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Environmental effects of ozone depletion and its interactions with climate change: progress report, 2011

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Abstract

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 believed previously. As a result of this, human health and environmental problems will be longer-lasting and more regionally variable. Like the other panels, the EEAP produces a detailed report every four years; the most recent was published in 2010 (Photochem. Photobiol. Sci., 2011, 10, 173-300). 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 next full quadrennial report will be published in 2014-2015.

Keywords

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PERSPECTIVE

Environmental effects of ozone depletion and its interactions with climate change: progress report, 2011

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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 believed previously. As a result of this, human health and environmental problems will be longer-lasting and more regionally variable. Like the other panels, the EEAP produces a detailed report every four years; the most recent was published in 2010 (*Photochem. Photobiol. Sci.*, 2011, **10**, 173–300). 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 next full quadrennial report will be published in 2014–2015.

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

• **Without the Montreal Protocol, erythemally weighted UV radiation‡ would have been increased by a factor of 3 or more at all latitudes by 2065, with values of the UV Index (UVI) exceeding 40 at the equator.** These high UVI values would have resulted in substantial harmful environmental impacts, while in winter at high latitudes there may have been some beneficial effects (see section 2). In the expected future, following the implementation of the Montreal Protocol, long-term absolute changes in both summer and winter clear-sky UVI will be less than 0.4 outside southern polar latitudes.[1]

• **A recent analysis of total ozone data from multiple satellite instruments (1979–2009), reported that an upward trend in total ozone over Antarctica since the late 1990s is detectable and is presumably due to reduction in CFCs.**[2] This positive trend was identified after removing the effect of circulation changes on ozone. However, significant uncertainties exist in the stability of the satellite instruments over the long periods considered, the combination of measurements from different satellites, and the isolation of effects from circulation. The latter is particularly difficult as changes in circulation may affect the temperature in the stratosphere and the formation of polar stratospheric clouds that are involved in the depletion of ozone. Further confirmation of these findings and/or longer data sets would be valuable. This finding does not preclude the formation of ozone holes in the future that would result in increased UV radiation levels over the southern high latitudes.

• **New modelling studies have further strengthened our understanding of the impacts of ozone depletion on climate-related factors.** These impacts include changes in: (a) atmospheric circulation (displacement of the mid-latitude jet),[3,4] (b) precipitation (*e.g.*, increases in the southern subtropics during the austral summer),[5] and (c) circulation in the ocean (*e.g.*, strengthening of the subpolar meridional ocean circulation and the Antarctic circumpolar current).[5] These changes may have impacts on air quality and ecosystems (see sections 3, 5, and 6).

Unprecedented chemical destruction of stratospheric ozone inside the Arctic polar vortex has been observed in March 2011, identifiable as an Arctic "ozone hole".[6] For the first time in the observational

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

record, destruction of ozone over the Arctic in the springtime was comparable to that over Antarctica. Unusually long-lasting cold conditions in the lower stratosphere led to destruction of more than 80% of the ozone between 18 and 20 kilometres above sea level. In sharp contrast with normal years when ozone amounts less than 275 DU are rare, in March 2011, over 40% of the vortex area had ozone levels less than that threshold (Fig. 1). Areas of low ozone that may extend to populated areas in the northern mid- and high-latitudes would result in significantly elevated UV irradiances compared with the normal Arctic spring, with consequences for human health and for ecosystems. However, the UV levels in the Arctic should be less extreme compared to Antarctica. The results show that ozone "holes" are possible even with temperatures much milder than those in the Antarctica. It is difficult to predict whether such severe Arctic ozone depletion may be matched or exceeded in the future. However, if it continues to occur, and particularly if it becomes more severe, effects of increased UV on organisms may be exacerbated by reduced protection due to decreases in snow- or ice-cover resulting from global warming.

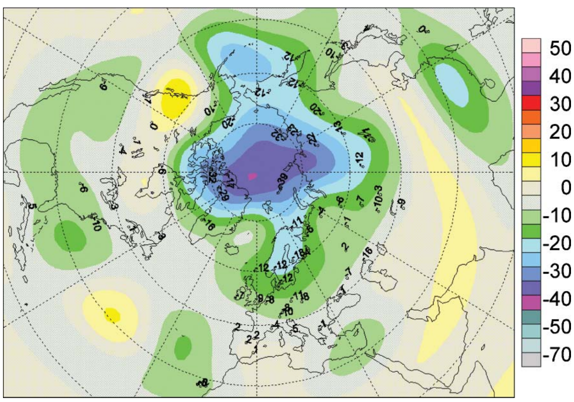

Fig. 1 Percent average reduction in total ozone over the northern hemisphere for March 2011. The highest loss (more than 80%) was observed between 18 and 20 kilometres above sea level over the Arctic. The map was produced by the WMO Northern Hemisphere Ozone Mapping Centre in Thessaloniki, Greece, by combining data from the GOME-2 satellite and Brewer/Dobson ground-based measurements. Reductions were computed relative to 1979–1981 average derived from TOMS total ozone measurements.

• **Surface UV radiation in the 21st century will be influenced by increases in stratospheric ozone due to reduction in ozone-depleting substances and by changes in ozone and cloudiness induced by increasing concentrations of greenhouse gases.** Models suggest that in the first half of the 21st century the recovery of ozone and changes in cloudiness will result in decreases in surface erythemal irradiance by 2–10% at mid-latitudes, and by up to 20% at northern and 50% at southern high latitudes. These decreases are dominated by the projected increases in stratospheric ozone. In the tropics, the projected changes are small (<2%) over this period.[7] By comparing model projections between 2100 and 1960, the effects of climate change on surface UV can be estimated, since the ozone depletion started after 1960 and ozone recovery would have been completed by 2100. By the end of the 21st century erythemal irradiance: (a) will remain below 1960 levels due to changes in clouds and greenhouse gas (GHG)-induced ozone transport at mid-latitudes, (b) will be reduced at high latitudes (particularly in the Arctic) by 5–10% due to changes in clouds, and c) will increase in the tropics by between 3 and 8% due to decreases in clouds and ozone, induced by GHGs.

• **Modelling the effects of UV radiation by weighting spectral irradiance measurements does not necessarily correspond directly to the actual environmental impacts.** Firstly, the shape and orientation of surfaces exposed is important: for example, solar UV radiation incident on a cylindrical surface is typically less than 50% of that on a horizontal surface.[8] Secondly, there may be additional uncertainties arising from incomplete knowledge of the wavelength dependence of the effects (*i.e.*, the shape of the weighting functions)[9,10] (see sections 2 and 3). Consequently, care must be taken when assessing the environmental impacts of UV changes using measurements of ambient UV irradiance.

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

• **Melanoma is now more definitively linked with solar UV-B exposure as a risk factor, particularly episodes of severe sunburn; its incidence continues to increase.** Recent findings support the evidence that UV-B radiation is critical for the initiation of cutaneous malignant melanoma (CMM).[11,12] The risk of melanoma is most closely related to episodes of severe sunburn, often occurring with deliberate over-exposure in fair-skinned individuals. As it is not possible to predict frequency of sunburn in future years, the corresponding impact on the incidence of CMM in relation to changes in solar UV-B radiation is uncertain. Marked increases in incidence of CMM, *e.g.* a doubling between 1978 and 2007,[13] have been noted in several countries,[14–16] but not to the same extent in younger age groups in locations with strong and well-established sun protection programmes.[17] The relative proportion of thick and thin melanomas has remained relatively constant,[18–20] although more of the thick tumours resulted in death.[20] A high number of common melanocytic naevi (moles) is a well-recognised risk factor for CMM.[21] In a recent study in France, children who practised outdoor sports had more naevi than those who did not,[22] while the use of sun protection in young children in Sweden led to the development of fewer naevi.[23]

• **Exposure to solar UV-B radiation causes the non-melanoma skin cancers (NMSCs), basal cell carcinoma (BCC) and squamous cell carcinoma (SCC). Where monitored, the annual incidence rate of these cancers has increased over the past 30 years and is projected to continue to increase, particularly in those aged over 50 years.** For example, the annual incidence of BCC increased by 80% between 1999 and 2008 in Santa Catarina (Brazil),[24] and of all skin cancers by 305% between 1974 and 2005 in Puerto Rico.[25] The lifetime risk of BCC in the Dutch population is estimated to be 1 in 5–6, with no indication of a plateauing in the incidence rate.[26] Two recent meta-analyses of all the relevant published studies to date showed that occupational exposure to UV radiation increased the risk of both SCC[27] and BCC.[28] In contrast, in the Danish population, outdoor workers had a significantly decreased risk of NMSC.[29] Although cutaneous malignancies are less frequent in those with deeply pigmented compared with fair skin, they are thought to rank amongst the top 10 malignancies in sub-Saharan Africa with significant under-reporting being likely.[30] In terms of world health and public health management, the NMSCs represent a major and increasing burden.

• **Exposure to solar UV radiation contributes to the development of Merkel cell carcinoma (MCC), an uncommon but aggressive tumour that occurs on sun-exposed body sites.**[31] MCC is found most frequently in elderly men, and survival is poorer than for melanoma.[32,33] The highest incidence of this malignancy has been reported in Western Australia (age-standardised rate of 0.82 per 100 000) and there is evidence that the incidence rate is increasing.[32,33] Solar UV may activate a virus-specific (polyomavirus) tumour antigen found in many MCC, thus providing a possible link between UV radiation and risk of MCC.[34] The incidence of MCC may increase in the future as a result of the depletion of the stratospheric ozone layer that has already occurred.

• **Common eye diseases resulting from chronic exposure to UV radiation, such as pterygium and cataract, create a large social and financial burden globally.** A detailed study of pterygium lesions (an invasive growth of the eye), traditionally classified as degenerative, showed that a significant proportion contained concurrent ocular tumours, including melanomas.[35] Epidemiological evidence suggests that conjunctival melanomas (on the external surface of the eye) but not intraocular (internal) melanomas are likely to be induced by exposure to solar UV radiation.[36] The molecular changes detected recently in conjunctival melanomas are different from those in intraocular melanomas, further suggesting that they have different causes.[36] In a prospective study involving almost 5000 individuals, the risk of developing cortical cataract was significantly higher in subjects using sun-sensitising medications.[37] Measurements of irradiance may not provide a good guide to risks of UV exposure to the eye, because they do not take account of the modifications in the received dose due to the facial profile and reflected UV radiation.[38] The impact of stratospheric ozone depletion on these eye diseases remains difficult to assess, either quantitatively (for example, uncertainty regarding wavelength-dependence and dose-responses for cataract and pterygium) or even qualitatively (for example, whether there is a definite association between UV exposure and ocular melanomas).

• **The potential benefit of vitamin D, produced as a result of exposure to solar UV-B radiation, should be balanced against the harmful outcomes of such exposure, including skin cancers and cataract.** High percentages of people, even in sunny climates, are considered vitamin D-insufficient, although inaccuracies in measurement limit the confidence in these findings.[39,40] Nevertheless, there is considerable interest in strategies to minimise vitamin D-deficiency. Theoretical calculations of synthesis of vitamin D achieved by solar UV-B irradiation[41–43] are now being replaced by what are likely to be more accurate estimates from real-life exposure to the sun. In experiments using irradiation of volunteers with simulated sunlight, it was shown that casual exposure to midday summer sun at mid-latitudes for about 30 min (unshaded sun exposure while dressed in summer clothing, three times weekly) raises production of vitamin D to sufficiently high levels in most fair-skinned individuals.[44] Many people can attain similar vitamin D levels in summer with more frequent exposures, and with more extended exposures at the weekends.[45] Most studies have shown that vitamin D-sufficiency in the summer does not necessarily guarantee adequate levels in the winter months.[45–48] Extended sunbathing in the summer should not be encouraged, and the decrease in vitamin D that occurs in the winter months at mid to high latitudes, due to the lack of solar UV-B irradiation at this time of the year, might be best countered by diet or the judicious use of vitamin D supplements.

• **Low levels of exposure to the sun and/or of vitamin D are associated with an increased risk of multiple sclerosis, diabetes and some infectious diseases.** Evidence from both animal models[49] and epidemiological studies[50–53] suggest that lower exposure to the sun and vitamin D-insufficiency are separately important to increasing the risk of developing multiple sclerosis (MS). In contrast, two animal models have shown that the onset of MS and the severity of the disease are diminished by vitamin D-deficiency.[54,55] Further uncertainty regarding the importance of vitamin D in modulating the activity of the disease in people with MS is indicated by clinical trials of vitamin D-supplementation, which have not shown an improvement in disease parameters.[56] Vitamin D-deficiency is associated with higher disease activity in people with the autoimmune disease, systemic lupus erythematosus (SLE),[57,58] including in the newly diagnosed, and is more common in anti-nuclear antibody (ANA)-positive healthy controls (at increased risk of SLE) compared with ANA-negative controls.[58] The incidence of diabetes (mainly type 2) is lower in people with active sun-exposure habits[59] or higher levels of vitamin D,[60] and one study showed an inverse relationship between the prevalence of type 1 diabetes and irradiance of erythemal UV-B in Newfoundland.[61]

An Australian study showed that the development of food allergies in Australia was more common for those born in the autumn/winter season, possibly due to lower vitamin D-status during early infancy.[62] The evidence in relation to asthma and sun exposure and/or vitamin D is weak and contradictory.[63,64]

Seasonal patterns in the incidence of tuberculosis suggest an increased risk of active disease with lower levels of UV exposure,[65] but clinical trials using vitamin D-supplementation in addition to regular antibiotic therapy, indicate a beneficial effect of vitamin D only in those with a specific vitamin D receptor genotype.[66] Lower vitamin D status has been associated with an increased risk of upper respiratory tract infections during winter,[67] and increased reactivation from latency of the human herpes virus, Epstein Barr virus.[68,69]

• **Although many health benefits have been proposed for vitamin D, some caution is required, particularly in situations where the vitamin D levels are increased through dietary supplements rather than by natural sunlight exposure.** In several cases, a U-shaped dose-response curve has been observed, indicating that a low and a high vitamin D status may not be beneficial. This has been shown for prostate cancer,[70] tuberculosis,[71] premature aging,[72] and mortality,[73,74] and is illustrated in Fig. 2.

• **Protection against the adverse effects of solar UV-B radiation is necessary when the sunlight is intense. Public health campaigns in several countries aim to inform the public about the risks and the most effective methods of protection but are not available in all regions of high risk.** Sunscreens lessen the risk of sunburn and

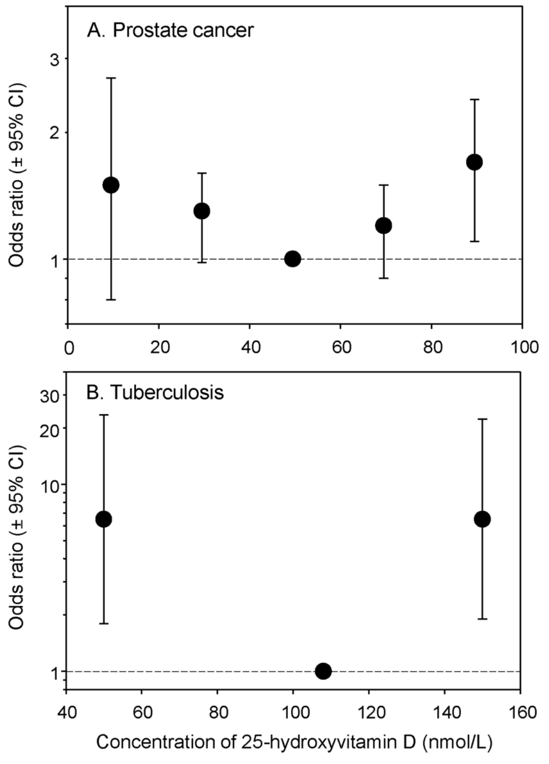

Fig. 2 Odds of prostate cancer (A) and tuberculosis (B) in relation to concentration of 25-hydroxyvitamin D [25(OH)D] in serum. Bars are 95% confidence intervals. (A) plotted from data in Table III of Tuohimaa *et al.*[70] using the median of the range of 25(OH)D concentration in each category; (B) plotted from data in Table 1 of Nielsen *et al.*[71] Median of reference category; upper and lower categories are taken as 50 nmol L^{-1} and 150 nmol L^{-1}.

SCC development; recently a trial of regular use of sunscreens in Queensland residents over a four year period reduced the incidence of new primary cutaneous melanomas.[75] Improved sun protection and awareness has been suggested as one reason for the decreasing incidence rates of melanoma in children in Australia and Sweden, from a peak in the mid-1990s.[76] On the other hand, holidays in sunny climates have become very popular, leading to a high risk of sunburn especially as many people on vacation wish to tan intentionally.[77] Measures used for protecting against solar UV need to target such behaviour. While the local UV Index should be informative, there is not widespread understanding of what it means and therefore sun and photoprotection behaviour are not modified according to the UV conditions.[78] In addition to staying indoors, seeking shade, covering up, wearing wrap-around sunglasses or UV-absorbing contact lenses[79,80] and using conventional sunscreens, more effective sunscreens and alternative strategies for photoprotection are in development.[81,82] Topically applied agents that have been tested in human subjects include the antioxidant nicotinamide (one of the group B vitamins),[83] and enzymes for repair of DNA.[84] Dietary components which may provide systemic photoprotection include green tea extracts, pomegranate juice, and omega-3 polyunsaturated fatty acids.[85] Zerumbone, an extract from a Southeast Asian ginger plant, protected against UV-induced cataract in a mouse model.[86] These strategies may have the potential to counter some detrimental health effects of stratospheric ozone depletion.

• **There is limited new information in the peer-reviewed literature regarding the toxicity of products being proposed as alternatives for ozone-depleting substances.** The lack of published information is principally due to two factors. First, many of the products being submitted for approval to regulatory agencies are not new but are re-purposed having received prior approval for another use or in another industrial sector.[87,88] For example, a number of the low toxicity replacements for halons used in fire suppression, such as water and detergent-based formulations, have an increasingly wide range of applications.[89] Such products are less likely to require additional toxicity information because the submissions focus on changes in exposure and how they might affect previous risk assessments. Secondly, when manufacturers develop new toxicity information, they are required to submit it to regulatory programmes such as SNAP (Significant New Alternatives Policy) but rarely publish it and, indeed, can designate it as confidential business information. The result is that the regulatory agencies can integrate such information into their risk assessments without disclosing the confidential details. For example, when concerns about the reproductive effects of brominated hydrocarbons, such as n-propyl bromide, led to their phase-out as substitutes for the ozone-depleting substances in certain sectors, much of the data upon which the SNAP decisions were based never entered the peer-reviewed literature.[90]

• **Changes in the climate resulting from depletion of stratospheric ozone and global warming might result in a rise in the incidence and prevalence of water-borne and vector-borne infections.** One example is that depletion of the ozone layer in the polar stratosphere has led to increased rainfall in the southern subtropics,[5] possibly increasing the risks of diarrhoeal diseases, malaria and dengue fever.[91–93] However, because of changes in societal behaviour, infrastructure, economic development and disease control, such adverse outcomes are uncertain at the present time.[94]

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

• **While depletion of stratospheric ozone results in increased UV-B radiation reaching the Earth's surface with well-documented impacts on biota,[95–99] new studies suggest that this ozone depletion also can influence biological processes by driving large scale climate change events.** There is evidence that the Antarctic ozone hole has been responsible for changes in atmospheric circulation in the Southern Hemisphere over the last half century, leading to increased wind speeds around the Antarctic coast[100] and altering precipitation in the subtropics.[5] In Antarctica, higher wind speeds appear to have caused drying of Antarctic coastal sites, leading to decreasing growth rates in Antarctic mosses,[101] as well as increasing salinity and changing diatom communities in East Antarctic lakes.[102] In the subtropical regions, ozone-related changes in precipitation may have consequences for water resources and terrestrial ecosystems in the Southern Hemisphere.[100]

• **Evidence continues to demonstrate that solar UV-B radiation is an important regulator of interactions between plants and consumer organisms, such as pests and pathogens.** Solar UV-B radiation can induce changes in plant chemistry that affect the abundance and performance of herbivorous insects. For example, attenuation of solar UV-B can increase reproduction of aphids on plants – a response associated with reduced amounts of phenolic compounds in the host plants.[103] Similarly, attenuation of UV-B can result in increased herbivory by thrips. This effect is at least partially attributable to changes in the expression of defence responses controlled by the plant hormone jasmonate.[104] In certain cases, the metabolic response that provides resistance against a biotic stressor, such as pathogen attack, is different from the one that confers protection against UV-B radiation. Under these circumstances, the acclimation strategy of plants may be directed toward biotic defence, thereby potentially increasing vulnerability to UV-B radiation.[105] Abscisic acid, a plant hormone, has been implicated in the mediation of the shifts in defence against biotic and abiotic stress.[105,106] These metabolic and sometimes morphological adjustments may also imply an energy cost to the plant in terms of redistribution of resources.[99,107,108] Laboratory studies indicate that UV-B radiation can affect the survival and behavioural patterns of predatory mites, which are natural enemies of plant feeders.[109,110] Collectively, these studies support the prediction that variations in solar UV-B radiation fluxes may affect trophic relationships in plant canopies in natural and managed ecosystems.

• **A major breakthrough has been made in the understanding of the molecular mechanisms that control plant responses to UV-B radiation.** As indicated in previous assessments,[99] significant advances have been made in recent years in identifying the mechanisms by which plants sense and respond to UV-B radiation. This year, these efforts led to the identification of UVR8 (UV RESISTANCE LOCUS 8) as a UV-B photoreceptor.[111] Absorption of UV-B induces instant monomerisation of the photoreceptor and the interaction of UVR8 with the protein COP1, which is a central regulator of light signalling in plants. This study, which is now supported by additional modelling evidence,[112] along with further characterisation of the signalling pathway,[113] and identification of new functions of UVR8,[114] provide a robust molecular framework which will greatly facilitate efforts to understand the mechanisms of plant response to changes in solar UV-B radiation.

• **Whereas some doubts have been cast about the accuracy of previous attempts to simulate the effects of ozone depletion on UV levels, a new computational assessment largely validates most experimental approaches that have been used thus far in plant research.** This study[10] compares potential errors that can occur in the use of UV emitting lamps in field experiments with plants, and points out situations that can lead to substantial errors in experimental designs of UV-lamp experiments.

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

• **The mechanisms by which UV-B radiation affects aquatic organisms are now well-known in many cases, but scaling-up to responses of whole ecosystems remains a major challenge. In addition, while there are many laboratory and small-scale field studies of UV effects, there have been no large-scale field investigations in the open ocean.** Investigation of the effects of enhanced exposure to UV-B at the ecosystem level is necessary to determine the impacts on aquatic ecosystem services, such as coastal protection, control of erosion, habitat-fishery linkages,[115] biodiversity maintenance,[116] and other ecosystem functions.[117,118] It is unknown whether altered ecosystems with different functional properties might arise as a result of differential sensitivities of species to UV-B radiation.[119] The deficiency of large-scale field investigations in the open ocean is due to the vast area to be covered and the lack of instrumentation to do this scale of research in the water column.[120–122] As a result, in the open ocean, there has been no substantial experimental work or long-term monitoring other than that using various satellite programs[123–125] to provide baseline biological data, and there likely will not be in the near future.[126,127]

• **Increased exposure of aquatic organisms to solar UV-B radiation has the potential to decrease production in the surface layer of the water column. This is because one of the outcomes of global climate change is a decrease in thickness of the upper mixed layer in the water column of lakes and oceans.** This may further decrease the amount of available nutrients (and thus photosynthetic production) within the upper mixed layer as it is isolated from the flux of nutrients from deep water.[128,129] Degradation of dissolved organic matter by UV-B radiation partially counteracts the lack of (or limitation of) nutrients, and increases biomass and productivity by bacteria and phytoplankton. This in turn also stimulates higher trophic levels and affects biogeochemical cycles. This has been shown not only in oceans,[130] but also in some lakes[131] and rivers.[132] A reduction in photosynthesis due to a decrease in nutrients and/or to an increase in UV-B exposure is likely to result in reduced carbon fixation (see also section 5), and therefore less food for other trophic levels. This may, in turn, have a negative impact on fish stocks.

• **Increased penetration of solar UV-B radiation into certain marine organisms may occur because of increased acidification of the upper mixed layer of the ocean which compromises the calcification of these organisms. This is due to the enhanced uptake of carbon dioxide from the atmosphere into the top layers of the ocean.** Many phytoplankton, macroalgae (seaweeds) and animals (sea shells, worms, corals, *etc.*) possess external calcified skeletons, which protect them from environmental impacts including solar UV-B exposure.[133] Increased acidification impairs the incorporation of calcium carbonate into the shells.[134–136] This decreased protection against UV-B can decrease photosynthesis, thereby reducing carbon fixation.[133,137] In addition, acidification can increase the dissolution of calcified structures in the sediments, which will decrease sequestration of carbon dioxide into the ocean.[138] Thus, as a result of these two processes, less carbon withdrawn from the atmosphere and less calcification of algal and animal species would decrease the "natural" protection of coasts (*i.e.*, compacting and cementing into durable reef formation), exposing beaches and coastal cities to potential damage.[139,140] Combined effects of UV radiation (both UV-A and UV-B) and climate change factors (such as increased carbon dioxide concentration, acidification and temperature) are likely to have complex interactions in aquatic primary producers. Increased temperature can partially counteract the negative effects of UV-B radiation as demonstrated in laboratory experiments and in natural assemblages.[141] One pathway appears to be through increasing the activity and gene expression of an enzyme involved in carbon fixation; thus resulting in increased photosynthesis and primary production.[142]

• **Increased export of UV-absorbing coloured dissolved organic matter from terrestrial and wetland ecosystems to inland and coastal oceanic waters and a resultant decrease in UV transparency of the water are predicted to occur as a consequence of extreme precipitation events in some regions**[143] (see also section 5). Coloured dissolved organic matter (CDOM) is so effective at absorbing UV radiation that it can be considered the ozone of aquatic ecosystems, which reduces the antimicrobial effects of natural solar radiation in surface water used in drinking water supplies.[91] Extreme precipitation, wind, and flooding events enhance runoff and flow of rivers to inland and coastal oceanic waters, which in turn increases CDOM, re-suspends sediments, and reduces transparency of these waters to UV radiation.[132] When re-suspended sediments are exposed to sunlight they may be an important source of both nutrients[144] and dissolved organic matter (DOM).[145] Studies on the Yunnan Plateau and Yangtze River indicate that particulates and phytoplankton, as well as CDOM, are important in controlling penetration of UV in rivers, while CDOM alone is most important in lakes.[146] UV exposure of aquatic plants may also alter both nutrient sources and colour of water in lakes.[147] Recent advances in optical techniques and fluorescence spectroscopy have enabled better quantification of the types, sources, and processing of CDOM in aquatic ecosystems.[148–153] Application of these methods in the future will help us better understand the causes, consequences, and fate of the large increases in DOM that have been observed in many regions and how they influence transparency of aquatic ecosystems to UV.[154]

• **The combined effects of UV-B exposure and elevated temperatures from climate change may alter the species composition of cyanobacteria, which may have significant impacts on the aquatic food webs.** In inland waters, increased prevalence of toxic cyanobacteria would compromise the freshwater available for human consumption.[155,156] For example, it has been shown that exposure to solar UV radiation combined with increased temperature has a very small or no negative impact on a globally important, potentially toxic species of cyanobacteria. However, reductions in photosynthetic efficiency, and changes to morphology and DNA were observed in other ecologically important cyanobacteria where the effects of solar UV radiation appear to be dependent on temperature.[157]

• **Aquatic vertebrates, such as amphibians and fish, are sensitive to UV radiation, but UV-induced damage may be reduced through behavioural responses and/or deposition of eggs at greater depths.** Recent studies have supported the sensitivity of the early life history stages of amphibians to UV radiation, but also the reduction of the potential for UV damage in natural ecosystems. Factors influencing potential damage are the depth at which eggs are deposited, attenuation of UV in the water column, and behavioural responses to UV radiation.[158] Molecular tools that consider genotoxicity, together with the use of environmentally realistic exposure to UV and knowledge of the defences of organisms against UV, are essential for assessing the potential impacts of UV radiation on higher trophic levels.[159]

• **Many invertebrates, including zooplankton, have a variety of successful defences that can reduce the negative impacts of elevated UV exposure. However, the interactive effects of UV and other environmental stressors, including nutrient and food availability, as well as temperature, may pose a greater threat than UV radiation alone.**[160] Zooplankton can detect and behaviourally avoid UV radiation in their daily vertical migration in more transparent lakes and oceans.[161] While differences in tolerance to UV among species do not necessarily lead to changes in community structure of zooplankton,[162] limitations of nutrients, availability of food, and cooler temperatures may all reduce tolerance to UV in zooplankton and larvae of invertebrates.[163–167] UV has a negative effect on calanoid copepods grazing at cooler temperatures.[168] Calanoid copepods are small crustaceans that are some of the most abundant metazoans on Earth (Fig. 3). Increased oxidative damage and developmental abnormalities of sea urchin embryos that were observed in field exposures in areas of high natural UV radiation in ozone-depleted regions may be aggravated by the loss of sea ice.[169] Recent modelling efforts targeting management strategies for penguins and seals indicate that the increase in UV-B radiation due to ozone thinning over Antarctica may have increased the mortality rate of Antarctic krill by as much as 10%.[170] Krill are a primary food source for these marine vertebrates.

Fig. 3 Calanoid copepods are some of the most abundant multi-cellular animals on Earth. They are the dominant primary consumers in the world's oceans and in many lakes. These small crustacean zooplankton influence water quality and are a critical component of aquatic food webs that may influence survival and recruitment of commercially important fish. Shown here are an adult male (left) and a female freshwater calanoid with eggs (right). Note the brighter colour of the male and the eggs *vs.* the female due to higher concentrations of UV-protective compounds. (Photo credit: Robert E. Moeller, with permission).

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

Interactions among stratospheric ozone changes, solar UV-B radiation, and climate change influence biogeochemical cycles in ways that can alter the balance of carbon dioxide uptake and release from the aquatic and terrestrial ecosystems. As summarised in the following bullets, understanding of the magnitude of biogeochemical responses in relation to these interactions remains very limited, and many mechanisms have yet to be incorporated in models of the global biogeochemical cycles.

• **The combined effects of polar stratospheric ozone depletion and climate change are decreasing the capacity of the oceans in the polar regions to take up carbon dioxide from the atmosphere.** Depletion of polar stratospheric ozone in conjunction with increasing concentrations of greenhouse gases can lead to enhanced wind-driven up-welling of carbon dioxide-rich deep water,[171] which alters the balance of CO_2 uptake and release from the oceans, resulting in localised reductions in the net uptake of CO_2[172] (see sections 1 and 6). Delayed recovery of polar stratospheric ozone due to climate change[173] may cause a positive feedback; potentially further increasing concentrations of CO_2 in the atmosphere. Future changes remain difficult to quantify due to uncertainties in the timing of recovery in stratospheric ozone[172–174] and the challenges of integrating all relevant biological and physico-chemical processes into models.

• **Reactions driven by solar UV radiation, coupled with a range of effects caused by climate change, can significantly alter carbon cycling in aquatic and terrestrial ecosystems by changing the nature and biological availability of organic carbon and nitrogen.** Climate change is altering precipitation patterns[5,175–177] and enhancing the frequency and amplitude of climate extremes.[176] These changes in continental hydrology show great geographical variation and modify the run-off of terrestrial organic carbon into aquatic systems. In aquatic systems, solar UV radiation has multiple effects on organic matter, including the enhanced dissolution of particulate organic carbon (POC) and nitrogen.[144,145,178] In addition, solar UV can alter the biological availability of organic carbon to heterotrophic bacteria, which in turn, may increase the microbial production of CO_2.[153,179–181] In terrestrial ecosystems, organic compounds (particularly lignin) in litter (dead plant material) are sensitive to degradation by solar UV radiation. Recent studies have shown that break-down by UV radiation can control the rate of abiotic degradation of plant litter,[173] and that photodegradation of lignin also enhances microbial decomposition of plant litter.[182–184] The net effect of these UV-induced processes suggests an increased release of CO_2 from aquatic and terrestrial systems, potentially contributing to future climate change.

• **The combined effects of changes in solar UV-B radiation and climate can reduce biological carbon fixation in aquatic systems and thus modify oceanic uptake of CO_2.** UV-induced photobleaching of coloured dissolved organic matter (CDOM)[179] enhances the exposure of marine organisms to UV-B radiation due to increased penetration of UV in the water column. Negative impacts on photosynthetic marine organisms caused by exposure to solar UV-B radiation (see section 4) reduce biological fixation of CO_2, which can result in reduced storage of carbon-containing detritus in deeper layers of water, although the balance of this and other biological and physico-chemical processes acting on carbon storage remains unclear. Photobleaching of CDOM may increase due to stratification (layering[185]) of the ocean related to climate change and acidification. Climate change may also reduce up-welling and availability of nutrients for phytoplankton,[186,187] resulting in further interactions with solar UV radiation on biological fixation of carbon.

• **UV-induced carbon emissions to the atmosphere are likely to increase with projected shifts to warmer and drier conditions, such as in the Mediterranean and in western North America; a trend towards increased droughts in the Amazon and East Asia will also likely contribute to the UV-induced carbon emissions.** Arid lands currently occupy more than 30% of the terrestrial land surface and are expanding.[188] There is increasing evidence that carbon cycling in these ecosystems is strongly linked to UV-induced processes,[189–193] although some short-term studies have highlighted the importance of other factors affecting loss of carbon.[194,195] Large emissions of carbon dioxide due to photodegradation of organic matter by UV have been shown in a broad range of ecosystems, including arid grasslands,[193] deserts, and prairies,[190] as well as in models for arid and arctic zones.[196] If current predictions of increased aridity for some zones are correct,[197,198] the ecological significance of these UV-driven processes for carbon loss from terrestrial ecosystems is expected to increase.

• **Exposure to solar UV radiation affects below-ground as well as above-ground processes in terrestrial ecosystems, with consequences for ecosystem carbon balance.** In non-arid terrestrial ecosystems, above-ground exposure of plants to solar UV radiation can influence below-ground growth of roots and function of roots, and the microbiology of the soil.[199] Exposure to experimental increases in UV-B radiation can affect microbial biomass near the roots and reduce soil-respiration in agricultural systems[190,200] and peatlands,[201] which can translate into modest increases in carbon in soil and emissions of non-methane volatile organic compounds.[202] Thus, it is increasingly clear that the balances between different mechanisms through which solar UV radiation influences the carbon balance of terrestrial ecosystems may be very different between arid and non-arid regions.

• **There is increasing understanding of natural sources of nitrous oxide (N_2O) from oceanic and terrestrial ecosystems.** The oceans account for around 30% of the natural sources of N_2O, an important greenhouse gas and important precursor for ozone-depleting gases.[199] It has recently been identified that Archaea (a widely distributed class of bacterioplankton) are a major source of this oceanic N_2O.[203]

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

• **Depletion of stratospheric ozone affects weather patterns and air quality at ground level.** Circulation in the lower atmosphere (and hence meteorological processes) in the southern hemisphere is altered by depletion of stratospheric ozone.[5,174] These effects include latitudinal shifts in wind currents (mid-latitudinal jets)[5] and increased precipitation (10% relative to the current climatology) in the southern subtropics.[5] It is well established that meteorological processes affect air quality. For example, in Melbourne, Australia, *ca.* 25% of the variance in ground-level ozone can be explained by local meteorological variables such as temperature and wind speed.[204] Similar results were reported for the northern hemisphere.[205] Changes in stratospheric ozone need to be considered as a long-term modifier of local weather patterns and associated air quality. These effects of stratospheric ozone should be incorporated into models used for predicting future air quality.

The projected recovery of stratospheric ozone has been calculated to offset much of the influence of climate change on meteorological processes during the 21st century in the southern hemisphere. These changes in atmospheric circulation and precipitation[174,206] are likely to affect long range transport and removal of pollutants from the troposphere, and therefore the intensity and frequency of occurrence of local pollution events. This will have implications for human health, plants, and environmental processes as discussed above (see sections 2–5). This should be considered in the predictions of future air pollution events.

• **Hydroxyl radicals (•OH) generated by UV-B-induced photo-dissociation of tropospheric ozone, are the main cleansing agents of the troposphere, and are responsible for the removal of many pollutants and some greenhouse gases from the atmosphere.** The new measurements of •OH bring observations into better agreement with models,[207] in particular for the inter-annual variability of global •OH amounts. These measurements better account for the global burden of methyl-chloroform and its rate of change due to •OH. They also increase confidence in modelled projections of future concentrations of •OH under different ozone-recovery and climate-change scenarios.

• **Recent evidence suggests that a significant fraction (up to 30%) of hydroxyl radicals in the troposphere can be produced from photo-dissociation of nitrous acid (HONO).** Because the photo-dissociation of HONO occurs mostly at UV-A wavelengths, this mechanism of •OH production is less sensitive to UV-B radiation (and hence depletion of stratospheric ozone) than previously recognised mechanisms. The sources of HONO have not been completely identified, but at least some may be of biogenic origin from soil microbes and leaves of plants exposed to UV-B[199] and may be affected by human activities, such as agriculture.[208] This source of •OH should be considered in future estimates of air quality.

• **Estimates of the human health and environmental impact of air pollution highlight the potentially large impact of the coupled effects of stratospheric ozone depletion and climate change.** UV-B radiation is an essential ingredient in the formation of many photochemical pollutants, including ground-level ozone and a large portion of fine particulates. Recent studies confirm the potentially large adverse effects of these pollutants on human health and vegetation. A study using atmospheric modelling has suggested that ground-level ozone was associated with an estimated 0.7 ± 0.3 million deaths/annum and particulate matter ($PM_{2.5}$) was associated with 3.7 ± 1.0 million deaths per annum.[209] These deaths are the equivalent of 6.3 ± 3.0 and 30 ± 7.6 million years of life lost, respectively. Although some controversy exists,[210,211] these results show the importance of UV radiation and changing climate in the causation of disease in humans. A meta-analysis of environmental effects of ozone[212] showed that statistically significant reductions in number of seeds (16%), number of fruit (9%) and weight of fruit (22%) result from exposures to ambient concentrations of ozone as compared to pre-industrial concentrations (<10 parts per billion (ppb)). Elevated concentrations (70–100 ppb) resulted in greater reductions in yield (27%) and weight of individual seeds (18%). Because of the importance of UV-B radiation in these processes, depletion of stratospheric ozone and interactions with climate change will have indirect but potentially large effects on the health of humans and crops.

• **Regulations directed at lowering ground-level ozone will have only a small effect on UV radiation transmitted to the surface. Therefore, quality of air at ground-level can be improved without significant increases in exposures to UV radiation.** A new modelling study for the eastern two-thirds of the United States indicates that reductions in the ground-level standard for ozone from 84 to 70 ppb will result in a population-weighted UV radiation increase of 0.19 ±0.06%,[213] about an order of magnitude lower than previously published estimates.[214]

• **Aircraft-based observations of the vertical distribution of UV radiation are becoming more widely available and will enable better predictions of the spatial and temporal distribution of pollutants of concern for human and environmental health.** These observations[215] reveal the vertical structure of UV radiation above and below clouds (actinic flux) and thus provide better evaluation of models of the photochemical processing of air pollutants in the troposphere.

• **Interactions between greenhouse gases, resulting from the coupling of stratospheric and tropospheric chemical processes, have been identified.** Increases in emissions of nitrous oxide (N_2O) lead to a partial decrease in concentrations of methane (CH_4). This interaction occurs *via* the effects of N_2O on stratospheric ozone depletion, UV radiation, and abundance of tropospheric •OH. The increase of N_2O from 260 ppb (pre-industrial times) to present-day 320 ppb has offset *ca.* 18 ppb of the methane concentration increase.[216] Although this offset is only about 1% of the current concentration of CH_4, such interactions between the chemical and climatic effects of various long-lived trace gases need to be considered as their concentrations continue to increase.

• **New data suggests no significant increased risks from trifluoroacetic acid (TFA) to humans and the environment.** Based on recent modelling, emissions of the HCFC and HFC precursors of TFA from east Asia have been adjusted to improve agreement with measured concentrations,[217] but estimates of total releases to the global environment remain unchanged. In a previous assessment of releases of these and related compounds that degrade to TFA,[218] risks to humans and the environment were assessed as negligible. The new information on regional releases does not change these assessments. Other fluorinated chemicals in commerce,[219] which are *not* substitutes for ozone-depleting substances (ODSs), are degraded in the troposphere with relatively short half-lives (1.1 to 135 days) but are not expected to produce TFA (T. Wallington, personal communication).

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

The currently elevated solar UV levels will result in relatively higher rates of degradation of materials exposed outdoors.

However, the presently available and new stabiliser systems and strategies for substitution of material are likely able to mitigate the effect and maintain useful lifetimes of materials at present levels. This will, however, add to the lifetime cost of using the improved materials.

• **Polymers commonly used in solar cells and optoelectronic devices are degraded by solar UV radiation, affecting their service lifetimes and cost.** Semi-conducting polymers such as poly(3-hexylthiophene) (P3HT) and poly(3-octothiophene) (P3OT), which are used in active layers of solar cells as well as the plastics used in enclosures of solar panels, degrade on exposure to solar UV radiation, thus limiting their service life.[220] While accelerated test methods specific to these materials are still being formulated,[220,221] preliminary results show the light-induced damage in P3HT polymer follows a free-radical process.[222] Complete action spectra for photodamage of these over the solar wavelength range are not yet available. However, in P3OT, exposure to blue light efficiently destroys its semi-conductor characteristics and is therefore more damaging compared to exposure to UV.[223] Multi-walled carbon nanotubes as well as hindered amine light stabilisers (HALS) that are effective with commodity polymers might also be good stabilizers for the P3HT polymer.[224] A better understanding of the photostability of materials used to produce photovoltaic panels will lead to improved technologies for generating clean energy that can help mitigate the effects of climate change and the interactions with ozone depletion.

• **Recent studies show that the effectiveness of nanoscale fillers as light stabilisers in plastics varies with the type and chemistry of the nanocomposite.** Nanoscale fillers (ultrafine particle additives) are increasingly used in formulations of plastics to obtain superior strength and mechanical properties. These are also expected to act as solar UV-stabilisers. Nanoscale zinc oxide (ZnO)-filled polyurethane coatings on steel[225] or in thin films of polyethylene,[226] nano-silica filled polyurethane coatings on polyethylene film[227] and nano-ZnO or nano-titanium dioxide (TiO_2) in clear wood coatings[228] all result in improved photostability of the underlying substrate. The coatings retard the degradation of the surfaces from exposure to solar UV radiation. However, in bulk polyethylenes filled with nanofillers of ZnO,[229] clay or silica,[230] and in polypropylene filled with nanosized calcium carbonate,[231] a decrease in photostability has been observed. These data suggest that the efficacy of nanofillers as light stabilisers observed in coatings or thin films cannot be generalised to include all bulk polymer nanocomposite systems.

• **Wood–plastic composites with a polyethylene surface layer protect the material from UV degradation.** Better technologies that control surface discoloration of wood following exposure to solar UV will increase the service life of these products. Recent work shows that bark extractives (compounds extractible by solvents) incorporated into surface coating formulations act as environmentally friendly stabilisers, and retard the UV-induced discoloration of wood.[232] A hydrophobic polyethylene surface cap layer on wood reduces the loss of natural extractives that act as antioxidants in wood/polyethylene composites.[233] As with surface wax treatment[234] or oxide-filled coatings[235] that stabilise wood against discoloration and reduction of strength, the cap layer also limits intrusion of water into the wood that otherwise promotes biodegradation.

• **A recent model that reliably predicts the surface temperatures reached by different materials exposed to solar radiation outdoors can be used to better interpret weathering data.**[236] Improved modelling of the weathering of materials is critical for designing better light-stabiliser technologies. Rates of UV-induced damage processes in materials increase with temperature[221] and will therefore also be affected by climate change. Using the surface temperatures of plastics exposed to solar radiation in place of the ambient air temperatures in weathering studies results in more accurate estimates of the photoreaction rates.

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