age-cohort) with change in overall rates reflecting a downturn in mortality in younger age groups.[19] The peak years for CM mortality were for those born in 1936-1940 in Oceania, 1937-43 in North America, 1945-53 in the UK and Ireland and 1957 in Central Europe.

One study showed that, following a diagnosis of CM, patients in Denmark still expose themselves to high levels of solar UV radiation without using personal protection, particularly when on holiday.[174] Similarly, children of people who have survived CM had higher levels of sun exposure and sunburn than average-risk populations in a study from California.[135] Contrary to a previous report,[44] higher levels of sun exposure prior to diagnosis of CM were not associated with reduction in subsequent mortality[185] when examined with a rigorous study design focused on this specific question. Furthermore, in a mouse model, repetitive exposure of primary CMs to UV radiation promoted spread to blood vessels and metastasis to the lung.[24]

2.3 **The incidence of non-melanoma skin cancers continues to increase, primarily in fair-skinned populations. Changes in patterns of sun exposure over time are resulting in a more rapid increase in the incidence of basal cell carcinoma (BCC) compared to that of squamous cell carcinoma (SCC).** In the USA there was a 14% increase in the age-adjusted rate of procedures (a proxy for incidence) for non-melanoma skin cancers (NMSC) between 2006 and 2012.[283] Extrapolating to the US population, the estimated total number of NMSCs was almost 5.5 million in 2012, with approximately 3.3 million people treated. Patterns of sun exposure have changed over time, with increased intermittent recreational exposure, most frequently occurring in locations with high ambient levels of UV radiation. As a consequence, the incidence of BCC is increasing at a faster rate than that of SCC in younger people.[89, 234] Sun protection programs that have been shown to be effective in lowering the incidence of NMSC should have a particular focus on leisure-time sun exposure in young people.

A study in South Africa showed that the mean age-standardised annual incidences (per 100,000 people, figures are female, ***male*** incidence) of BCC, SCC and CM in 2000-2004 were highest in groups classified in the study as white (BCC: 113, ***198***; SCC: 32, ***70***; CM: 17, ***21***), followed by the coloured (BCC: 27, ***59***; SCC: 15, ***26***; CM: 4, ***6***), Asian (BCC: 5, ***8***; SCC: 3, ***4***; CM: 1, ***1***) and then black (BCC: 2, ***3***; SCC: 2, ***3***; CM: 1, ***1***) population groups.[247] SCC and BCC were most commonly found on the head.

A recent review of studies quantifying the direct costs of NMSC to health care systems found that these costs were highest for the USA (nearly 600 million € annually) followed by Australia (around 350 million € annually), although after adjustment for population, costs were greatest for Australia, followed by New Zealand, Sweden and Denmark.[140] Skin cancer prevention initiatives were shown to be highly cost-effective and possibly cost-saving.

2.4 **Both UV-A and UV-B radiation can lead to the formation of skin cancer.** While UV-B irradiation is well known to cause DNA damage, UV-A (315-400 nm) irradiation also causes cellular damage through the generation of reactive oxygen species, as well as causing immunosuppression. There is increasing evidence to suggest that UV-A irradiation can also cause the production of thymine dimers in DNA of basal keratinocytes and influence gene expression.[225] UV-A radiation may be implicated in the development of both CM and NMSC through its role in inhibition of nucleotide excision repair.[104]

2.5 **Several eye diseases, including cancers of the eyelid and the surface of the eye, cortical cataract and pterygium, are strongly related to exposure to UV radiation. The evidence is less clear for other diseases of the eye, such as nuclear and posterior subcapsular cataract, ocular melanoma and age-related macular degeneration.** Exposure to UV radiation causes cancers of the eyelids, principally BCC.[187] The causative role of exposure to UV radiation in ocular squamous neoplasia may involve a combination of DNA damage, local and systemic immunosuppression, and reactivation of latent viruses.[133] Specific genetic and epigenetic changes in genes involved in oxidative stress may increase susceptibility to UV radiation-induced development of cortical cataracts.[321, 353] In China, there was an increase in disability-adjusted life years (DALYs) for cataract of 92 per 100,000 people for every 1000 J/m^2 increase in ambient erythemal UV radiation estimated from satellite data.[388] For the population aged ≥75 years this figure increased to 1,342 DALYs per 100,000 people.

The risk of exfoliation syndrome (an age-related disease that is the most common identifiable cause of glaucoma) increased with greater time outdoors and a history of work over water or snow, and reduced with the use of sunglasses in a clinic-based case-control study in the USA and Israel.[254] Blue light, rather than UV radiation, may play a previously-unacknowledged role in the pathogenesis of uveal melanoma,[216] as well as age-related macular degeneration.[371]

2.6 Less time outdoors appears to be a major risk factor for the development of myopia, but whether this is an effect of UV radiation is not clear. In a birth cohort study, myopia (defined as a mean refractive error of both eyes ≤-0.5 diopters) in young Australian adults was significantly less common in participants with objective evidence of greater sun damage to the eye (measured as the area of conjunctival autofluorescence),[231] and was significantly more common in individuals with vitamin D deficiency.[375] These findings support the hypothesis that outdoor light exposure may be protective against myopia, with the relevant wavelengths, or the role of UV radiation, not yet determined.

2.7 Exposure to solar UV radiation can alter the immune response to a variety of microorganisms in animal studies, and recent reports support a similar role in humans. The risk of recurrence of infection with herpes simplex virus in the eye was increased three-fold in people in North Carolina who had the highest outdoor exposure (8 hours or more per week outdoors when the UV Index was ≥4) compared with those having the least outdoors exposure (7 hours or fewer outdoors when the UV Index was <4).[220] In studies in Korea[183] and Taiwan,[365] the occurrence of shingles, caused by the reactivation of herpes zoster (chicken-pox) virus, was more common in the sunny months than in the winter, possibly due to the immunosuppression induced by exposure to higher levels of solar UV radiation.

In a systematic review of 24 randomised trials, the effectiveness of the BCG vaccine against tuberculosis (TB) decreased with closer proximity to the Equator and increasing levels of UV radiation, possibly due to UV-induced suppression of the immune response to the vaccination.[224] Furthermore, in a study over 28 years in Birmingham, UK, there was strong evidence for seasonality of TB, with notifications being 24% higher in the summer than in the winter.[192] The lesions of dermal leishmaniasis (a parasitic infection spread by sandflies) that can arise after an apparent cure from visceral leishmaniasis, appear on sun-exposed areas of the body.[240] Exposure to solar UV radiation is thought to play a key role, acting by suppressing immune responses in the skin at the exposed body sites.

A study in the USA found a significant positive correlation between average annual levels of UV radiation for each State and the incidence of oral and pharyngeal cancer in people with fair skin, but not in those with deeply pigmented skin.[136] There was also a positive correlation between levels of UV radiation and incidence of cervical cancer in white women. Human papilloma virus (HPV) is commonly found in each of these cancers; the variation in incidence in relation to levels of UV radiation suggests that exposure to solar UV radiation may induce the production of soluble mediators that promote HPV-associated tumorigenesis at non-exposed body sites.

2.8 **Despite much research into a wide range of disease outcomes, the role of vitamin D in human health, beyond its importance for calcium homeostasis and maintenance of bone, has not been confirmed.[18]** Recent reviews[160, 251] show that vitamin D deficiency (concentration of 25-hydroxyvitamin D [25(OH)D] in serum or plasma of less than 50 nmol/L) is common worldwide, although the use of different assays for which accuracy is not assured makes it difficult to fully assess the magnitude of the problem. One study showed high prevalence of vitamin D deficiency in young children in Iran that was the result of high levels of air pollution, leading to low levels of exposure to UV radiation.[189] New work is providing greater guidance on how much sun exposure is required for the avoidance of vitamin D deficiency, including in people with different skin types.[355] In Australia, a program of sun exposure led to increased 25(OH)D levels in older people in residential care but was only effective when started in spring or autumn, and some individuals did not achieve vitamin D sufficiency.[99]

Many observational studies show that low serum 25(OH)D concentrations are associated with increased risk, progression, severity and mortality for many disorders, including cancers,[330] autoimmune diseases such as lupus,[83, 374] inflammatory bowel disease[217] and multiple sclerosis,[12] poor cognitive function,[182] attention deficit hyperactivity disorder[137, 186] and myopia.[375] Other studies show no effect of vitamin D. Intervention studies using supplementation with vitamin D show no benefit for most health outcomes tested.[18] The major determinant of serum 25(OH)D concentration in many populations is recent sun exposure or time outdoors.[219] This means that serum 25(OH)D, as well as being the usual measure of vitamin D status, is a marker for recent sun exposure and time outdoors. Intervention studies using supplementation with vitamin D test a specific effect of vitamin D. However, associations with 25(OH)D may be due to the link with other factors related to recent sun exposure and time outdoors such as physical activity or exposure to UV radiation, rather than vitamin D status *per se*. The lack of a beneficial effect of supplementation with vitamin D suggests that there is, in fact, no causal association between higher vitamin D status and better health, but that other factors associated with the level of 25(OH)D may be important for health. Alternatively, supplementation studies may have had null results due to study designs where the supplementation dose was too low, for too short a time, in people without vitamin D deficiency at the beginning of the study, or the sample size of the study was too small. In a few supplement studies there has been evidence of improvement in disease symptoms, for example for lupus,[83, 374] and autism[289] but the designs used in the studies do not allow firm conclusions to be drawn. The role of vitamin D in health and disease, the optimal level and size of any effect, remains unclear.

Sun exposure and/or vitamin D during pregnancy may be particularly important for the health of offspring. Vitamin D status in pregnancy was inversely related to the risk of attention deficit hyperactivity disorder in the offspring[238] in one study, but was not in another, and low 25(OH)D level in umbilical cord blood has been correlated with an increased risk of transient wheezing and atopic dermatitis in early childhood. [22] Higher maternal vitamin D status was associated with an increased risk of depression in the offspring in another report.[322]

A few studies show that both low and high levels of 25(OH)D are associated with increased risk of an adverse health outcome, such as all-cause mortality,[7] or an adverse effect of higher 25(OH)D levels for prostate cancer,[370] and hypertension[188] suggesting that optimal levels are not necessarily high levels.

2.9 **Other potential benefits and risks of exposure to UV radiation are being revealed. Higher sun exposure is associated with reduced risk of some cancers and autoimmune diseases, but whether this is a causal association is not clear.** In Finland, fishermen, but not their wives, had higher incidence of lip cancer but lower incidence of colon cancer than the general Finnish population.[339] Whether these cancers are linked to the higher exposure to UV radiation, or the presumed higher consumption of fish, was not explored, although the discrepancy in risk between the men and their wives might lend weight to a UV-related explanation rather than a dietary cause. In the USA, incidence of several sub-types of non-Hodgkin lymphoma was significantly lower in the highest compared to the lowest quintile of ambient UV radiation (average daily cloud-adjusted noon-time UV irradiance at 305 nm (UV-B) over 1982-92) for the residential location, with some effects more pronounced in fair- compared to dark-skinned populations.[56] Similarly, incidence rates for multiple myeloma, a cancer of the plasma cells often spreading to bone marrow, were greater at higher latitudes and there was an independent inverse association between UV-B irradiance and incidence of multiple myeloma.[235] In contrast, another study showed that higher residential erythemal UV radiation was associated with increased risk of B-cell acute lymphoblastic leukemia in children aged less than five years; there was a threshold effect, with risk increasing at levels of ambient UV radiation above 100 J/cm^2.[79]

Several studies report an association between higher levels of sun exposure or ambient UV radiation and reduction in inflammatory bowel disease: risk of Crohn's disease,[178] and hospitalisation and need for bowel surgery for both ulcerative colitis and Crohn's disease.[208] The well-described seasonal variation in disease relapses in people with multiple sclerosis shows latitudinal variation, with a shorter gap between relapses in people living at higher latitude.[319] There is a strong latitudinal gradient of increasing rates of hospital admission for anaphylaxis (a severe allergic reaction) in children in Chile; that is, with increasing latitude above 34ºS and lower levels of solar UV radiation.[169]

An inverse association between mortality from all causes and levels of UV radiation or personal sun exposure have been described for dialysis patients,[304] female participants of a large cohort study in Sweden at the 20-year follow-up,[212] and in premature babies (23-28 weeks gestation) in the first 28 days of life.[292]

Many commonly used drugs can be phototoxic or cause photosensitivity. Photosensitivity reactions are reported with angiotensin II receptor blockers, used to treat hypertension.[346] In addition, long-term use of these drugs is associated with an increased risk of CM.[297] Long-term use of diuretics may increase the risk of SCC and BCC.[297] Additional advice on sun protection should be provided when these drugs are prescribed.

Higher levels of UV radiation have been associated with lower levels of serum folate,[152] including in women of childbearing age.[49] Whether this effect is sufficient to alter the risk of disorders such as neural tube defects in humans is not clear. The combination of high dietary folate intake and high levels of exposure to UV radiation may potentiate DNA damage[55] and risk of BCC.[96]

2.10 Infrequent use and poor understanding of labels and application of sunscreens are common, resulting in people overestimating their sun protection. There is mixed evidence on the long-term benefits of use of sunscreens for the prevention of skin cancers. Sunscreens are not used commonly in some countries.[164, 221, 296] Even where their use is common, sunscreens are often applied at a thickness that is one-fifth to one-half of that required to achieve the rated sun protection factor (SPF).[193, 259] Poor application may continue even after training,[36] but new approaches to training for application may improve effective protection.[180] The use of higher SPF sunscreens (e.g. SPF 50+) may compensate to some extent for the application thickness being less than optimal. New sunscreens provide better protection within the UV-A waveband, but, for a given SPF, increasing protection within the UV-A is accompanied by reduced protection within the UV-B waveband.[116]

A randomised controlled trial in an older Australian cohort showed that regular daily use of sunscreen reduced the risk of actinic keratosis (a scaly growth on the skin that may be a pre-malignant stage of SCC), SCC, and CM.[172] In contrast, increasing use of sunscreens from 1997-2007 in a large cohort of Norwegian women was associated with an increased risk of sunburn,[132] and a meta-analysis of observational data from Europe, America, and Oceania showed no significant increase in risk or benefit of sunscreen use for CM.[367]

A wide range of oral/nutritional photo-protective agents are being investigated.[66, 261] There is considerable interest in the development of natural biocompatible sunscreens,[290] including plant extracts[5, 6, 58] and compounds ingested by marine animals (e.g. mycosporine-like amino acids) that probably function as sunscreens in tissues exposed to UV radiation.[150, 151, 249, 272] Recent work also notes adverse health effects, such as allergic and photo-allergic contact dermatitis from use of synthetic sunscreens,[88, 159] that sunscreens may be endocrine disrupters,[222] and have adverse effects on marine ecosystems (see section 4.6 below).

2.11 **Sunglasses and contact lenses provide excellent protection from UV radiation, although in some countries labelling of sun protection factors may be inaccurate.** A proposed new UV protection label for eyewear, the eye-sun protection factor (E-SPF), integrates transmission of UV radiation through the lens and reflection of UV radiation from the back of the lens (caused by coatings on both sides of the lens to reduce glare).[41] Validation of its biological relevance is now required.[196] A high proportion of sunglasses purchased from unauthorized dealers in developing countries do not comply with international standards for UV protection.[37] Testing of four commercially available soft contact lenses showed that they blocked 89-99% of UV-B radiation.[266] Use of UV-blocking contact lenses and spectacles was associated with reduced UV-induced damage as measured by autofluorescence in the conjunctiva near the nose but not in that on the outer side of the eye.[364]

2.12 **Research on the interactions between UV radiation and the effects of climate change on human health remains sparse.** UV radiation may alter the physiology of some mosquitoes leading to an increased tolerance to some chemical insecticides and this effect may be accentuated by environmental pollution.[329] The importance of these interactions for future control of vectors of diseases is not clear.

In a study of people with white skin in the USA, the incidence of BCC increased in relation to increasing levels of lifetime residential ambient UV radiation and was also higher in the fourth (compared to the first) quintile of ambient temperature.[121] It is difficult to predict from this ecological study whether there might be interactions between exposure to UV radiation and warmer temperatures due to climate change that could affect the risk of skin cancer. In another study, temperature was an important determinant of time spent outdoors in cooler, but not hotter, climates.[366] Thus, at locations where climate change leads to ambient temperatures in a "comfortable" range, people are likely to spend more time outdoors and have higher exposure to UV radiation. In contrast, if climate change leads to temperatures outside this range, people are more likely to spend more time indoors, and receive less UV radiation (also see a further discussion in section 4.5 below).

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

3.1 **Agriculture and food security are likely to be more adversely affected as a result of projected changes in climate and levels of UV radiation, but some beneficial outcomes may also become evident.** Projected increases in intensity and frequency of unfavourable climate events such as heatwaves, flooding, and recurring dry seasons (see sections 1.4 above and 3.10 below) together with changing levels of UV radiation that are linked to climate change, will have adverse effects on production of crops. On the other hand, in addition to an improved understanding of the way in which interactions between exposure to UV radiation and climate change can alter plant response, opportunities for exploiting some of the resultant modifications of plants are relevant with respect to food production, nutrition, and resilience of plants to stress in general. However, crop plants are usually cultivated in dense stands, where beneficial effects of solar UV-B radiation on e.g., immunity of plants, could be lost.[26, 362]

Further work has been directed to productivity, quality traits of plants, and adaptive mechanisms[9, 311] in order to address the effects of UV radiation and rising temperatures on plants. Across a range of plant species, increasing temperature during early development of plants enhances growth, while exposure to realistic levels of UV-B radiation[311, 313] counteracts the growth response. Other growth stages, such as the onset of flowering, are delayed by elevated levels of UV-B radiation, with resultant decreases in fruit and seed production ([215] and references therein). These modifications during plant growth may become more common in areas that are receiving high levels of UV radiation, mostly because of projected decreases in cloud cover and aerosols in some regions.[285] Current high UV radiation levels also occur in certain high-altitude and low latitude locations.[246]

UV-B-mediated shifts in allocation of resources (such as sugars, mineral ions, and water) within the plant may have important consequences for agriculture. Redirection of these resources away from defense mechanisms and toward processes for rapid growth in response to attenuation of UV-B radiation in high-density stands[230] may have negative consequences for plant health in agricultural settings.[382] Further research on the molecular connections between perception of UV-B radiation and the regulation of plant immunity may provide clues to improve resistance of crop plants to pests and pathogens under conditions of high-density agricultural practices.

The use of pesticides in agriculture continues to be a concern. It is known that UV radiation facilitates the breakdown of pesticides[81, 270] and may in some cases increase toxicity of certain pesticides and/or their degradation products (see section 5.5 below). The detrimental effects to the plant may result in an increase in the permeability of membranes leading to increased uptake of pesticides when plants are exposed to elevated levels of UV radiation.[2, 207] Because of the potential harmful effects of pesticides on the environment, more selective biological methods of control are being developed. Use of certain fungi (entomopathogenic) constitute one biological control measure, although unfortunately they also can be very sensitive to UV-B radiation. This will decrease their usefulness as biological controls in regions of enhanced UV-B radiation.[78, 124]

3.2 **In terms of plant adaptation, there are several implications for food production and altered plant attributes as a consequence of exposure to UV radiation and a rapidly changing and variable climate.** While plant response can indicate mechanisms of adaptation, some of these adaptations are also of interest from an agricultural, horticultural, and nutritional perspective ([48, 354, 362], and references therein) and can be managed by changing certain practices of crop management for beneficial outcomes. For example, stimulation by UV radiation of polyphenolics can be used to increase the nutritional quality of plant products and plant tolerance to stress conditions by manipulating exposure of crops to UV radiation through e.g., opening of the plant canopy or use of filters.[26, 318, 354]

Other examples include the modulating effect of UV radiation on growth of grape vines and subsequent alterations in composition of the berry fruit and resulting juice or wine. These changes can be used by growers to experimentally manipulate conditions to alter taste, quality of the berry, and appearance of the wine, and cross-tolerance to environmental stressors,[61, 226, 323] including fungal infections[16, 128] and temperature.[323] In many geographical regions, a concern arising from increasing temperature is that certain crops, including grape vines, show more rapid ripening that affects quality of wine (e.g. increased alcohol content in wine[226]). However, when multiple, interacting environmental variables are taken into account, such as exposure to increasing temperature and elevated levels of carbon dioxide, UV-B radiation may also alleviate oxidative damage as well as offset the hastening of ripening by the increased levels of carbon dioxide and temperature.[226]

3.3 **Some male and female plants have been reported to respond differently to temperature and UV radiation.** Changes in sex ratios in these plants as a result of exposure to UV-B radiation and temperature may modify ecosystems and spatial distribution of plant habitats. For example, in certain trees and shrubs, male (pollen-producing) plants establish and grow more rapidly than females (seed producing), perhaps because less energy is allocated to reproduction than in female plants. Tolerance of environmental stresses, such as UV-B radiation, water-deficiency, increased salinity, and temperature, also appears to differ in populations of male and female plants so that the proportion of gender across a population can be changed. Male plants may be more tolerant of stresses than females.[184, 204, 241, 269] This greater stress tolerance can result from increased temperature and UV-B radiation.[268] However, the temperature-driven enhanced production of protective flavonoid compounds in female plants[269] further illustrates sex differences. Thus modifications at certain life stages in male and female plants reflect complex interactions between exposure to enhanced UV-B radiation and rising temperature, and may therefore alter the balance of plant gender and establishment of a species.

3.4 **Solar UV radiation can increase rates of decomposition of plant litter via photodegradation, especially in ecosystems with arid and semi-arid climates (i.e., grasslands, savannas, and deserts).** Litter from different plant species varies considerably in its rate of degradation and the precise chemical changes of litter resulting from photodegradation remain unclear.[48] Lignin is thought to be a primary molecular target of photodegradation,[14, 48, 106] but variation among species in susceptibility of litter to photodegradation appears not to be solely related to lignin levels[190] or its optical properties that influence penetration of UV radiation.[86] Results from a meta-analysis[190] suggest that density of litter and thus the surface area of litter exposed to UV radiation can be an important attribute influencing photodegradation of litter (see section 5.3 below). UV radiation directly degrades lignin structures[210] and indirectly alters other cellular constituents, such as cellulose and hemicellulose, and these chemical changes may then enhance microbial decomposition of litter (refs[106, 23] but see also[211]).

3.5 **UV radiation influences decomposition of litter by several interacting and possibly synergistic abiotic and biotic mechanisms.** The indirect enhancement effects of UV radiation on litter can apparently persist for some time and potentially carry over from seasonal dry periods (i.e., summer when UV radiation levels are typically high) to cooler, moist periods (winters) when temperature and moisture conditions are more favourable for microbial decomposition.[130] This enhanced stimulation of microbial decomposition by UV radiation also appears to extend to partially decomposed soil organic matter.[372] Results from a recent meta-analysis[351] suggest that the combined effect of UV radiation on abiotic (photodegradation) and biotic (microbial) decomposition processes contributes to greater mass loss of litter than photodegradation alone; and lignin loss is greater when photodegradation interacts with microbial decomposition (see also section 5 below). An increased understanding of the mechanisms of the effects of UV radiation on decomposition of litter will increase our ability to predict how climate change will affect this process.

3.6 **Climate change can potentially mediate the effects of UV radiation on decomposition of litter by various direct and indirect pathways.** However, few studies have experimentally examined the interactive direct effects of climate change and UV radiation on litter decomposition (see section 5.3 below). Results from an experimental study of Mediterranean grasslands (see section 5.3 below) indicate that reduced rainfall and increased temperature decreased the rates of decomposition in both standing and ground litter of a perennial grass species (*Stipa tenacissima*). In addition, ambient UV radiation increased the rate of decomposition but only under dry, warm conditions.[4] These findings suggest that, at least in these ecosystems, the relative importance of UV-driven photodegradation may increase with climate change with potential consequences for carbon cycling and sequestration. Climate change may also influence litter decomposition indirectly via changes in vegetation composition, structure, and fire (see sections 1.6 above and 3.10 below).

3.7 **The molecular mechanisms by which terrestrial plants respond to changes in UV-B radiation are becoming better understood.** Since the mechanism of perception of UV-B radiation by the UVR8 photoreceptor protein was elucidated in plants,[280] there has been substantial progress in the understanding of the downstream signaling events that lead to physiological responses, including the activation of protection mechanisms (reviewed in [181]). This improved understanding of the perception of UV-B radiation and signaling in plants has important implications for biotechnology. Biotechnological applications of this knowledge include the enhancement of desirable responses to UV-B radiation in crops (such as accumulation of pigments and antioxidants in fruits and vegetables and other crops)[27, 48] and the development of novel tools that allow manipulation of cellular activities by light.[386]

3.8 **There is further evidence that plants use solar UV-B radiation as a signal of light availability and intensity of competition from other plants.** Although high levels of UV-B radiation can be harmful for some organisms, it is becoming increasingly clear that terrestrial plants have effective protective mechanisms against the damaging effects of UV-B radiation. These mechanisms include the accumulation of protective UV-absorbing pigments in epidermal cells and the cell walls of plants,[48, 51, 70, 119, 157, 236, 281] activation of antioxidant systems[93] and increased expression of genes involved in DNA repair mechanisms. In certain species, the UV-absorbing pigments can be adjusted on a diurnal basis in response to changes in solar UV radiation.[31, 33] Many of these protective responses are regulated by the UV-photoreceptor, UVR8.[342] In addition, plants use UVR8, along with other photoreceptor proteins, to sense changes in the light environment caused by the proximity of other plants[153, 230]). Under low light conditions that inactivate UVR8 (shade), resources are redirected from defense to rapid growth.[230] This strategy helps the plant to compete for light with its neighbours, but also makes it more vulnerable to the attack of pathogens and pests.

3.9 High sensitivity to UV-B radiation has been demonstrated in some invertebrates. Terrestrial arthropods (such as insects, spiders, and millipedes) can be affected by UV-B radiation via effects on their food sources (mainly plants, e.g.,[27, 94, 274]). It has usually been assumed, without much hard evidence, that the exoskeleton affords good protection against the direct effects of UV-B radiation for most terrestrial arthropods. However, high sensitivity to UV-B radiation occurs in aphids[52, 98, 387] and mites[242, 325, 327]. Some arthropods also sense and respond to solar UV-B radiation with avoidance behavior.[25]

Adult damselflies are able to coat the mouthparts of ectoparasitic water mites with melanin (invertebrate melanotic encapsulation) as an effective response to deter these parasites. However, if damselfly larvae are exposed to UV-B radiation, they produce more melanin in their exoskeleton to protect from UV-B damage. As a result, adults are smaller and have a reduced immunity response (30% reduction in melanotic encapsulation). This constitutes the first evidence for a UV-driven impaired immune response in an insect.[90]

3.10 Ozone depletion is changing global climate (wind patterns, temperature, and precipitation) across the globe with consequences for agriculture, ecosystems, and human health. These ozone-related changes are manifest at the Earth's surface in the Southern Hemisphere during summer (December-February) and in the Northern Hemisphere in spring (April-May)[48, 59, 92, 106, 111, 282, 316, 377, 389] with widespread implications for terrestrial and aquatic ecosystems, human health and food security, some of which are detailed below.

Changing wind patterns and intensity: More intense mid-latitude winds linked to ozone depletion could reduce or enhance the ability of the oceans to sequester carbon.[106, 199, 282] Enhanced wind-driven upwelling of carbon-rich deep water would result in less uptake of atmospheric carbon dioxide (CO_2) by oceans, reducing their potential to absorb carbon.[48, 106] However, winds can also transport more dust from drying areas, such as South America, into the oceans, enhancing fertilisation by iron and resulting in more plankton and greater carbon uptake[106, 282, 363]. These stronger more southerly winds have also been shown to have positive impacts on some foraging sea birds[45, 108, 357] with the sub-Antarctic wandering albatross showing a 15% increase in both body weight and breeding success.[357] However, for the flightless southern rockhopper penguins, the poleward shift of the jet stream is predicted to reduce the number of days with westerly winds in the future, leading to fewer days with favourable foraging conditions.[91]

Changing temperatures: Ozone depletion at the south pole is associated with cooling of East Antarctica (see [282]) while ozone depletion at the North Pole is associated with springtime cooling over China, Greenland and north eastern Canada[59] but northern Europe and Siberia show enhanced springtime warming. These changes in temperature have likely reduced melting of the ice sheet in polar regions and resulted in changed phenological (e.g. mismatches between plants and their pollinators). Depletion of Antarctic ozone has possibly offset a substantial portion of the summer warming that would otherwise have occurred in Eastern Australia, Southern Africa and South America, due to increasing greenhouse gases (ref [29] and section 1.9 above). As ozone concentrations recover, this amelioration may reduce with potential implications for populations of these regions.

Changing precipitation: Ozone depletion is similarly associated with changing precipitation across the globe.[59, 92, 138, 281, 377, 389] More springtime precipitation occurs at high latitudes in the North Atlantic Ocean (70˚W to 20˚E) and in Siberia (50-120˚E), associated with extremely low polar stratospheric ozone. Regional changes in precipitation will likely alter levels and transparency of water and hence exposure to UV radiation in aquatic ecosystems by the mechanisms mentioned in section 4.1 below. As detailed in our last assessment,[48] terrestrial ecosystems in the Southern Hemisphere are being affected by these ozone-related climate changes. Wetter summers have seen increased tree growth in Eastern New Zealand[345] and expansion of agriculture in South-eastern South America.[138] Conversely, in Patagonia and East Antarctica, declining growth of trees and moss beds has been linked to reduced availability of water.[48, 71, 282]

Changes in wind patterns, temperature, ocean salinity and precipitation are known to have an impact on agriculture and food security, human health, marine and terrestrial ecosystem health.[175] However, there have been relatively few studies (i.e., none for the Northern Hemisphere) that directly consider these climate-related effects of ozone depletion. Ecological and health studies aimed at revealing such effects would probably be most effective if they focused on regions with statistically significant correlations between springtime depletion of ozone and either summertime surface temperature (in the Southern Hemisphere) or springtime surface temperature (in the Northern Hemisphere).

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

4.1 Climate change is altering the exposure of aquatic ecosystems to UV radiation through a variety of mechanisms. Incident UV radiation is no longer increasing due to stratospheric ozone depletion, and a slow return to pre-1980 levels of stratospheric ozone is expected in the coming decades. However, exposure to UV radiation in inland, coastal, and open ocean waters continues to be altered by changes in ice and snow cover, cloud cover, increases in thermal stratification of the water column induced by warmer air temperatures, and by heavy precipitation that reduces the UV transparency of water.

Climate change is altering the concentrations of UV-absorbing substances such as terrestrially-derived dissolved organic matter (DOM) in inland and coastal waters by altering the amount, timing, and type of precipitation and frequency of extreme precipitation and drought events.[176, 340] Increases in precipitation, including extreme events and flooding, increase concentrations of DOM and turbidity in inland and coastal aquatic ecosystems, reducing their UV transparency (Figure 2).[361]

Figure 2. Plume of turbid water entering the east basin of New York City's Ashokan Reservoir following an extreme runoff event. The increase in extreme precipitation events in many regions of the world will decrease UV transparency, the potential for solar disinfection of parasites and pathogens, and increase the cost of effective disinfection of drinking water sources. See text for details. Photo credit: Randall Hurlbert.

An 18-year study in Sagami Bay, Japan, found that seasonal reductions in UV transparency and shallower mixing depths are related to increases in DOM concentrations and to weather patterns associated with the Pacific Decadal Oscillation index (an ocean-based oscillation that influences regional weather as does El Niño).[198] Increases in DOM and changes in UV transparency can alter microbial food webs[294] and distribution and abundance of zooplankton.[73, 101, 112, 170, 201] Dietary photoprotective compounds can decrease the threat of damage by UV radiation and reduce the need for behavioural responses in zooplankton.[170]

The fate of DOM in inland waters is also important for the global carbon cycle, because inland waters release large amounts of CO_2 (≈ 2 petagrams (Pg) per year), much of which is derived from DOM.[76] While microbial activity has generally been thought to be the primary mechanism of breakdown of DOM in aquatic ecosystems, recent data suggest that solar UV radiation may be responsible for 70-95% of the breakdown of this substantial pool of organic carbon in aquatic ecosystems in the Arctic.[76, 77] This sunlight-driven degradation of DOM has important implications for biogeochemical cycles and greenhouse gas production as discussed in more detail in section 5.2 below.

The seasonal duration and thickness of ice cover in aquatic ecosystems is decreasing globally, increasing exposure to UV radiation.[147] In the Arctic, the areal extent and thickness of sea ice continue to decline. Recent modeling efforts estimate that exposure to the UV-B wavelength range in the surface waters of the Arctic Sea may increase as much as tenfold between 1950 and

2100 due to the melting of sea ice.[114] Copepods, which are the dominant grazers in the oceans, ascend to shallower waters about the time of ice-out in the Arctic, which has the potential to increase their exposure to UV radiation. Increases in photoprotective compounds in the copepods at this time of year reduces the potential for damage by UV radiation.[171] In the Antarctic there is a different pattern of sea ice. The areal extent of Antarctic Sea ice has been increasing by about 1% per year,[308] but the thickness of the ice has been decreasing at an accelerating rate with as much as 18% loss within two decades in some regions.[253] Recent modeling indicates that polar stratospheric ozone depletion may alter the areal extent of sea ice; however, the direction of this effect is still a matter of debate.[111, 308] In contrast, other modeling has shown that while ozone depletion is altering the temperature and salinity of the Southern Ocean, effects on Antarctic Sea ice are not likely.[111] In the Arctic, models that compare the increase in seasonal loss of sea ice in the late twenty-first versus the late twentieth century predict that climate change-induced sea ice loss will reduce ozone by 13 Dobson Units during the spring.[324] This small percentage loss in ozone is not likely to lead to important feedbacks between ozone depletion and sea ice. These potential feedbacks between ozone and sea ice are covered in more detail in sections 1.2, 1.8, and 1.9 above.

4.2 **Increasing air temperatures have led to a warming of surface waters in lakes and oceans, increasing the strength of thermal stratification and exposure of surface-dwelling organisms to UV radiation.** Mean annual temperatures of oceanic surface water have warmed by about 1°C over the last 125 years with increases in thermal stratification and a reduction in the depth of the upper mixed layer, as well as deep ocean warming.[113] Since most of the primary producers are found in this sunlit zone, they are effectively exposed to higher levels of visible light and UV radiation. Stronger stratification also reduces the upwelling of nutrients from deeper water, decreasing productivity and altering the species composition of primary producers.[368] There is also some evidence that, by reducing the average exposure of algae to UV radiation, greater concentrations of DOM may thus decrease the photoprotection and UV tolerance of algae. Under some conditions these algae may be circulated into the near surface waters where they are exposed to high UV radiation and subsequently more readily damaged.[155]

4.3 **In contrast to the warming of most ocean waters, there is a significant cooling in the North Atlantic between Greenland and Ireland.** This is due to a weakening of the Gulf Stream that heats the North Atlantic, the American East coast, and Northern Europe,[252] and a decline in the Atlantic Meridional Overturning Circulation (AMOC).[267] These changes in oceanic currents and surface temperatures alter thermal stratification and thus exposure of marine organisms to UV radiation.

Warming of the climate is altering the strength, depth, and duration of thermal stratification in inland water bodies as well. This will change exposure to UV radiation with the response varying with the depth, surface area, and water clarity of the ecosystem.[53, 195] Deeper, warmer lakes (e.g., tropical lakes and reservoirs) are increasingly becoming stratified sooner and remain so for longer than shallower, cooler lakes.[195] Transparency of water modulates the amount of solar UV radiation penetrating the water column and is also a primary modifier of thermal stratification.[154] While lower transparency reduces exposure to UV radiation on a depth-averaged basis, it can also warm surface waters, cool bottom waters, and increase stratification. Reduced transparency in clear-water systems substantially increases the duration of stratification and delays the onset of ice cover,[154] thereby extending the ice-free season. Longer ice-free periods and increased thermal stratification increase exposure of surface-dwelling organisms to UV radiation, alter vertical habitat gradients of food and predation in the water column, and modify nutrient cycling and gas exchange rates including those for greenhouse gases. These changes in aquatic ecosystems have the potential to reduce biodiversity through increased exposure to UV radiation, increase greenhouse gas production, and create mismatches between consumers and their food resources that can decrease consumer abundance.

4.4 **Acidification of the oceans and associated increases in concentrations of CO_2 in the oceans interacts with the effects of UV radiation, climate change, and other stressors in affecting marine organisms.** A recent review highlights the fact that acidification of the oceans is exacerbated by inputs of CO_2 derived from degradation of DOM as well as from the atmosphere.[239] In coastal regions, increased runoff containing DOM and nutrients associated with climate-driven extreme precipitation events can further increase concentrations of CO_2 in seawater and accelerate acidification beyond that expected from elevated atmospheric CO_2 alone.[239]

Rates of growth and/or photosynthesis in ecologically important algae can be inhibited by interactions between the effects of UV radiation and acidification[369] as well as by interactions between these two stressors and limitation of nutrients.[205] In contrast, the elevated concentrations of CO_2 associated with acidification may ameliorate the negative effects of photo-inhibition by UV radiation in some marine diatoms by increasing photosynthesis as long as exposure to UV radiation is not so high as to cause damage.[67]

4.5 **An increase in the prevalence of water-borne parasites is a likely response to reduced solar disinfection from decreased penetration of UV radiation in aquatic ecosystems induced by increases in precipitation and runoff from terrestrial ecosystems.** It has long been recognised that viral, bacterial, and protozoan pathogens and parasites are inactivated by exposure to solar UV radiation. Decreases in the UV-transparency of inland and coastal waters related to increases in inputs of DOM suggest that inactivation of parasites and pathogens by solar radiation is becoming progressively less effective.[362] Outbreaks of water-borne pathogens are frequently preceded by high precipitation events.[82] While mobilisation of pathogens from terrestrial ecosystems to inland waters is thought to account for a substantial portion of these outbreaks, the sensitivity of many pathogens to UV radiation coupled with reductions in solar disinfection related to decreases in the UV transparency of inland and coastal waters may also be a contributing factor.

A variety of environmental factors as well as characteristics of parasites and pathogens may influence the effectiveness of solar disinfection by UV radiation in surface waters (see section 5.5 below). Pathogenic bacteria[250] and fungi[50] are inactivated by natural and simulated solar radiation, and this inactivation may be reduced by shading of UV radiation due to DOM and algal blooms.[39] Hydrodynamic modeling based on data from Lake Tahoe indicates that variations in depth of the thermocline and vertical mixing alter exposure to UV radiation and are thus an important element in the effectiveness of solar disinfection of parasites.[168]

In contrast to the UV-disinfection of surface waters, exposure to high levels of UV radiation can either stress or suppress the immune system of hosts, making them more susceptible to infection. For example, high levels of UV radiation combined with warm temperatures may increase infection of freshwater fish by the protozoan parasite that causes white spot disease.[80] Similarly, exposure of larval damselflies to UV radiation can suppress the immune response of adults, reducing their ability to defend against parasitic mites (see section 3.9 above).[90]

4.6 **The effects and transport of pollutants in aquatic ecosystems are altered by UV radiation.** Our general knowledge of interactions between UV radiation and pollutants is limited because they have not been studied for many compounds. UV radiation can either enhance or reduce the effects of pollutants (see section 5.5 below). Studies of the interaction of UV radiation and four toxic compounds on the growth and metabolism of algae revealed both synergistic and antagonistic effects.[194] The mechanism of action of UV radiation may involve more than just photosynthesis. For example, the uptake and thus toxicity of copper in aquatic plants can be enhanced by exposure to UV radiation.[275] Pesticides may also inhibit the repair of UV-induced DNA damage in embryos of African clawed frogs,[379] as well as decrease the ability of their tadpoles to behaviourally avoid UV radiation.[378]

The toxic effects of oil spills are enhanced by UV radiation due to radical formation, alone or in combination with warming of the climate. In contrast, UV radiation has been shown to alleviate the negative effects of the combination of oil and ocean acidification on bacterial communities,[72] and to play a role in photodegrading antibiotics in the environment.[35]

Mercury is an important aquatic pollutant and the toxicity and transport in the food web depends on the form of the mercury compound, with toxicity being especially severe for organic methylmercury. In nature there is a balance between production of methylmercury and its breakdown by either bacterial or photochemical processes. Photochemical degradation of methylmercury is assumed to be the more dominant of these two pathways in lakes. UV-B radiation is the most active component of the solar spectrum in the photodegradation of methylmercury in Norwegian lakes;[262] likewise in laboratory studies.[286]

Anthropogenic sunscreens (commercially produced sun lotions) contain a variety of chemicals that include organic compounds such as oxybenzone (benzophenone-3, or BP-3) that absorb damaging UV radiation, or inorganic compounds such as titanium dioxide or zinc oxide that reflect UV radiation. With the hundreds of millions of tourists that crowd beaches and use these sun lotions each year, there is the potential for these chemicals to accumulate to concentrations that may damage inland and coastal aquatic ecosystems. The organic compound BP-3 is toxic to coral planula larvae as well as to cells of corals.[97] When exposed to BP-3, even in the µg/L range, larvae of coral lose their motility and their algal symbionts, and suffer substantial damage to DNA and tissues, which leads to increased mortality. Since BP-3 is photo-toxic, these negative effects of BP-3 are worse in the sunlit waters where coral larvae are found.[97] In the presence of solar UV radiation, titanium dioxide nanoparticles produce the strong oxidising agent hydrogen peroxide. While these nanoparticles are coated to prevent human skin damage in sun lotions, the coatings dissolve in natural waters and thus become more reactive. Combined laboratory experiments and field sampling at a beach in the Mediterranean Sea demonstrated that the levels of hydrogen peroxide produced in the presence of UV radiation by titanium dioxide in sun lotions can damage phytoplankton.[293] These nanoparticles and other chemical compounds may concentrate in the surface microlayer where critical processes such as gas exchange and solar flux are regulated, as well as accumulate in the sediments where they may harm sediment-dwelling organisms.[293, 338] Other sun lotions release inorganic compounds that include not only toxins, but also phosphorus and nitrogen that are important nutrients that may increase primary productivity.[338] While our knowledge of the effects of sun lotions on aquatic ecosystems is very limited, the available data suggest that chemicals released by sun lotions may damage corals and alter phytoplankton dynamics, leading to negative effects on aquatic ecosystems and their food webs.

4.7 **Several recent advances have been made in our understanding of how exposure to UV radiation can alter species interactions from phytoplankton to invertebrates and vertebrates in aquatic ecosystems, and also how some responses to UV radiation are temperature-dependent.** Even closely related species may differ in their sensitivity to UV-B radiation owing to variation in the type and amounts of UV-absorbing compounds and detoxifying enzymes that they each have.[38] Photoprotective defense mechanisms differ widely among species of phytoplankton[148] and invertebrates.[326] UV-induced changes in the composition of species at one trophic level can have consequences for other trophic levels. For example, concentrations of fatty acids in sub-Antarctic phytoplanktonic algae, important to grazing zooplankton, increase when these algae are grown without UV-B radiation.[146]

The role of UV radiation in the vision, communication, and performance of vertebrates is becoming more widely recognised. For example, it was recently found that hooded seals have enhanced vision in the UV wavelength range.[162] The development of UV markings used in communication among coral reef fish is absent in captivity and dependent on exposure to UV radiation on the reef.[123] When exposed to UV radiation, spring-born mosquitofish reared at temperatures higher or lower than their 28ºC optimum exhibit decreases in swimming performance and higher metabolic rate accompanied by increased damage to proteins and lipids in their tail muscles. The responses by fish born later in the year are less temperature dependent.[131] These new findings indicate that effects of UV radiation are altered by the ability of aquatic organisms to detect, respond to, and defend against solar UV radiation, and that these responses can be temperature-dependent.

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

5.1 Climate change could enhance the production of short-lived halogens that cause depletion of ozone in the stratosphere and troposphere. Short-lived halocarbons (with lifetimes <6 months; e.g., methylene chloride, bromoform) that cause depletion of ozone are produced in marine environments;[165, 312] for example, at the sea surface microlayer,[62] and when terrestrial dissolved organic matter (DOM) is introduced into seawater.[233] These short-lived brominated and iodinated halocarbons are formed via reactions associated with the natural breakdown of DOM in marine systems.[209, 277] Some of these products can reach the stratosphere where they participate in destruction of ozone.[277] Climate-induced increases in runoff of DOM from land to ocean[110] are likely to enhance the formation of these short-lived halocarbons with potentially important consequences for depletion of ozone in both the stratosphere and troposphere.[165, 312]

5.2 Ultraviolet radiation stimulates the production of carbon dioxide from terrestrial dissolved organic matter due to melting permafrost, and contributes to a significant positive feedback on global warming. Terrestrial permafrost contains nearly 1,500 Petagrams (1 Pg $=10^{15}$ g) of organic carbon.[298, 347] The release of CO_2 from thawing permafrost in the Arctic is known to be increasing[110] and is considered to be a major positive feedback in climate change by amplifying global warming.[298] A range of processes is responsible for this release of CO_2, but central in this change is the increased transport of terrestrial dissolved organic matter (DOM) into streams, rivers and lakes due to melting permafrost.[76, 347] Recent evidence has highlighted the role of solar radiation in the degradation of terrestrial DOM to produce CO_2.[76, 77] In parallel, the mechanisms and organic precursors underlying photodegradation of terrestrial DOM are becoming better understood.[305, 306] Photodegradation accounts for 70-95% of total breakdown of DOM in Arctic lakes and rivers, and is therefore a major factor driving the release of CO_2 from thawing permafrost.

5.3 Land-use and climate change alter vegetative cover and affect UV-mediated carbon turnover of plant litter in terrestrial ecosystems. Substantial differences in vegetative cover occur in terrestrial ecosystems due to influences from natural climatic factors coupled with human activities such as agriculture, deforestation, or intentional planting of exotic species.[85] Plant cover is a major determinant of the amount of UV radiation and total solar radiation reaching the soil surface,[10] which means that plant cover modulates the effect of UV radiation on carbon turnover.[15, 32] Reductions in plant-cover due to decreased rainfall increases direct photochemical degradation of carbon compounds in soil and may indirectly enhance microbial litter decomposition.[4, 130] Afforestation (planting of woody species in areas that were previously unforested), which increases plant cover, dramatically reduces carbon loss and photodegradation in arid land ecosystems.[10] In ecosystems with marked seasonality of rainfall, UV radiation in particular has been shown to stimulate litter decomposition (see section 3.4 above).[23, 86]

5.4 Increases in the frequency, intensity, and extent of fires due to anthropogenic climate change and other human activities alters the effects of UV radiation on carbon cycling in terrestrial ecosystems. Estimates of the severity of extreme events highlight drought and consequent increased fire frequency as potentially having the largest impact on the carbon cycle in the coming decades.[118] Fires (Figure 3) can interact with effects of UV radiation on carbon cycling in a number of contrasting ways. Burning of above-ground biomass produces CO_2, methane and other greenhouse gases and increases intercepted solar irradiance at the soil surface, all of which lead to increased fluxes of carbon into the atmosphere. In contrast, fires also generate short-lived aerosols that reduce UV and visible radiation and act as cloud-condensation nuclei (see sections 1.6 above and 6.8 below). Fires can increase diffuse radiation that would enhance uptake of CO_2 by plants.[271] Charred biomass on the land surface includes a broad spectrum of organic constituents (including black carbon), which have different photoreactivities,[348] and which can emit gaseous products from photodegradation. This charred organic matter can then run off into streams, lakes, and coastal inland waters, where photochemical mineralisation and biological degradation can occur. Taken together, the interaction of UV radiation and fires is complex, but suggests that increased frequency of fires, particularly large-scale intense fires, will amplify the importance of UV-driven carbon losses due to changes in exposure and the characteristics of post-fire organic matter (also see discussion in sections 1.6 and 3.6 above).

Figure 3. Climate change is leading to increased frequency and extent of high-latitude fires that interact in various ways with changing UV radiation (Photo courtesy of Brian Stocks, Canadian Forest Service, Sault St. Marie, Ontario, Canada)

5.5 The fate and transport of pesticides, pharmaceuticals, heavy metals, nanomaterials, and pathogens are affected by UV-induced photochemical processes. UV radiation induces photoreactions that dissipate pollutants and pathogens. For example, protection from UV radiation by overlying plastics enhances residues of some photosensitive pesticides in water and on crops.[3, 356] Pharmaceuticals, heavy metals, nanomaterials, organic pollutants, and pathogens enter aquatic environments where they are degraded by exposure to UV radiation. This photodegradation involves both direct photolysis and photoreactions sensitised by terrestrially-derived DOM[21, 106, 229, 273, 309] (and see section 4.4 above). UV-initiated photoreactions play a key role in the release of nanomaterials from their composites with polymers in commercial products,[191] carbon nanotubes,[166] and graphene oxide.[167] Future concentrations of certain environmental contaminants will thus depend on their release into the environment coupled with climate change events and photodegradation by UV radiation.

5.6 The production of methane and other trace gases from the foliage of a wide variety of plant species under realistic levels of ultraviolet radiation has been confirmed to be negligible for the global methane budget. Leaves from a wide range of species of plants were evaluated for emissions of greenhouse gases under environmentally relevant levels of UV-B radiation.[120] All had measurable, but small, emissions of methane, carbon monoxide, and ethane. These fluxes are consistent with previously published studies,[46] thus confirming that the global contribution of methane from this source is small (≤1 Teragram [1 Tg = 10^{12} g] y^{-1}), representing less than 0.2 % of global sources.[120]

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

6.1 Ground-level ozone concentrations may increase substantially over large geographic regions due to a combination of stratospheric ozone recovery and climate change in the coming decades. Model simulations indicate that ground-level ozone would have decreased in northern mid-latitudes due to stratospheric ozone depletion, but this decrease was offset by changes in atmospheric circulation.[158] As stratospheric ozone recovers, future background (non-polluted) ground-level ozone concentrations are expected to increase due to slower destruction by decreased UV radiation,[384] and from increased transport of ozone from the stratosphere to ground-level. These increases in background ozone are likely to have negative implications for agriculture and ecosystem health. In addition, significant increases in ground-level ozone are expected due to increased storm-associated lightning,[30] although the magnitude of this effect is uncertain due to a lack of understanding of the process for production of nitrogen oxides (NOx) by lightning. These changes in ground-level ozone are in addition to any increases due to anthropogenic[232] and biogenic emissions which are expected to be temperature-dependent.[376] In urban areas, high emissions of NOx may counteract some of these effects and urban ozone concentrations may decrease.

6.2 Significant positive long-term trends in concentrations of ozone at the earth's surface have been observed over the last 25 years at most locations.[74] The exceptions are for Europe since 2000, and the east coast of the USA since the 1990s, where trends were negative.[74] In the Southern Hemisphere the increase was small but statistically significant. It remains unclear what is driving these trends. Model simulations for the west coast of the USA suggest that there has been an increase in ozone due to the export of NOx from Asia during 2005-2010, offsetting about half of the tropospheric column ozone reductions attained by reductions in local emissions.[344] However, stratospheric-tropospheric ozone transport can also contribute to this trend.

6.3 **An analysis of records of ground-level ozone in the UK concludes that the magnitude of estimated long-term trends depends strongly on the metrics used to quantify ozone patterns and amounts.**[223] Trends depend on how ozone metrics are computed, e.g., from ozone peak levels, averages, or other algorithms (SOMO10, SOMO35).[358] The choice of metric has implications for assessing the effectiveness of regulations and air quality improvements, and their relationship to background ozone concentrations that are beyond local/national regulation.

6.4 **Increasing evidence indicates that the known sources and sinks of hydroxyl (•OH) radicals are insufficient to explain OH concentrations of •OH actually observed or inferred in the atmosphere.** UV-generated •OH radicals perform a critical function by accelerating the removal of many compounds from the atmosphere. Global observations of chemicals removed by •OH (e.g., methyl chloroform) indicate little or no difference in •OH concentrations between the Northern and Southern Hemisphere, while models predict ~25% more •OH in the Northern Hemisphere due to larger emissions of nitrogen oxides (NOx).[256] Direct •OH measurements in locations with high amounts of biogenic hydrocarbons (e.g. isoprene) and low anthropogenic pollution (low NOx) also show larger amounts of •OH than predicted – likely produced by complicated radical recycling chemistry recently identified in laboratory experiments.[1, 122, 244, 257, 284] Additional sources include photolysis of ozone on the surface of cloud droplets[8] and the reaction of methyl peroxy radicals with bromine monoxide.[303] Measurements also show that the total rate of removal of •OH (the reactivity of •OH) is larger than predicted, further indicating the occurrence of recycling of •OH or other sources.[149, 156, 206, 245, 360] Better quantification of chemical reactions of •OH will improve our ability to predict future atmospheric composition in response to changing emissions of critically important gases, e.g., methane, sulfur and nitrogen oxides, as well as HFCs and HCFCs.

6.5 **Halogens contribute to the atmospheric oxidation (self-cleaning) capacity in marine environments, and new data suggest that they also contribute inland.** Nitryl chloride ($ClNO_2$) has been identified in the nocturnal atmosphere in a range of environments including over the coast and well inland. While stable in the dark, $ClNO_2$ is photolysed at sunrise releasing Cl atoms that are significant oxidants at that time.[310] Natural and anthropogenic emissions of short-lived halogens appear to supplement •OH in the atmospheric removal of critically important gases (methane, sulfur, and nitrogen oxides, HFCs and HCFCs; see section 5.6 above).

6.6 **A new study demonstrates a clear linkage between tropospheric oxidation capacity and stratospheric UV transmission even when modulated by factors other than ozone.** Simulations of the 1991 eruption of Mt. Pinatubo confirmed that SO_2 gas and sulfate particles injected into the stratosphere by the volcano caused a substantial reduction in tropospheric UV radiation, leading to lower •OH and higher methane concentrations over much of the globe for several months after the eruption.[28]

6.7 **UV radiation is known to be a critical driver of the formation of photochemical smog, e.g. ozone and aerosols. UV radiation may also play a**

role in the destruction of aerosol particles. A new modeling study suggests that UV radiation also destroys some organic aerosols, a removal process comparable with hitherto recognised losses such as removal by rain.[161] Such processes, if confirmed, could have a profound effect on the spatial and temporal distribution of aerosols, their effects on human health, and their response to UV radiation and other environmental changes.

6.8 **Air pollution, which includes UV-generated ground-level ozone and particulate matter, is expected to worsen in many locations and improve in others, with direct consequences for human health.** A recent global burden of disease study using a business-as-usual emission scenario projected that premature mortality due to outdoor air pollution could double by 2050, mostly in Asia.[202] In the USA and EU, regulators have concluded that adverse health effects in some cases occur at air pollution concentrations lower than those of the currently established standards.[341, 359] However, recent studies have questioned the strength of the evidence supporting causal relationships between short- or long-term exposures to ozone, and e.g., cardiovascular effects.[139, 260, 263] The problem with all of these analyses lies in their complexity: choices of data bases, models and statistical methods that can substantially affect the conclusions.[237]

6.9 **Based on current data, the amount of trifluoroacetic acid (TFA) formed from HCFCs and HFCs in the troposphere is too small to be a risk to the health of humans and the environment.** The fates and effects of TFA in the environment have been critically assessed.[317] In summary, the formation of TFA from the degradation of HCFCs and HFCs continues to be a concern, in part because of its very long environmental lifetime. TFA is produced naturally and synthetically and is widely used in the chemical industry. In addition, TFA is a potential environmental breakdown product of a large number (>one million) of chemicals, many of which are in commerce. These chemicals include pharmaceuticals, pesticides, and polymers. While the contribution to global amounts of TFA from HCFCs and HFCs is well understood, that from these other chemicals is very uncertain. TFA salts are stable in the environment and will accumulate in terminal sinks such as playas, salt lakes, and oceans where the only process for loss of water is evaporation. Total contribution to existing amounts of TFA in the oceans as a result of the continued use of HCFCs, HFCs, and HFOs up to 2050 was estimated to be a small fraction (<7.5%) of the ≈ 0.2 µg acid equivalents/L estimated to be present at the start of the millennium. TFA, as an acid or as a salt is of moderate to low toxicity to a range of tested organisms. Based on worst-case exposure scenarios for salts of TFA, risks to mammals, plants growing in soil, and aquatic organisms is *de minimis*. Risks are potentially greater for plants exposed directly to TFA acid but the short times of exposure in most natural environments will likely mitigate adverse effects.

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

7.1 **In addition to UV radiation, air pollutants in urban areas may contribute very significantly to the discoloration of plastics routinely exposed to**

outdoor conditions even in the absence of direct solar radiation. In weathering of materials outdoors, solar UV radiation is generally the most important agent responsible for discoloration and loss of mechanical strength.[332] In a 2-year outdoor exposure study of 17 types of plastics, where the direct solar radiation and precipitation were excluded, diffuse light and pollutants, especially NO_2 and O_3, were found to be the dominant secondary agents of damage. These were more important than temperature or relative humidity in causing the yellowing of plastics in art and heritage uses.[255] Concentrations of traffic-generated air pollutants need to be taken into account in weathering studies, especially in urban areas.

7.2 **Carbon black pigment, when used together with some UV stabilisers, enhances their stability synergistically.** Carbon black is a good UV stabiliser in plastics[54, 143] as well as in rubber products. Recently, synergistic stabilisation of polyethylene by a combination of 1.5% carbon black and 0.1 to 0.2% (w/w) of the popular hindered-amine light stabilisers (HALS) was reported.[179] In accelerated weathering studies indicators of weathering such as gel content, carbonyl index, elastic modulus and elongation at break were the lowest for the HALS/carbon black system. The mechanism of the synergism has not as yet been fully elucidated. With dark-coloured plastic products, carbon black can be used to extend service lifetimes outdoors.

7.3 **Polypropylenes containing recycled plastic show changes in bulk morphology that results in a reduced outdoor service life.** Replacing a part of the virgin resin with recycled polypropylene in molding products is commonly practiced and is both economical and environmentally desirable. The mechanical properties of thick (>3 mm) molded polypropylene with recycled polypropylene content of up to 40% is not very different from that of samples made from virgin polypropylene. However, the outdoor durability of the former was shown to be much poorer with exposure to solar UV radiation, based on decreased mechanical properties,[373] than that for virgin polypropylene. Also after 12 hours of accelerated UV irradiation, the decrease in toughness of molded laminates was larger by 13% for polypropylene with 30% recycled content compared to that for virgin polypropylene. Despite the ‘green’ advantage of using more recycled content, at least for polypropylene, it reduces the service life of the product.

7.4 **In cable-jackets with the new aluminum-based fire retardants, initial degradation by UV radiation yields a filler-rich surface layer that screens the underlying polymer from further degradation.** There is a growing trend in the industry to phase out polybrominated fire retardant additives. Ethylene vinyl-acetate copolymer, with aluminum hydroxide (~40 % w/w) filler as the fire retardant, is used in cable jacketing. During exposure to UV radiation, the material undergoes heterogeneous degradation with the filler progressively migrating to the surface. This yields a protective surface layer that is enriched with aluminum oxide.[102, 200] Where the underlying material is thick enough to provide the needed mechanical integrity to the cable, this phenomenon provides incidental UV stability at no additional cost.

7.5 **Some residual additives may enhance the degradation by UV radiation of light-sensitive polymer layers in organic photovoltaic cells.** Emerging organic photovoltaic technology, including that of polymer photovoltaic (PV) cells is expected to pose a strong challenge to silicon counterparts. However, improving their durability to ensure a long (>20 year) service life is critical for their commercialisation. The mechanisms of photodegradation have been studied of the light-sensitive polymers of organic PV cells[42, 95, 291] as well as the durability of their plastic encapsulants.[20, 213, 279] In a recent report, residual additives left in the light-sensitive polymer during manufacture, and which are confined and sandwiched between plastic laminates, were shown to promote accelerated degradation of these polymers.[337] Complete removal of these additives prior to sealing the light-sensitive layers during fabrication of the cells may help avoid this complication and extend service life.

7.6 **Colour changes in wood exposed to solar UV radiation correlates well with the extent of lignin photodegradation.** UV-induced degradation of the lignin in wood exposed to solar radiation results in yellowing.[383] Surface yellowness index and the extent of lignin degradation (measured spectroscopically) during solar UV-induced degradation in several hardwood species were found to be correlated.[47, 57, 214] Since colour measurements are more convenient, they could be used as a good surrogate for detecting changes in the surface chemistry of weathered wood.

7.7 **Surface treatments, especially nanomaterial-based coatings, show continuing promise as UV stabilisers for wood.** Nanomaterial UV stabilisers perform exceptionally well in a variety of wood species. The high specific surface area of nanoparticles provides efficient light-shielding at low weight fractions of the filler. Graphene,[350] zirconium dioxide,[350] iron oxide,[126] titania,[352] and cerium oxide[218] can control UV-induced yellowing in several wood species. Similarly, surface modification of wood with nanocellulose crystals[343] and epoxidised soybean oil[287] also result in good UV stabilisation. There can be adverse environmental implications of large-scale use of nanofiller technologies as the particles can be released during use. However, these approaches are yet to be developed for commercial use and the effects on the environment and human health of potential release of the nanoparticles due to weathering are not yet known.

7.8 **The efficacy of thermal surface modification of wood to control solar UV-induced damage remains unclear.** Thermal modification of wood was developed as a means of improving structural properties and biodegradation of wood outdoors. As the wood is used outdoors, how UV stability is affected by heat treatment has been of recent interest. Two reports[69, 334] indicated an increase in the rate of discoloration and degradation of lignin in heat treated hard- and soft-wood species upon UV irradiation; others[333, 335] found the opposite. The stabilisation might be either species-specific or process-dependent. This is a promising environmentally-friendly technique for protection from UV radiation of selected types of wood.

7.9 **Modifying textile fibres with nanoparticles effectively improves their UV protective function.** Nanoparticles used as fillers in textile fibres dramatically decrease the transmission of solar UV radiation. The incorporation of nanoparticulate titanium oxide,[177] cerium oxide,[218] and silver[276, 328] into natural textile fibres at <5 % (w/w), lead to very significant reductions in the transmission of solar UV-A radiation through the fabrics. The service life of treated fabric is not reliably known (see section 2.11 above).

7.10 The protection against exposure to UV radiation provided by cotton fabrics can be increased by an order of magnitude by treatment with graphene nanoplates. Cotton fabric typically used in garments allows ~15% of solar UV radiation to pass through.[315] Good UV radiation absorbers coated on the fibre or fabric can further reduce this value. Surface modification of cotton fabric with graphene nanoplates increase the ultraviolet protection factor (UPF) 10-fold[265] at 0.4% (w/w) graphene. Using a chitosan dispersant with 1% (w/w) graphene enhanced it 60-fold.[331] With growth in graphene technology, the technique has commercial potential. However, the thickness and weave of the fabric also strongly determines protection from UV radiation. As is the case for fabrics treated with certain nanoparticles, the service life of treated fabric is not reliably known.

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