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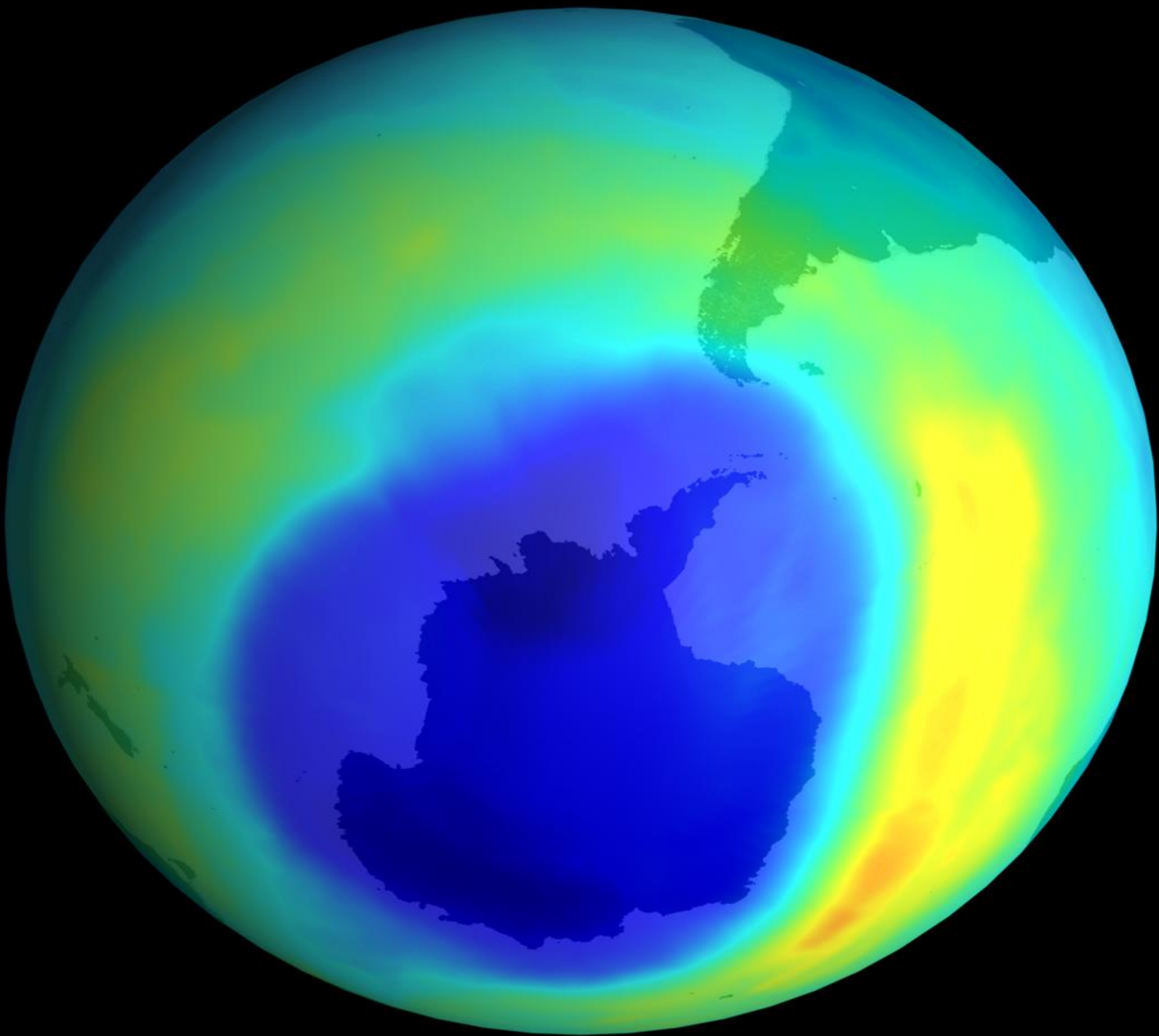

ENVIRONMENTAL EFFECTS OF OZONE DEPLETION AND ITS INTERACTIONS WITH CLIMATE CHANGE: 2014 ASSESSMENT

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ENVIRONMENTAL EFFECTS OF OZONE DEPLETION AND ITS INTERACTIONS WITH CLIMATE CHANGE: 2014 ASSESSMENT

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

Copies of the report are available from
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Front Cover
The ozone hole over Antarctica expanded to a record size of approximately 28.3 million square kilometers on Sept. 3, 2000. The previous record was approximately 27.2 million square km on Sept. 19, 1998. The size of the ozone currently has stabilized, but the concentrations in the center continue to fall. The lowest readings in the ozone hole are typically observed in late September or early October each year. Image from the TOMS science team & and the Scientific Visualization Studio, NASA GSFC

Environmental effects of ozone depletion and its interactions with climate change: 2014 assessment

Introduction

This quadrennial Assessment was prepared by the Environmental Effects Assessment Panel (EEAP) for the Parties to the Montreal Protocol. The Assessment reports on key findings on environment and health since the last full Assessment of 2010, paying attention to the interactions between ozone depletion and climate change. Simultaneous publication of the Assessment in the scientific literature aims to inform the scientific community how their data, modeling and interpretations are playing a role in information dissemination to the Parties to the Montreal Protocol, other policymakers and scientists.

The 2014 Assessment will be published in the journal, Photochemical & Photobiological Sciences, **14**, 2015.

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Review meeting
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ABBREVIATIONS AND GLOSSARY

Abbreviation	Complete term
1,25$(OH)_2$D	1,25-dihydroxyvitamin D
25(OH)D	25-hydroxyvitamin D
Airshed	Airshed, an area where the movement of air (and, therefore, air pollutants) can be hindered by local geographical features such as mountains
AK	Actinic keratosis
AMD	Age-related macular degeneration
AMP	Anti-microbial peptide
ANSI	American National Standards Institute
AO	Arctic Oscillation. A large-scale variation in Arctic wind patterns
AOD	Aerosol optical depth
APase	Alkaline phosphatase
APC	Antigen presenting cell
ASL	Above sea level
BCC	Basal cell carcinoma(s)
Br	Bromine (an ozone depleting chemical)
BRAF	B-Rapidly Accelerated Fibrosarcoma, a gene that is commonly mutated in melanoma
BrO	Bromine monoxide
BSWF	Biological spectral weighting functions
BWF	Biological weighting function
CAS	Chemical Abstracts Service
CAT	Catalase
CC	Cortical cataract(s)
CCl_4	Carbon tetrachloride (an ozone depleting gas)
CCM	Chemistry-climate model (used to predict future changes in atmospheric composition)
CDFA	Chlorodifluoroacetic acid
CDK	Climatic droplet keratopathy
CDKN2A	Cyclin-dependent kinase inhibitor 2A; a gene commonly mutated in melanoma
CDK4	Cyclin-dependent kinase 4; mutations in the gene are found in melanoma

Abbreviation	Complete term
CDOC	Coloured dissolved organic carbon
CDOM	Coloured (or chromophoric) dissolved organic matter
CDR	Carbon dioxide reduction
CFC	Chlorofluorocarbon. Ozone depleting substance (e.g., CFC1_2: dichlorodifluoromethane. CCl_2F_2), now controlled under the Montreal Protocol
CH	Contact hypersensitivity
CH_4	Methane (a greenhouse gas)
$CHCl_3$	Chloroform (an ozone depleting gas)
CIE	*Commission Internationale de l'Eclairage* (International Commission on Illumination)
Cl	Chlorine (an ozone depleting substance)
CMF	Cloud modification Factor
CMM	Cutaneous melanoma
CO	Carbon monoxide
CO_2	Carbon dioxide (a greenhouse gas)
COS	carbonyl sulfide
COT	Cloud optical depth
CPD	Cyclobutane pyrimidine dimer
Cu	Copper (Cu(I) and Cu(II) being different oxidation states)
DIC	Dissolved inorganic carbon
DMS	Dimethylsulfide
DMSP	Dimethylsulfoniopropionate
DNA	Deoxyribonucleic acid
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
DON	Dissolved organic nitrogen
DSB	Double strand break
DTH	Delayed type hypersensitivity
DU	Dobson unit (used for the measurement of total column ozone (1 DU = 2.69×10^{16} molecule cm^{-2})
DVM	Daily vertical migration

Abbreviation	Complete term
EAE	Experimental allergic encephalitis
EDUCE	European Database for Ultraviolet Radiation Climatology and Evaluation
EESC	Equivalent Effective Stratospheric Chlorine. A term used to represent the total chlorine concentration in the stratosphere from all sources of ozone depleting substances (including CFCs, HCl, Cl_2, $ClONO_2$, etc) and a scaled contribution from other halocarbons and bromine, taking its ODP into account
ENSO	El Niño Southern Oscillation. A large-scale climate variability in the Pacific region
EP	Earth Probe (a NASA satellite)
EPA	Environmental Protection Agency
EV	*Epidermodysplasia verruciformis*, a rare recessive genetic hereditary skin disorder associated with a high risk of carcinoma of the skin
Fe	Iron (Fe(II) and Fe(III) being different oxidation states)
FMI	Finnish Meteorological Institute
GHG	Greenhouse gas
Glu I	A pathogenesis-related (PR) protein
GNA11	Guanine nucleotide-binding protein subunit alpha-11, a gene coding for proteins involved in various transmembrane signaling systems.
GNAQ	Guanine nucleotide-binding protein G(q)
GST	Glutathione-S-transferase
GWP	Global warming potential. A measure of the warming effectiveness of a gas compared with CO_2
HALS	Hindered Amine Light Stabilizer
HCFC	Hydrochlorofluorocarbon. Interim replacements for CFCs with small ozone depletion potential (e.g., R22: chlorodifluoromethane $CHClF_2$) to be phased out
HFC	Hydrofluorocarbon, long-term replacements for CFCs
HFO	Hydrofluoro-olefine, replacements for CFCs. An example is 2,3,3,3 tetrafluoropropene (HFO-1234-yf)
Hg	Mercury (Hg0aq and Hg(II) being different oxidation states)
HIV	Human immunodeficiency virus
H_2O_2	Hydrogen peroxide
HNV	Hematopoietic necrosis virus
HONO	Nitrous acid
HPV	Human papillomavirus

Abbreviation	Complete term
HSV	Herpes simplex virus
HY5	Transcription factor HY5, which is a key downstream effector of the UVR8 (UV-regulatory protein) pathway
IBD	Inflammatory bowel disease
Ig	Immunoglobulin
IL	Interleukin
Ink4a	Murine inhibitor of kinase 4a protein (gene in italics)
IPCC	Intergovernmental Panel on Climate Change
IPF	Immune protection factor
kda	Kilodalton
KNMI	Dutch National Institute for Weather, Climate and Seismology (Netherlands)
L•	Lipid radical
LER	Lambertian equivalent reflectivity
MAAs	Mycosporine-like amino acids
Mb	Megabase, equal to 1 million base pairs
MC1R	Melanocortin 1 receptor, a gene coding for proteins involved in regulating colour of mammalian skin and hair.
MCC	Merkel cell carcinoma
MDD	Minimal vitamin-D dose
MED	Minimal erythema dose
MHC	Major histocompatibility complex
MS	Multiple sclerosis
mtDNA	Mitochondrial DNA
N_2O	Nitrous oxide (a greenhouse gas that is also a source of NO_2)
NAO	North Atlantic Oscillation. A large-scale variation and redistribution of atmospheric mass in the Atlantic region producing large changes in the Northern hemisphere dynamics.
NASA	National Aeronautic and Space Administration (USA).
NaTFA	Sodium trifluoroacetate
NC	Nuclear cataract(s)
NCAR	National Centre for Atmospheric Research, USA
NH	Northern Hemisphere

Abbreviation	Complete term
NIMBUS-7	A NASA satellite
NIVR	Netherlands Agency for Aerospace Programmes
NMHCs	Non-methane hydrocarbons
NMSC	Non-melanoma skin cancer
NO	Nitric oxide (an ozone depleting gas)
NO_2	Nitrogen dioxide (an ozone depleting gas)
NOAA	National Oceanic and Atmospheric Administration, USA
NOAEL	No observed adverse effect level, a level of exposure below which no adverse effects are observed in a test organism, similar to NOAEC
NOEC	No observed effect concentration, a concentration of exposure below which no effects of any kind are observed in a test organism
NOEL	No observed effect level, a level of exposure below which no effects of any kind are observed in a test organism, similar to NOEC
NO_X	Nitrogen oxides
NP	Nanoparticle
O_3	Ozone
OA	Organic aerosols
OCA	Oculocutaneous albinism
OCS	Carbonyl sulfide
ODP	Ozone depletion potential. The ratio of the impact on ozone of a chemical compared to the impact of a similar mass of CFC-11. Thus, the ODP of CFC-11 is defined to be 1.0
ODS	Ozone depleting substance(s) (e.g., CFCs)
•OH	Hydroxyl radical (and important atmospheric cleaning agent)
OMI	Ozone Monitoring Instrument (on board the Aura satellite)
OTR	Organ transplant recipients
P	Phosphorous
PAH	Polycyclic Aromatic Hydrocarbon
PAM	Pulse amplitude modulated (fluorescence), a measure of the efficiency of photosynthesis
PAR	Photosynthetically Active Radiation, 400-700 nm waveband
PAUR II	Photochemical Activity and solar Ultraviolet Radiation campaign 2

Abbreviation	Complete term
pCO_2	Partial pressure of carbon dioxide
PEC	Predicted environmental concentration
PER	Photoenzymatic repair
PFBI	Perfluoro-n-butyl iodide, a substitute for CFCs used as a solvent for cleaning during the maintenance of aircraft
Pg	Peta gram ($1x10^{12}$ grams)
PHR1	The gene encoding CPD photolyase
PLE	Polymorphic light eruption
PM	Particulate matter (aerosols in the atmosphere)
PM2.5	Particulate matter in air that smaller than 2.5 µm and is inhaled deeper into lungs than larger particles (PM10)
PM10	Particulate matter in air that smaller than 10 µm
PNEC	Predicted no effect concentration
POC	Particulate organic carbon
POM	Particulate organic matter
POP	Persistent organic pollutant
ppm (ppb)	Parts per million. A mixing ratio of 1 molecule of a substance per million molecules of air. Similarly, ppb is parts per billion, one molecule per billion molecules of air.
PR	Pathogenesis-related proteins
PS	Polusulphone, a thermoplastic that contains sulfur and is resistant to high temperatures
PSC	Posterior subcapsular cataract(s)
PSC	Polar stratospheric cloud (ice crystals which form at high altitudes in Polar regions when the temperature is below a critical threshold)
PSI	Photosystem I
PSII	Photosystem II
Ptc	Murine patch protein (gene in italics)
PTCH	Human patch protein (gene in italics)
QBO	Quasi biennial oscillation (a shift in wind patterns - especially over the tropics - with a period of approximately 2.2 years)
RA	Rheumatoid arthritis
RAC1	Ras-related C3 botulinum toxin substrate (gene in italics); mutations of the gene are found in melanoma

Abbreviation	Complete term
Radiative Forcing	A measure of the influence a factor (e.g., GHGs, ice albedo, tropospheric aerosols, etc.) has in altering the balance of incoming solar and outgoing infrared irradiance ($W\ m^{-2}$) in the Earth-atmosphere system. It is an index of the importance of the factor as a potential climate change mechanism. Radiative forcing is approximately proportional to temperature changes at Earth's surface, so a positive radiative forcing is associated with heating in the troposphere
RAF	Radiation amplification factor (a measure of sensitivity to ozone change)
RCP	Representative concentration pathways: Scenarios for future climate resulting from different combinations of economic, technological, demographic, policy, and institutional futures, defined by their total radiative forcing (cumulative measure of human emissions of GHGs from all sources expressed in $W\ m^{-2}$) pathway and level by 2100.
ROS	Reactive oxygen species (•OH for example)
RR	Relative risk, usually of increased risk above background of contracting a disease. The RR of background incidence of the disease is 1
RT	Radiative transfer
SAGE	Stratospheric Aerosol and Gas Experiment, a satellite-based instrument
SCC	Squamous cell carcinoma
SCCC	Squamous cell carcinoma of the cornea and conjunctiva
SD (SE)	Standard Deviation, a measure of the variance of a value. Standard Error is a similar term
SED	Standard erythemal dose
SH	Southern hemisphere
SPF	Sun protection factor
SOD	Superoxide dismutase
SODIS	Solar disinfection
SO_X	Oxides of sulfur
SSA	Single scattering albedo, quantifies the absorption efficiency of aerosols
STAT	Signal transducer and Activator of Transcription, a gene that regulates many aspects of growth, survival and differentiation in cells
SZA	Solar zenith angle in degrees (= 90°, the solar elevation angle from the horizontal)
TB	Tuberculosis
TFA	Trifluoroacetic acid
Th1	T-helper 1
Th2	T-helper 2

Abbreviation	Complete term
TiO_2	Titanium dioxide
TOC	Total ozone column
TOMS	Total Ozone Mapping Spectrometer, a satellite-based instrument
Treg cell	T-regulatory cell
Troposphere	Lowest part of the earth's atmosphere (0-16 km)
UCA	Urocanic acid
UML	Upper mixed layer, of water in lakes or the ocean
UNEP	United Nations Environment Programme
UV	Ultraviolet. Wavelengths from 100 nm to 400 nm. Ozone and other atmospheric gases progressively absorb more and more of the radiation at wavelengths less than 320 nm. Only those greater than 290 nm are transmitted to the Earth's surface
UV-A	Electromagnetic radiation of wavelengths in the 315 to 400 nm range (weakly absorbed by ozone)
UV-B	Electromagnetic radiation of wavelengths in the 280 to 315 nm range (strongly absorbed by ozone)
UV-C	Electromagnetic radiation of wavelengths in the 100 to 280 nm range (solar UV-C is not transmitted to Earth's surface)
UV_{eff}	UV irradiance weighted by the spectral sensitivity of an effect, integrated over wavelength.
UV_{ery}	Erythemally-weighted UV irradiance, where the irradiance is weighted by the erythemal action spectrum
UVI	UV index. A measure of erythemally-weighted UV for providing information to the public. UVI values greater than 10 are considered "extreme" by the WHO. If UV_{ery} is specified in units of W m^{-2}, then UVI = 40 x UV_{ery})
UVR	Ultraviolet radiation
UVR8	UV-regulatory protein
VDR	Vitamin D receptor
VOC	Volatile organic compound (s)
WHO	World Health Organization
WMO	World Meteorological Organization
WOUDC	World Ozone and UV Data Centre
XP	*Xeroderma pigmentosum*, recessive genetic disorder of DNA repair in which the ability to repair damage caused by UV radiation is compromised
ZnO	Zinc oxide

Environmental Effects of Ozone Depletion and its Interactions with Climate Change: 2014 Assessment. Executive Summary

Ozone Depletion and Climate Change

- **The Montreal protocol continues to be effective.** The Scientific Assessment Panel of the Montreal Protocol on Substances that Deplete the Ozone Layer concludes that atmospheric abundance of most controlled ozone-depleting substances (ODSs) is decreasing. There are several indications that the global ozone layer is beginning to recover from ODS-induced depletion. However, the variability of the atmosphere and the influence of climate change have hindered a definitive attribution of the observed global ozone increases since 2000 to the concomitant ODS decreases. In Antarctica, large ozone depletion continues to occur each year. In the Arctic, ozone depletion is generally less pronounced than in Antarctica but more variable: the very high stratospheric ozone concentrations observed in the spring of 2010 were followed by record-low concentrations in spring 2011.

- **As a result of the success of the Montreal Protocol in limiting ozone depletion, changes in UV-B irradiance measured at many sites since the mid-1990s are due largely to factors other than ozone.** Increases in UV-B irradiance (280-315 nm) ranging from 5 to 10% per decade have been reported for several northern mid-latitude sites, caused predominantly by reductions in cloudiness and aerosols. However, at some northern high latitude sites, UV-B irradiance has decreased during that period mainly due to reduction in snow- or ice-cover. Because of the large natural variability, any responses of UV-B irradiance to stabilisation of the concentrations of stratospheric ozone and possible beginning of a recovery are not yet detectable in the measurements.

- **Large short-term increases in UV-B irradiance have been measured at some locations in response to episodic decreases of ozone at high latitudes.** For example, the low ozone in spring 2011 in the Arctic increased the erythemal (sunburning) dose averaged over the duration of the low-ozone period by 40-50% at several Arctic and Scandinavian sites. Corresponding increases over Central Europe were estimated to about 25%.

- **Future levels of UV-B irradiance at high latitudes will be determined by the recovery of stratospheric ozone and by changes in clouds and reflectivity of the Earth's surface.** In Antarctica, reductions of up to 40% in mean noontime UV Index (UVI) are projected for 2100 due to the continuing recovery of ozone. These reductions are comparable in magnitude with the increases in UVI that occurred in the past due to ozone depletion. Because of the anticipated increases in cloud cover, the UVI is projected to decrease by up to 7% at northern high latitudes. Reductions in surface reflectivity due to ice-melt will continue to contribute to reductions in UVI by up to 3% in the margins of the Antarctic continent and by up to 10% in the Arctic, but confidence in the magnitude of these effects is low.

- **With continued effective implementation of the Montreal Protocol, future changes in UV-B irradiance outside the Polar regions will likely be dominated by changes in factors other than ozone.** By the end of the 21st century, the effect of the recovery of ozone on UV-B irradiance will be very small, leading to decreases in UVI of between 0 and 5%. Additional decreases of up to 3% in the UVI are projected due to the anticipated increases in cloud cover. Future changes in UVI would be likely dominated by decreases in aerosols, resulting in increases in the UVI, particularly in densely populated areas. For example, increases in the UVI of up to 40% are projected for parts of Asia, reversing the large reductions in UVI that have probably occurred in this region during the second half of the 20th century. The confidence in these effects of aerosol is very low due to uncertainties in the projected amounts and optical properties of aerosols, as well as in future policy on emission controls.

Human Health

- **Changing behaviour with regard to sun exposure by many fair-skinned populations has probably had a more significant effect on human health than increasing UV-B irradiance due to ozone depletion.** The increase in holiday travel to sunny climates, wearing clothing that covers less of the body, and the desire for a tan are all likely to have contributed to higher personal levels of exposure to UV-B radiation than in previous decades. Such changes in behaviour have both adverse and beneficial consequences for health.

- **Immediate adverse effects of excessive UV-B irradiation are sunburn of the skin and inflammation of the eye (photoconjunctivitis or photokeratitis). Long-term regular low-dose or repeated high-dose exposure to the sun causes melanoma and non-melanoma (basal and squamous cell) carcinomas of the skin and cataract and pterygium (a growth on the conjunctiva) of the eye.** The incidence of each of these skin cancers has risen significantly since the 1960s in fair-skinned populations, but has stabilised in recent years in younger age groups in several countries, perhaps due to effective public health campaigns. Cataract is the leading cause of blindness worldwide.

- **The major known beneficial effect of exposure of the skin to solar UV radiation is the synthesis of vitamin D.** Vitamin D is critical in maintaining blood calcium levels and is required for strong bones. People vary in how efficiently their skin makes vitamin D from sun exposure and perhaps in their physiological needs for this vitamin. Vitamin D deficiency might increase the risk of an array of diseases such as cancers, autoimmune diseases and infections. At present it is not clear if the low level of vitamin D is a cause of these diseases, occurs as a consequence of them, or is a marker of other factors that predispose to ill-health.

- **Strategies to avoid over-exposure to solar UV radiation include staying indoors, seeking shade, wearing protective clothing, brimmed hats and sunglasses, and applying sunscreens. These methods should aim to balance the harmful and beneficial effects of sun exposure.** Such a balance may be difficult to achieve in practice as the recommended time outdoors will differ between individuals, depending on personal factors such as skin colour, age, and clothing as well as on environmental factors such as location, time of day, and season of year. Current uncertainties centre on defining an optimal level of vitamin D and the amount and pattern of sun exposure required to achieve the optimum in different individuals. Thus, devising appropriate health messages for the public at the present time is not straightforward.

- **Climate change may affect personal sun-exposure behaviour, but the impact is likely to vary according to season and location.** For example, increasing temperatures may lead to decreased time outdoors in climates where it is already hot, but more time outdoors in cooler climates.

Terrestrial Ecosystems

- **The effects of UV-B radiation on plants are influenced by various abiotic and biotic factors in ways that can have both positive and negative consequences on plant productivity and functioning of ecosystem.** Ozone depletion, increased exposure to ultraviolet-B radiation, and climate change affect biological systems that result in intricate feedbacks and complexity. In mid-high latitudes of the Southern Hemisphere plant productivity has likely decreased slightly due to the increased UV radiation as a result of the ozone depletion. On the other hand, exposure to UV-B radiation can promote plant hardiness, and enhance plant resistance to herbivores and pathogens. It can also improve the quality, and increase or decrease the yields of agricultural and horticultural products, with subsequent implications for food security.

- **Exposure to UV-B radiation can increase or decrease rates of decomposition of dead plant matter (litter), depending on prevailing climate and the chemistry and structure of the litter.** In arid and semi-arid ecosystems (grasslands, savannas and deserts), photodegradation generally increases rates of decay of plant litter and is now being considered as an important driver of decomposition, although uncertainty exists in quantifying its regional and global biogeochemical significance. Changes in the decomposition of plant litter from exposure to UV-B and also UV-A (315-400 nm) and visible radiation have potential consequences for the cycling and storage of carbon and other nutrients.

- **Solar UV radiation has the potential to contribute to climate change via its stimulation of emissions of carbon monoxide, carbon dioxide, methane, and other volatile organic compounds from plants, plant litter and soil surfaces** Mechanisms and sources of emissions of trace gas have been identified in plants and ecosystems. UV radiation together with other abiotic factors, in particular temperature, stimulates these emissions. The magnitude, rates and spatial patterns of the emissions remain highly uncertain at present. These UV radiation processes could increase emissions of trace gases that affect the atmospheric radiation budget (radiative forcing) and hence changes in climate.

- **While UV-B radiation does not penetrate into soil to any significant depth, it can affect a number of belowground processes through alterations in aboveground plant parts, microorganisms, and plant litter.** These include modifications of the interactions between plant roots, microbes, soil animals and neighbouring plants, with potential consequences for soil fertility, carbon storage, plant productivity and species composition.

- **Terrestrial ecosystems in the Southern Hemisphere are being affected by the Antarctic ozone 'hole.'** Resultant changes in precipitation patterns have been correlated with ecosystem changes such as increased tree growth in Eastern New Zealand and expansion of agriculture in South-eastern South America. Conversely, in Patagonia and East Antarctica, declining tree and moss bed growth have been linked to reduced availability of water. A full understanding of the effects of ozone depletion on terrestrial ecosystems in these regions should therefore consider both UV radiation and climate change.

Aquatic Ecosystems

- **Climate change and UV radiation affect phytoplankton productivity and species composition of marine ecosystems.** Phytoplankton (primary producers) are decreasing along the West side of the Antarctic Peninsula due to increased solar UV-B radiation and rapid regional climate change. Change in ice phenology as well as light and nutrient availability may affect species composition. Organisms mitigate UV-B radiation-induced damage by repair mechanisms or by producing UV-absorbing compounds.

- **Interactions between climate change and UV radiation are having strong effects on aquatic ecosystems that will change in the future due to feedbacks between temperature, UV radiation and greenhouse gas concentrations.** Higher air temperatures are increasing the surface water temperatures of numerous lakes and oceans, with many large lakes warming at twice the rate of air temperatures in some regions. Species composition and distribution of many marine ecosystems may change with warmer oceans. For others such as corals, the warming may alter their tolerance of other stressors. This warming also can shift the thermal niche of organisms towards the pole and causes changes in community structure.

- **Warming of the ocean results in stronger stratification that decreases the depth of the upper mixed layer.** The decrease in the depth of the upper mixed layer exposes organisms that dwell in it to greater amounts of solar visible and UV radiation which may overwhelm their capability for protection and repair. Enhanced stratification also reduces upward transport of nutrients across the thermocline from deeper layers. In the polar waters, increasing temperature results in explosions of phytoplankton growth under the ice and around the ice edges.

- **Increased concentrations of atmospheric CO_2 are continuing to cause acidification of the ocean, which alters marine chemical environments with consequences for marine organisms.** Acidification interferes with the calcification process by which organisms, such as phytoplankton, macroalgae and many animals including molluscs, zooplankton and corals, produce exoskeletons protecting themselves from predators and solar UV radiation. Consequently, they become more sensitive to UV radiation, so that they calcify even less and decrease their production of biomass.

- **Climate change-induced increases in concentrations of dissolved organic matter (DOM) in inland and coastal waters reduce the depth of penetration of UV radiation**. Increased extreme precipitation events and enhanced growth of terrestrial vegetation produce greater fluxes of UV-absorbing DOM from the landscape. This creates a refuge for UV-sensitive organisms including some invasive species. Decreased penetration of UV radiation also reduces the natural disinfection of surface water containing viruses, pathogens, and parasites.

Biogeochemical Cycles

- **Climate change modulates the effects of solar UV radiation on biogeochemical cycles in terrestrial and aquatic ecosystems resulting in UV-mediated positive or negative feedbacks on climate.** For example, where photochemical priming plays an important role, changes in continental runoff and ice melting, due to climate change, are likely to result in enhanced UV-induced and microbial degradation of dissolved organic matter (DOM) and release of carbon dioxide (CO_2). Such positive feedbacks are particularly pronounced in the Arctic resulting in Arctic amplification of the release of CO_2 (see next point).

- **Solar UV radiation is driving production of substantial amounts of carbon dioxide from Arctic waters**. The production is enhanced by the changes in rainfall, melting of ice, snow and the permafrost, which lead to more organic material being washed from the land in to Arctic rivers, lakes and coastal oceans. Solar UV radiation degrades this organic material, which stimulates CO_2 and CO emissions from the water bodies, both directly and by enhanced microbial decomposition. New results indicate that up to 40% of the emissions of CO_2 from the Arctic may come from this source, much larger than earlier estimates.

- **The changes in climate associated with the Antarctic ozone 'hole' include changes to wind patterns, temperature and precipitation across the Southern Hemisphere.** More intense winds lead to enhanced wind-driven upwelling of carbon-rich deep water and less uptake of atmospheric CO_2 by the Southern Ocean, reducing the oceans potential to act as a carbon sink (less sequestering of carbon). These winds also transport more dust from drying areas of South America into the oceans and onto the Antarctic continent. In the oceans this can enhance iron fertilisation resulting in more plankton and increased numbers of krill. On the continent the dust may contain spores of novel microbes that increase the risk of invasion of non-indigenous species. The ozone 'hole' has also helped to keep East Antarctica cold, but conversely has helped to make the Maritime Antarctic region one of the fastest warming regions on the planet. These climate-related impacts of ozone depletion on ecosystems may also interact with changing UV radiation, leading to tipping points.

- **The carbon cycle is strongly influenced by interactions between droughts and intensity of UV-radiation at the Earth's surface.** Increased aridity due to climate change and severity of droughts will change the amount of plant cover, thereby increasing UV-induced decomposition of dead plant matter (plant litter). These increased losses could have large impacts on terrestrial carbon cycling in arid ecosystems.

- **Lignin present in all terrestrial vegetation plays a significant role in the carbon cycle, sequestering atmospheric carbon into the tissues of perennial vegetation**. Although it is well known that lignin is one of the components of dead vegetation most resistant to biotic decomposition, new results have shown that lignin is readily decomposed with exposure to solar UV radiation. Consequently, UV-induced degradation of plant litter is correlated with its lignin content, reducing long-term storage of carbon in terrestrial systems.

Air Quality

- **UV radiation is an essential driver for the formation of photochemical smog, which consists mainly of ground-level ozone and particulate matter. Recent analyses support earlier work showing that poor outdoor air quality is a major environmental hazard.** Greater exposures to these pollutants have been linked to increased risks of cardiovascular and respiratory diseases in humans and are associated globally with several million premature deaths per year**.** Ozone also has adverse effects on yields of crops, leading to loss of billions of US dollars each year. These detrimental effects also may alter biological diversity and affect the function of natural ecosystems.

- **Future air quality will depend mostly on changes in emission of pollutants and their precursors; changes in UV radiation and climate will also contribute.** Significant reductions in emissions, mainly from the energy and transportation sectors, have led to improved air quality in many locations. Air quality will continue to improve in those cities/states that can afford controls, and worsen where the regulatory infrastructure is not available. Future changes in UV radiation and climate will alter the rates of formation of ground-level ozone and some particulate matter and must be considered in predictions of air quality and consequences for human and environmental health.

- **Decrease in UV radiation associated with recovery of stratospheric ozone will, according to recent global atmospheric model simulations, lead to increases in ground-level ozone over large geographic scales.** If correct, this would add significantly to future ground-level ozone trends. However, the spatial resolution of these models is insufficient to inform policy, especially for urban areas.

- **UV radiation affects the atmospheric concentration of hydroxyl radicals, ·OH, which are responsible for the self-cleaning of the atmosphere.** Recent measurements confirm that on a local scale, ·OH radicals respond rapidly to changes in UV radiation. However, on large (global) scales, models differ in their predictions by nearly a factor of two, with consequent uncertainties for estimating the atmospheric lifetime and concentrations of greenhouse gases and key air pollutants. Projections of future climate need to consider these uncertainties.

- **No new negative environmental effects of the substitutes for the ozone depleting substances or their breakdown-products have been identified.** However, some substitutes for the ozone depleting substances will continue to contribute to global climate change if concentrations rise above current levels.

Materials

- **A trend towards environmentally sustainable materials in building has increased the use of wood and wood-plastic composites.** Despite this trend, the use of rigid PVC, the most-used plastic in building, will continue to be popular at least in the medium term. Improvements are being developed that make PVC easier to process and environmentally friendly. The effects of solar UV radiation and climate change on the lifetime of PVC building products continue to be a concern.

- **The role of solar UV radiation in creating microplastics debris in the oceans from the weathering of plastic litter on beaches is an emerging environmental issue.** These microplastic particles concentrate toxic chemicals dissolved in seawater and are ingested by zooplankton, thus providing a potential mechanism for transfer of pollutants into the marine food web. While the process has not been studied in any great detail, the production of microplastics will likely increase at high solar UV-B radiation levels and/or elevated temperatures.

- **Nanoscale inorganic fillers can provide superior stability against solar UV irradiation relative to conventional fillers in coatings and plastics.** Nanoparticle fillers in coatings, especially those in clear-coatings on wood or fibre-coatings of textiles, also provide enhanced stability. With nanoparticles that absorb UV radiation, such as the mineral rutile, the stabiliser effect is particularly evident. The benefits of nanofillers in bulk plastics, however, are less clear and more information is needed to assess their efficacy. Nanofillers may provide a low-cost means of stabilising some polymer and wood-based products and help increase service lifetimes in the face of variations in UV radiation or climate change.

- **Clothing and glass can provide protection against exposure to solar UV radiation**. Textile fabrics block the personal exposure to solar UV radiation, whereas glass usually blocks mainly UV-B radiation. Effectiveness of specific fabrics depends on the weave characteristics but can be further improved by surface-treating the fibres with a UV absorber. Glazing for windows is being developed to further improve their thermal properties and also results in increased filtering of the UV radiation with benefits for health of humans and indoor components of buildings and artwork.

Chapter 1. Ozone depletion and climate change: impacts on UV radiation

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Summary

We assess the importance of factors that determine the intensity of UV radiation at the Earth's surface. Among these, atmospheric ozone, which absorbs UV radiation, is of considerable importance, but other constituents of the atmosphere as well as certain consequences of climate change can also have major influences. Further, we assess the variations of UV radiation observed in the past and present, and provide projections for the future. Of particular interest are methods to measure or estimate UV radiation at the Earth's surface. These are needed for scientific understanding and, when they are sufficiently sensitive, they can serve as monitors of the effectiveness of the Montreal Protocol and its amendments. Also assessed are several aspects of UV radiation related to biological effects and health. Implications for ozone and UV radiation from two types of geoengineering methods that have been proposed to combat climate change are also discussed.

In addition to ozone effects, UV changes in the last two decades derived from measurements have been influenced by changes in aerosols, clouds, and surface reflectivity, and possibly by solar activity. Positive trends of UV radiation observed after the mid-1990s over northern mid-latitudes are mainly due to decreases in clouds and aerosols. Despite some indications from measurements at a few stations, no statistically significant decreases in UV-B radiation attributable to the beginning of the ozone recovery have yet been detected.

Projections for erythemal irradiance (UVERY) suggest the following changes by the end of the 21st century (2090-2100) relative to present time (2010-2020): (1) Ozone recovery (due to decreasing ozone-depleting substances and increasing greenhouse gases) would cause decreases in UVERY, which are highest (up to 40%) over Antarctica. Decreases are small (less than 10%) outside the southern Polar Regions. A possible decline of solar activity during the 21st century might affect UV-B radiation at the surface indirectly through changes induced in stratospheric ozone. (2) Projected changes in cloudiness would lead to relatively small effects (less than 3%) except at northern high latitudes where increases in cloud cover could lead to decreases in UVERY by up to 7%. (3) Reductions in reflectivity due to melting of sea-ice in the Arctic would lead to decreases of UVERY by up to 10%, while at the margins of Antarctic the decreases are smaller (2-3%). Melting of sea-ice would expose the ocean surface formerly covered by ice to UV-B radiation up to 10 times stronger than before. (4) Expected improvement of air-quality and reductions of aerosols over most populated areas of the northern hemisphere may result in 10-20% increases in UVERY, except over China where even larger increases are projected. The projected

aerosol effect for the southern hemisphere is generally very small. Aerosols are possibly the most important factor for future UV levels over heavily populated areas, but their projected effects are the most uncertain.

Introduction

For the purposes of the current assessment (2010-2014), which addresses negative and positive effects of solar UV radiation on humans, terrestrial and aquatic ecosystems, materials, and air quality (see other Chapters), we assess short- and long-term changes in ambient UV radiation at the Earth's surface resulting from changes in atmospheric ozone and climate. Effects of ozone on climate and climate on ozone are also discussed. Absorption by ozone is the dominant factor controlling the levels of surface UV-B (280 – 315 nm) radiation for cloud-free and low-aerosol conditions. With the continuing success of the amended and adjusted Montreal Protocol in reducing the concentrations of the ozone depleting substances (ODSs) the focus is now on the detection of possible decreases in UV-B radiation in response to the first signs of recovery of the ozone layer. Changes in climate caused by the increasing concentrations of greenhouse gases may also affect the UV radiation at the Earth's surface indirectly, as detailed below.

Current status of atmospheric ozone

Since the last assessment of ozone depletion[264] efforts to quantify the geographic and temporal variability of ozone have continued through ground- and satellite-based measurements. This extension of observations of ozone by four years has increased the statistical confidence in the estimated long-term changes in total ozone column (TOC). There are indications that the global ozone layer is beginning to recover from depletion caused by ODSs. However, the variability of the atmosphere, the uncertainty of measurements, and the influence of climate change prevent unequivocal attribution of the observed increases in ozone since 2000 to decreases in ODSs.[240, 265]

Ozone at mid-latitudes and the tropics. The present (2008-2012) mean values of ozone relative to the 1964-1980 mean are smaller by ~3.5% in the Northern Hemisphere mid-latitudes (35°N - 60°N) and by ~6% in the southern hemisphere mid-latitudes (35°S - 60°S). In the tropics (20°S - 20°N), no significant changes have occurred in total ozone over this period. The observed average changes in total ozone over time, relative to the 1998-2008 mean, in different latitude bands are shown in Fig. 1.

Following the decline in total ozone between the 1960s and 1990s, levels of total ozone outside the polar regions have stopped decreasing since the late 1990s, consistent with the slow decline of ODSs over the same period.[232] Several datasets indicate that total ozone has increased by ~1% since 2000 in the latitude band 60°S - 60°N in response to stratospheric ozone recovery. However, there is disagreement about the magnitude and statistical significance of this increase.[265] Presumably any increase in ozone would have resulted in a corresponding decrease in surface UV-B radiation at the Earth's surface, by analogy with the increases in UV-B radiation observed for the ozone decline.[263]

Amounts of total ozone are subject to large year-to-year variability caused by variations in atmospheric circulation. Examples include the unusually high values in 2010 and low values in 2011 in the northern hemisphere mid and high latitudes. Because of these large variations, the relatively small increases in total ozone expected by the recent decline of ODSs are still not statistically significant.[33, 42] Without removal of these circulation effects, attribution of ozone recovery to decreases in ODSs would not be detectable even in Antarctica before the period 2017-2021.[94, 95] Separation of recent changes of ozone into contributions by ODSs, greenhouse gases (GHG), and natural low-frequency variability

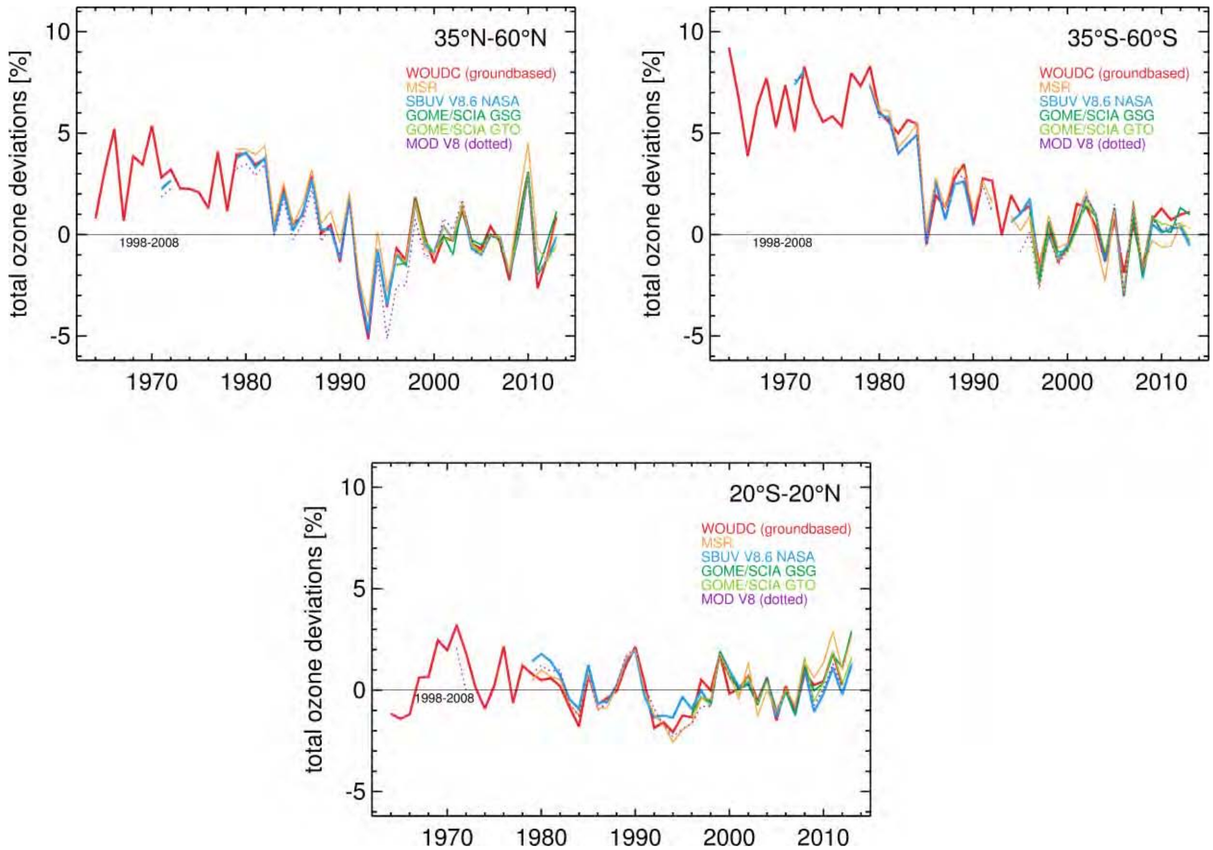

Fig 1. Total column ozone annual mean deviations relative to the 1998-2008 mean for different latitude bands as derived from different ground- and space-based datasets. Adapted from WMO 2015[265]

remains challenging. For example, after removing the variations caused by the solar variability from satellite data for total ozone, the residuals averaged over the band 60°S- 60°N show a decline of about 5% between 1980 and 2000, followed by a partial recovery after about 2000.[276] However, significant sporadic reductions in total ozone have been observed in geographically localised areas at high latitudes in South America[56] and in northern high- and mid-latitudes,[152] showing that the ozone depletion problem is not yet fully solved.

Analysis of the variability of extreme values in the longest time series of total ozone (Arosa, Switzerland, starting in the 1920s) has revealed an increasing frequency of both low-ozone and high-ozone events, which dominate trends in the 1970s and 1980s. After removal of the extreme events from the original time series, the overall downward trend in the period 1970-1990 is reduced from 2.4% per decade to 0.9 % per decade.[196, 197] However, since the extremes are relative to the long-term climatology, the values that were removed also include small values that have been caused by the increase in ODSs during that period. A similar study for Sonnblick, Austria, over a shorter period (1994-2011), revealed a decline in the frequency of low-ozone events and an increase in high-ozone events.[76]

In the northern hemisphere, the increase in tropospheric ozone from precursors (CO, NO_x, and hydrocarbons) since pre-industrial times nearly equals the decrease in stratospheric ozone from increases in ODSs. In the southern hemisphere, the decrease in stratospheric ozone dominates the total ozone column. Currently, the impact of increasing N_2O, a source gas that leads to formation of reactive nitrogen in the stratosphere, on ozone almost cancels the globally averaged increases from climate change effects[193] (see discussion below).

Our present understanding is that the present levels of global total ozone are still less than the mean levels in the period 1960-1980. Over most latitudes, total ozone values have stabilized after the mid-1990s, but the year-to-year variability has increased relative to the period before 1990, precluding the unequivocal detection of possible increases expected from the observed decline of ODSs concentrations.

Ozone at high latitudes

Over the high latitudes (63°-90°) of both hemispheres, ozone depletion continues to occur during winter and spring. Compared to average values before 1980, the 2010-2013 mean total ozone is lower by ~27% in the southern hemisphere in October and by ~10% in the northern hemisphere in March.[265]

The Antarctic ozone hole has continued to appear each spring. The evolution of total ozone in Antarctica over the last decade has been significantly affected by variations in stratospheric temperature and circulation, which have masked the effect of the decreases in ODSs since the early 2000s. With an accurate account of circulation-induced changes, a small (3-8%) increase in total ozone over Antarctica during the last decade is now apparent.[135, 203, 204] Even without accounting for these circulation effects, reductions in the severity of ozone depletion in Antarctica since the 1990s are now becoming clear.[265] However, uncertainties in methods and measurements preclude a definite conclusion that the recent increases of ozone in Antarctica are due to declining concentrations of ODSs alone.[265]

Any reversal of total ozone trends is not yet apparent in the Arctic spring, where the largest ever ozone loss was observed in 2011.[134, 188] The concentration of ozone in the Arctic stratosphere during spring of 2011 was the lowest since satellite records began in 1979. The minimum daily average column ozone (297 Dobson Units (DU)) was observed in March 2011.[19] This value is 18 DU below the previous record-low observed in March 2000, and 100 DU (25%) below the average for 1979–1988. At some locations and times, amounts of total ozone observed between February and April 2011 were more than 50% below the climatological mean.[11] The fraction of the Arctic vortex area with total ozone below 275 DU is typically near zero for March, but reached nearly 45% in March 2011.[152] In that year, the minimum total ozone in spring was continuously below 250 DU for about 27 days, and values between 220 and 230 DU were observed for about one week in late March,[152] leading to increases in UV-B radiation, as discussed later.

This large chemically-mediated loss of ozone in the Arctic was the result of an unusually prolonged cold period in the lower stratosphere and an anomalously strong Arctic vortex, which weakened the transport of ozone from middle latitudes[111] and facilitated the formation of polar stratospheric clouds (PSCs). These clouds provide surfaces for heterogeneous reactions that activate stratospheric chlorine, which in turn destroys ozone in catalytic cycles. Temperatures below the threshold for the formation of PSCs of about −77°C occurred between December 2010 and early April 2011. Over 80% of the ozone present in January from about 18 to 20 km altitude had been chemically destroyed by late March, which is roughly twice that in the previous record-setting winters of 1996 and 2005.[152] Chemical and transport anomalies for 2011 stand out as extreme events, greater than 2σ (standard deviation), while the total anomaly was nearly 3σ,[111] The amount of ozone loss and the chemistry of the Arctic stratosphere in the spring of 2011 was remarkably similar to that commonly observed in Antarctica, justifying the conclusion that there was an Arctic ozone hole in 2011.[82]

There are indications that this Arctic ozone depletion event contributed to the smaller total ozone values recorded at mid-latitude locations. Measurements at 34 European stations revealed that the total ozone over Western Europe from late March to late April 2011 was 15%-25% less than the mean value for this period over the last decade.[183]

There is no indication that the extreme meteorological conditions that led to the loss of ozone in the Arctic in 2011 were driven by climate change.[188] Severe ozone depletion as occurred in 2011 or even worse could possibly happen over the next decades under similar conditions of long-lasting cold stratospheric temperatures.[225] The effect of these large reductions of ozone on surface UV-B is discussed later.

Effects of depletion and recovery of ozone on climate

Changes in stratospheric ozone influence climate both directly through radiative effects and indirectly by affecting stratospheric and tropospheric circulation.[265] Ozone depletion has been the dominant driver of globally averaged cooling that occurred in the lower stratosphere during the last part of the 20th century,[93] but no statistically significant temperature change has occurred there since the mid-1990s.[215, 238] Episodic warming over this period has occurred due to aerosols after major volcanic eruptions.[215] Cooling of the stratosphere due to ozone depletion over Antarctica is, in turn, the dominant driver of circulation changes in the southern hemisphere troposphere during summer (see also Chapters 3 and 5). According to model simulations, these changes have led to changes in surface wind patterns, pole-ward shifting of the midlatitude maximum of precipitation[119] and increases of moisture in subtropics.[106, 118, 119, 200, 229, 256] Opposite effects for the southern hemisphere circulation and climate would be expected for the future from the projected recovery of stratospheric ozone. However, increases in GHGs would compensate partly these ozone recovery-induced effects on climate.[6, 120, 161, 187, 222, 227] For more detailed discussion on the effects of ozone depletion and recovery on climate see the WMO Scientific Assessment of Ozone Depletion: 2014.[265]

Indirect effects of climate change on surface UV radiation

Climate change may have indirectly influenced the levels of UV radiation in the past by altering the amounts of ozone, UV-absorbing tropospheric gases, aerosols, and clouds in the atmosphere. These influences will likely continue into the future.[110, 265] Future changes in the reflectivity of the Earth's surface, either due to melting of sea-ice and ice-caps at high latitudes[252] or due to reduced snow-cover may also be important. Cooling of the stratosphere resulting from increased concentrations of CO_2 and other GHGs will lead to greater concentrations of ozone in the future because the destruction rates of ozone in the cooler middle and upper stratosphere, outside the Polar Regions, will decrease. However, at high latitudes, where temperatures in the lower stratosphere may drop below the threshold for the formation of PSCs, heterogeneous chemistry on the surfaces of these clouds in the presence of chlorine can potentially lead to rapid loss of ozone. An example of these processes is the annually recurring springtime Antarctic ozone-hole. For the Arctic, chemistry-climate models (CCM) suggest that, while in the near future there is a chance of low springtime ozone in individual years, there is no indication of a formation of regular Arctic ozone holes.[141] Although a much wider area may be susceptible to heterogeneous processes later this century, the projected smaller concentrations of chlorine by that time are expected to moderate the potential for loss of ozone.

Increasing concentrations of GHGs will increase the strength of the primary large-scale transport and overturning of the upper atmosphere (the Brewer-Dobson circulation), leading to decreases of ozone in the tropics and increases outside the tropics. Emissions of CH4 and N2O would also affect the evolution of global stratospheric ozone, particularly in the second half of the 21st century, when concentrations of ODSs are expected to be small.[265] The increases of ozone outside the tropics caused by rising concentrations of GHGs will be partly offset by additional chemical destruction arising from anthropogenic emissions of N2O.[191]

Clouds respond to climate-forcing mechanisms in multiple ways, and feedbacks of clouds can be positive or negative. Climate change is projected to reduce the amount of clouds in the future over most of the tropics and mid-latitudes, due mostly to reductions in low clouds.[110] Changes in clouds in the marine boundary layer are most uncertain. Over higher latitudes (>50°), increases in fraction of cloud cover and optical depth are projected. These would increase the amount of solar UV radiation scattered back to space and, therefore, reduce the UV radiation reaching the Earth's surface. Furthermore, clouds play a critical role in the climate system, since they can increase the planetary albedo, thereby counteracting global warming, but they can also contribute to warming of the troposphere through absorption of infrared radiation emitted from the surface.

Reductions in the fraction of ice and snow cover, as well as changes in their characteristics (e.g., thickness of ice, depth of snow) may influence the exposure of ecosystems to solar UV radiation mainly through: (a) less UV radiation reaching the Earth's surface due to reduced surface reflectivity (see Surface reflectivity, below) leading to less exposure; and/or (b) greater exposure to UV radiation for systems formerly under the ice or snow if that protective cover diminishes. Complete removal of ice would lead to much greater exposure to UV-B radiation, because transmittance of UV-B radiation through the existing snow-covered ice is much smaller than 1%.[144] Recent observations in the Arctic suggest that the summer melt season starts earlier, the winter freeze occurs later, the areal extent of the ice has decreased, and more ice is failing to last through the summer.[44, 136, 153, 179] Under such conditions, it has been estimated that over the course of one melt season nearly 40% more solar radiation would enter the ocean system.[181] In recent years the extent of the northern ocean's ice cover has declined, with large interannual variability;[21] while in Antarctica the sea-ice has been expanding since the 1980s.[179]

The combined direct or indirect effects of these climate change-related factors would likely influence the levels of solar UV radiation in the future and modulate the effects of the projected recovery of ozone. This interaction, which depends on latitude and on the emissions of GHGs, increases the complexity of assessing the future levels of solar UV radiation at the Earth's surface. Projections for these factors by climate models can be used to estimate the UV radiation in the future; however, with large uncertainty, as discussed later.

Other factors affecting UV radiation

As UV radiation propagates through the atmosphere, in addition to being affected by ozone, it is modified through absorption and scattering by atmospheric constituents, including aerosols and clouds, and by reflections on the Earth's surface. The effects of the most important factors are discussed in the following sections based on established knowledge and on new findings, in order to assess the relative importance of those factors on UV irradiance that reaches the surface in the context of ozone and climate changes. In addition to UV-B irradiance, the erythemally weighted irradiance (UVERY) and the UV Index (UVI), both defined below in "Biological effects of UV radiation", are used in the following as these quantities appear frequently in the cited literature.

Aerosols

Aerosols (particles suspended in the atmosphere) interact with solar photons and thus can have a significant effect on atmospheric transmission of solar radiation (see also Chapter 6). These particles may be natural (e.g., wind-generated dust and sea salt), anthropogenic (e.g., sulfate, soot, and organic particles), or a mixture of both. The particles scatter and absorb sunlight, with relative probabilities that are complex functions of their size, shape, and chemical composition. They have important effects on air quality and climate, and a considerable body of knowledge has been developed on their sources, properties, and sinks.[109, 166] Observational methods include evaluation of trends in visibility,[34, 62, 201, 202, 251, 266] in-situ determination of size-resolved chemical and thermodynamic properties,[32, 43, 114, 142] and remote global-scale detection from ground-based networks and satellite platforms. The AERONET network provides total (scattering + absorption) aerosol optical depth, τ, at a wavelength of 340 nm as well as several visible wavelengths; but absorption optical depths, τ_{abs}, are only available at wavelengths of 440 nm and longer.[63, 88] Satellite-based instruments measuring aerosols include the MISR, MODIS and CALIOP.[117, 174, 194] Global climatologies of aerosols have been developed based largely on satellite observations.[126, 273]

Many observations have documented reductions in ground-level UV irradiances in the presence of aerosols.[30, 86, 133, 263] Reductions range from a few percent or less at non-polluted locations, such as New Zealand,[146, 155] to over 50% in polluted cities, such as Mexico City,[176] and can be more than 90% for biomass burning aerosols, such as in Russia in 2010.[36] The reductions are typically greater at UV than at visible wavelengths, implying that the aerosol optical depth (AOD) is larger at these wavelengths as well. Quantitative effects depend on aerosol type, and enhancements compared with clear-skies may even occur in some conditions, such as in bright scattering hazes.[61] Extrapolation from visible wavelengths is often based on a simple power model for AOD:

$$\tau \propto \lambda^{-\alpha},$$

where α, the Ångström exponent, parameterizes the strength of the wavelength dependence and has typical values between 0.5 and 2.0 at visible wavelengths.[63] Extrapolation to UV wavelengths is often a reasonable approximation for scattering but less so for absorption, which is more dependent on chemical composition. Some aerosols (e.g., sea salt, sulfate, and nitrate) have negligible absorption at visible as well as at UV-A (315 – 400 nm) and UV-B wavelengths. For dust and soot, the absorption spectrum is sufficiently broad that UV properties can be estimated by extrapolation from visible wavelengths. However, for organic aerosols, the state of knowledge is extremely poor, as these particles, depending on their origin and environmental conditions (e.g., humidity), have highly variable chemical composition. So called “brown carbon,” mostly composed of combustion-derived organic aerosols, is now recognized as a significant contributor to climate radiative forcing due to its absorption of solar radiation at visible wavelengths[72], and is likely to have even larger effects on UV spectra. Measurements on organic particles derived from burning of biomass show Ångström exponents for absorption as high as 6-7 when extrapolated into the UV range,[103, 127] and UV mass absorption coefficients in the range 1-10 $m^2 g^{-1}$, the latter value approaching that of black carbon.

The total AOD includes both scattering and absorption, but it is predominately the absorption that is most important in reducing the intensity of UV at the Earth’s surface. For example, decreases in AOD account for 4.2% of the UV-A irradiance increase at Thessaloniki during 1998-2006, while the additional

2% increase can only be explained if the absorption efficiency of aerosols has also decreased over that period.[122] The relative importance of scattering is defined by the single scattering albedo (SSA),

$$\omega_o = \frac{\tau_{sca}}{\tau_{sca} + \tau_{abs}} = \frac{\tau_{sca}}{\tau},$$

so that the scattering component is $\omega_o \times \tau$ while the absorption component is $(1 - \omega_o)\times\tau$. Based on radiative transfer model calculations (TUV, http://acd.ucar.edu/TUV) with typical input parameters (TOC: 300 DU, solar zenith angle (SZA): 20°, surface reflectivity: 0.05,), Fig. 2 illustrates how clear-sky surface erythemal irradiance (UV_{ERY}) depends on the total AOD and on SSA, for different target orientations. With non-absorbing aerosols (ω_o = 1), reductions are small and enhancements can even occur for vertically oriented cylindrical surfaces. In contrast, strongly absorbing aerosols (ω_o = 0.6) cause significant reductions in radiation regardless of target geometry.

Direct measurements of ωo at UV wavelengths are difficult because the absorption by aerosols co-occurs with scattering, and with absorption by gases, especially ozone, but, also NO2, or SO2 at UV-B wavelengths. Fig. 3 presents a summary of such studies. Values below 400 nm cluster near ωo ≈ 0.8 - 0.9, below typical visible values of about 0.9 or larger. The different results are almost certainly due to different aerosol types present, and more recent studies noted strong UV absorption in biomass-burning aerosols.[36, 50, 103]

A likely explanation for this enhanced absorption of UV is the presence of organic material in the particles. A major new insight of the past decade is that organic aerosols (OA) are more abundant than previously thought, often exceeding the concentrations of sulfate aerosols.[97, 114, 274] They have both natural and anthropogenic sources, the largest being the photo-oxidation of hydrocarbons emitted by vegetation, but other major sources include combustion of biomass, and the production and use of fossil fuels. Many UV-absorbing organic chromophores have been identified in collected aerosol and rain samples, including conjugated carbonyls and nitrates,[23], nitroaromatics,[59, 275] and organic peroxides.[66] Laboratory-generated OA, such as from smog chamber simulations of the oxidation of biogenic hydrocarbons, are found to absorb below 400 nm but not necessarily at visible wavelengths.[140] Atmospheric aging of OA also appears to increase UV absorption[244], although photo-bleaching has also been reported.[199] Therefore, OA have the potential to induce large variations in surface UV radiation, but quantification is still very uncertain and caution should be used when estimating changes in UV radiation in regions where large concentrations of these organic particles are found.

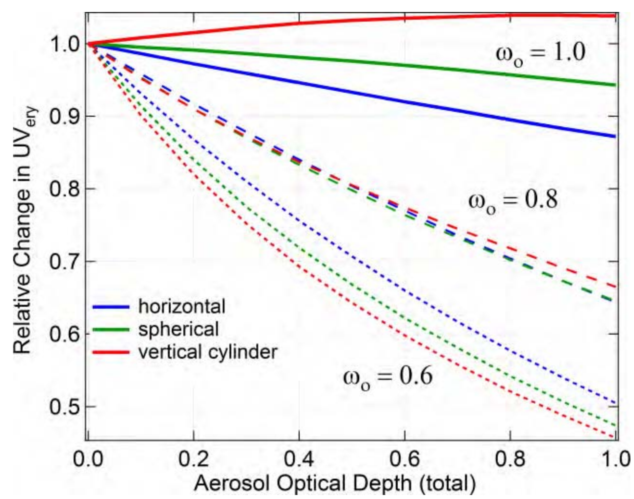

Fig 2. Variation of UV_{ERY} with aerosol optical depth, for different values of the single scattering albedo, ωo, and different receiver geometries (horizontal, spherical, and vertical cylinder).

Trends in aerosols over the past few decades have been derived from analysis of surface radiation network data and satellite-based observations. Decreases in aerosols have occurred over the US and much of Europe[35, 233] and the associated brightening has been detected at visible and UV wavelengths.[58, 164, 271] However, increases in aerosols have occurred in South and East Asia.[268, 273] In some cases, the mass concentrations of aerosols have decreased but the AOD has still increased due to a shift in the size distribution of the aerosol particles.[254] Historical (1850-2000) reconstructions of anthropogenic and biomass burning aerosols have been derived summarising the known historical changes.[139]

Future trends of aerosols are of great interest to climate studies, and scenarios spanning a large range of uncertainties have been developed.[14, 228] Global emissions of sulfate may already have peaked two decades ago and may now be decreasing, while those of fossil fuel black and organic carbon are expected to peak in the next few decades. Evaluation of the effects on UV radiation is relatively straightforward for sulfate and black carbon, but is highly uncertain for organics, especially if these absorb UV as discussed above.

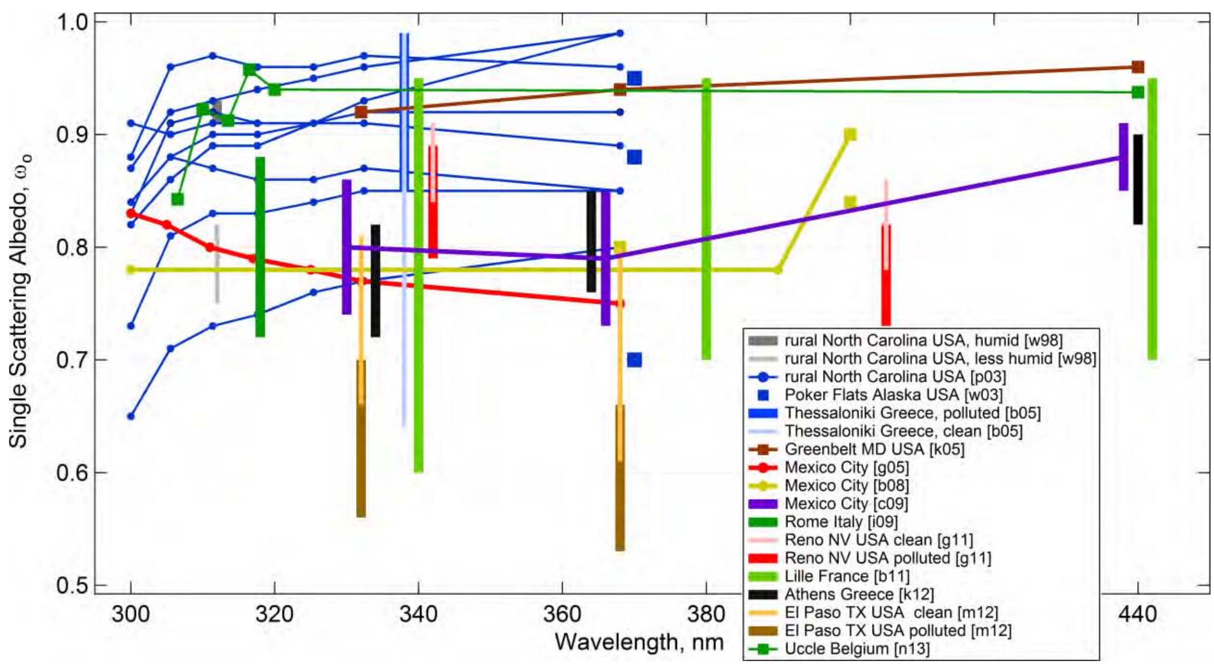

Fig. 3 Summary of available measurements of aerosol single scattering albedo, ω_o, at ultraviolet wavelengths from various sources: w98;[261] p03;[184] w03;[262] b05;[8] k05;[130] g05;[89] b08;[12] c09;[49] i09;[107] g11;[90] b11;[25] k12;[123] m12;[162] n13.[169]

In many cases, it is difficult to separate anthropogenic from natural influences, for example, changes in dust or sea salt from winds affected by climate change, or changes in biogenic aerosols following deforestation or other major changes in land use. This adds uncertainty to future projections because of the challenges in modeling the complex interactions.

Clouds

Clouds play an important role in modifying the solar UV radiation that is received at the Earth's surface, generally leading to attenuation, but in some conditions to enhancement. A recent example of the latter is from measurements in Spain, which have shown that clouds can enhance UVERY by up to 22%.[57] Reductions of irradiance depends on cloud cover, depth and type (water/ice), and can be moderated by surface reflectivity, particularly when the latter is high (e.g., snow, ice), leading to increased irradiance at the surface through multiple scattering of radiation (see discussion in next section). Effects of clouds are more pronounced in the visible than in UV wavelengths. Even under skies covered completely with clouds, the UVI can still be high: maximum UVI values close to 10 and average values of about 3 were measured at an urban location in Brazil (19.9°S; 858 m altitude) under overcast conditions, predominantly of cumulus clouds.[223] Typical noon UVI values at this location under cloud-free skies are about 8.3. Cirrus clouds are formed of relatively large ice crystals which efficiently scatter the solar radiation towards the ground, with only small losses compared with the clear-sky case. According to model calculations based on global estimates of optical depth of cirrus clouds averaged over the period 1984-2007, surface UV-B radiation has been attenuated on average by up to ~2% compared to clear skies.[124]

In the Arctic region, clouds could be affected by the loss of sea-ice. Based on satellite data for the period 2000–2010, a 1% decrease in sea-ice cover leads to a 0.36–0.47% increase in cloud cover, suggesting that a further decline in sea-ice cover would result in an even cloudier Arctic.[148] Due to the complexity of the processes involved, it is difficult to simulate the impact on UV radiation from the combined reduction in sea-ice and increase in cloudiness.

The spatial and temporal inhomogeneity of clouds makes it difficult to accurately assess and quantify their effects on radiation. Thus empirical parameterizations are often used to describe their effect, such as the cloud modification factor (CMF), which is defined as the ratio between the measured surface irradiance to the corresponding clear-sky value. It describes the average effect of clouds, implicitly taking into account the optical thickness of clouds (COT). A clear exponential dependence between the CMF derived from UV measurements and the COT from a Cimel sun-photometer was found; for COT between 10 and 50 the CMF ranged from 0.7 to 0.25.[4]

Since our last assessment[243] there has been little new information on how clouds affect the solar UV radiation received at the Earth's surface. Experimental evidence is constrained by the uncertainty in the measurements and by the complexity of the cloud characteristics. Climate change is projected to alter the amount of clouds over particular areas and, as the ozone layer recovers, clouds will have an important role in controlling the future levels of solar UV radiation that would be available for the ecosystems.

Surface reflectivity

The reflectivity of the Earth's surface, usually referred to as "surface albedo", is defined as the ratio of the reflected to the incident amount of radiation. The radiation reflected upwards from the surface undergoes subsequent scattering by air molecules and particles, resulting in enhancement of the irradiance at the surface. These effects are greater when the surface is covered by highly reflecting material, such as snow or ice. Most materials have low UV reflectivity, with only snow and ice having UV reflectivity greater than 0.5, whereas many surfaces have relatively high reflectivity in the visible. Consequently, effects of ice and snow are more readily apparent for radiation in the UV than in the visible region. The sea-surface also reflects radiation impinging on the water, but less effectively compared to snow and ice. The roughness of surfaces also affects their reflectivity. The fraction of reflected radiation generally increases with the angle of incidence of the photons; hence it depends on season and latitude. In the Arctic and Antarctica, this effect becomes more important due to the larger SZAs and the prevalence of diffuse radiation in these regions. Spectral measurements of UV irradiance at Ny Ålesund, Svalbard, (79°N) revealed an enhancement in clear-sky irradiance at 320 nm of about 15% between two sites affected differently by the reflectivity of the snow-covered surface and the partially ice-covered ocean.

The effect was doubled under overcast conditions.[128] Deposition of black carbon aerosols on snow or ice may substantially reduce the reflectivity, resulting in weaker solar irradiance at the surface. For example during the snow-melt period, the reflectivity at Sodankylä, Finland, decreased from 0.65 to 0.45 at 330 nm and from 0.72 to 0.53 at 450 nm, partly due to deposition of black and organic carbon.[163]

In mountainous regions, reflections of radiation may occur both on the surface (usually covered by snow) and from the top of clouds located below the altitude of the site, while multiple reflections may occur between snow-covered surfaces and the base of the clouds. These complex processes can result in considerable enhancements of incident irradiance. At Sonnblick, Austria, clouds below the observatory increased the average reflectivity by 0.28 ± 0.15, leading to increases in irradiance between 2% and 14% in most (~75%) of the investigated cases. Compared to snow-free conditions, enhancement of 22% in irradiance at 305 nm arose from a mean reflectivity of 0.68 under clear-sky conditions. Analysis of total sky images revealed that enhancements can also be observed when the solar disk was obstructed by clouds or under overcast skies.[224]

In the context of climate change, reductions in surface reflectivity due to melting snow or ice would result in reduction of irradiance over land, but to enhancement of irradiance received at and under the sea-surface in regions where sea-ice disappears. This situation may occur, for example, in the Arctic during the summer period in the 2030s.[252] Model simulations for several scenarios suggest that snow depth in April on Arctic sea-ice would decrease over the 21st century due mainly to the loss of sea-ice area in autumn and, to a lesser extent, in winter,[101] which results in smaller snow accumulation. When snow depth becomes shallower, reflectivity is reduced and, in turn, the UV radiation at the surface is also reduced, while more radiation is transmitted through the ice below the snow.

The sea-ice cover of the Chukchi and Beaufort Seas in the Arctic is currently undergoing a fundamental shift from multiyear ice to first-year ice, which is generally thinner and spatially heterogeneous with a more complex pattern of reflection and transmission of solar radiation.[79, 181] When annual Arctic sea-ice starts melting, it becomes less reflective than old ice, leading to reductions in UV irradiance at the surface. In Antarctica, sea ice is generally expanding rather than shrinking. This expansion is not uniform, but varies regionally. Glaciers in western Antarctica have become thinner[230] and loss of ice sheets is projected for the future in this region.[115, 198]

Reductions in surface reflectivity are expected to play an important role for the levels of UV radiation in the future over areas that in the past were covered by ice or snow, such as the high and polar latitudes and the high mountains. Implications can be expected for ecosystems in these areas, either from the reduced (mainly terrestrial systems) or from the enhanced (mainly aquatic systems) exposure to UV radiation. Over other regions, except over smaller, high-reflecting areas (e.g., salt lakes affected by dust deposition), the changes in reflectivity are likely to be small and thus unlikely to have a significant effect on UV.

Solar activity

Solar activity, particularly the 11-year solar cycle, influences UV-B radiation that penetrates to the surface of the Earth, mainly through changes induced in stratospheric ozone, rather than directly due to increased solar emission. In the upper stratosphere, solar activity affects the photochemical production of ozone by UV-C (200-280 nm), while in the lower stratosphere it affects ozone predominantly by changing the atmospheric circulation.[104] This latter effect is the most important for UV radiation at Earth’s surface because it occurs in the layer where ozone is abundant.

Recent observations from the SIM and SOLSTICE instruments onboard the SORCE satellite revealed an 'exceptionally' low minimum in the solar activity, with larger reductions in the emitted UV-C radiation during the declining phase of the 11-year solar cycle (2004-2008) than at the same phase of previous solar cycles.[150] These reductions were about 8 times larger than expected by semi-empirical models.[91, 92] The inconsistencies of these observations with the perception of variations in solar irradiance from earlier measurements and models have been assessed recently,[67] along with the relevant implications for the variability of sratospheric and total ozone. Inclusion of these new observations of solar variability in photochemical models and in CCMs revealed decreases of ozone in the upper stratosphere and mesosphere (related to photochemical processes), allowing penetration of more UV-B radiation to lower altitudes in the stratosphere and below. However, it has been suggested that penetration of UV-C in the lower stratosphere will enhance the ozone production there (self-healing effect), and in turn reduce UV-B radiation penetration to Earth's surface.[91, 234] The net effect on UV-B has not yet been quantified.

Recent studies[1, 149, 151, 175, 231] suggest that solar activity may evolve into a declining phase in the course of the 21st century resulting in weaker emission of solar UV radiation. CCM simulations for the future showed that such strong reductions in UV-C radiation would lead to significant decreases in the production of stratospheric ozone from the photolysis of oxygen. This would slow down the recovery of stratospheric ozone by more than 10 years or even cancel it,[2] leading to greater levels of UV-B radiation at the ground for as long as the concentrations of stratospheric ozone remain small. These effects are most pronounced in the region between about 40°S and 40°N, where UV-B radiation is already high, and would be likely reinforced by the projected strengthening of the Brewer-Dobson circulation.

Detection of the effects of solar activity on surface UV radiation measurements is difficult, as they are masked by stronger natural variations due to other factors. An average decrease of about 1.8±1.0% in ground-level irradiance from solar maximum to solar minimum for the UV-A and 2.4±1.9% for the 400–600 nm spectral band was reported by correlating 17 years of spectral solar irradiance measurements at the South Pole with the 10.7 cm solar radio flux (indicative of the 11-year solar activity).[78] As the effects appear too large to originate directly from differences in the radiation emitted by the Sun, it was suggested that these decreases are partly due to a small variation in atmospheric attenuation with the solar cycle, with the greatest attenuation occurring at solar minimum. However, there is no experimental proof of this suggestion.

Although direct influence of solar activity to UV radiation at the surface is small, indirect effects, through changes in the production of ozone, can be more important. If a substantial solar minimum occurs in the future, it may influence global climate and the ozone layer, and could lead to increases in UV-B radiation at the surface.

UV radiation changes and trends derived from measurements

Measurements of UV radiation

Ground-based. With few exceptions, e.g., [15, 38] coordinated measurements of UV radiation from the ground started in the late 1980s after the discovery of the ozone hole.[69] It is therefore not possible to directly assess changes in UV radiation for the entire period between the 1960s (i.e., the time before concentrations of ODSs in the atmosphere became important) and the present. Several ground-based networks now provide data records in excess of 20 years with instruments deployed in the U.S.,[81, 125] Canada,[74, 96] South America,[28, 60] Europe,[131, 164, 211, 220, 245] New Zealand,[155, 156] Australia,[87] the Arctic,[20] and Antarctica.[17] Relatively few measurements have been performed historically in Africa, the Middle East, and Asia, but several programs have recently been established in Nepal,[218] Thailand,[26, 112] and China.[105] By the mid-1990s, the technology of UV radiation measurements with spectroradiometers had already reached a level of accuracy that would allow the detection of changes in UV of a few percent at stations with appropriate quality control protocols.[257] A European project has been completed which aimed to provide traceable solar UV irradiance measurements with an uncertainty of less than 2% (http://projects.pmodwrc.ch/env03/). However the methods developed in this activity have not yet been implemented in operational UV monitoring.

Recently, array spectrometers have been adapted for spectral irradiance measurements in the UV. These instruments have been used to quantify the effects of solar UV-B radiation in terrestrial ecosystems (see Chapter 3). However, being single monochromators, they are susceptible to stray light problems in the UV-B.[129, 212] Efforts have been made to determine the uncertainty of this type of instruments.[45, 46] Because of their large uncertainties compared to scanning spectroradiometers, these instruments are not yet widely used in UV monitoring programs.

Spectroradiometric measurements of UV irradiance on a flat, horizontal surface are most common and generally considered the most accurate method to quantify UV radiation. However, this geometry is not the most appropriate to gauge exposure levels of humans and most animals because the anatomical distribution of UV exposure is highly heterogeneous, poorly correlated to surface irradiance, and, in the case of humans, influenced by factors such as posture, orientation to the Sun (see Fig. 2), skin color, clothing, and other sun-protective behaviors.[247] In principle, the most accurate method to quantify human exposure is to measure the incident solar spectral radiance distribution (which may originate from the Sun, the sky, and radiation scattered upward from the ground) and integrate this distribution over all exposed parts of the human body.[214] The development of a system capable of measuring sky radiance at different zenith and azimuth angles within seconds rather than minutes enables new possibilities to study the spectral influence of fast changing cloud conditions without the disadvantages of scanning instruments.[195] This method is still under development and has not yet been reported for exposure studies. In an alternative approach,[247] measured global-horizontal, direct-normal, diffuse-horizontal and upwelling irradiance, were combined with a three-dimensional numerical model of the human body to calculate exposure. An important conclusion of this study as well as of Seckmeyer et al.[214] was that the contribution of diffuse UV radiation to total sun exposure is larger than commonly expected, explaining almost 80% of the cumulative annual exposure dose.

Satellite based. The estimation of UV irradiance at the ground has been repeatedly undertaken from various satellite-borne sensors.[7, 54, 147] As these products are mainly derived by models fed with measured or estimated radiation-related parameters, they are associated with relatively large uncertainties, which vary according to location, season, atmospheric situation and the characteristics of the satellite instrument. Known sources of errors that affect the accuracy of the derived surface UV irradiance include: absorption and scattering by tropospheric aerosols, inhomogeneities of clouds, assumptions or estimations of the surface reflectivity, variability of altitude within the sub-satellite pixel, various modeling parameterizations, and the inability by current satellites to distinguish between clouds and surfaces covered with snow and/or ice. It is important to note that ground-based observations are point measurements while satellite observations are representative for a pixel of several square kilometers. This difference must be taken into account when comparing satellite- and ground-based measurements; particularly when the ground-based instrument is located in a non-homogenous area (e.g., mountains).

In the previous assessment[243] it was noted that, although satellites have the advantage of near global coverage, satellite-borne instruments cannot adequately probe the boundary layer (approximately the lowest 1-2 km) of the atmosphere. Therefore, they tend to overestimate UV radiation when absorbing aerosols are present,[7] particularly under clear skies. In a recent study in Santiago, Chile, a city with heavy air pollution and complex surrounding topography, this effect was quantified, reporting an average overestimation of UVI by about 46% from the Total Ozone Mapping Spectrometer (TOMS) for the period 1995-2007, and by about 47% from the Ozone Monitoring Instrument (OMI) for the period 2005-2007.[28] These results were qualitatively confirmed by two other studies.[47, 54] Similar results were found for four locations in Thailand,[26] with average biases between 40% and 60%. Smaller biases were reported for locations with smaller aerosol concentrations. In France, UVI derived from OMI and the Global Ozone Monitoring Experiment, (GOME-2) was found larger by about 6% during 2008-2009,[113] while in Southern Spain for the period 2004-2008, the average bias was about 12%, rising to 19% for days with large aerosol optical depth (>0.25 at 440 nm).[3] The UVI derived from TOMS has been also compared with ground-based data at 27 stations of the USDA network, showing results consistent with the above studies, with an average positive bias in the satellite estimates of the order of 15% over all sites. Under clear skies, the biases can be either negative (up to 3.4%) or positive (up to ~24%), depending on the amounts of tropospheric aerosols and UV-absorbing air pollutants.[267]

Comparison of satellite retrievals of UV irradiance from OMI with UV spectra measured at six Austrian sites with altitudes ranging between ~600 and ~3100 m concluded that the satellite estimates were significantly smaller (average ratio 0.89, range 0.6-1.35) for most stations due to erroneous correction for effects of clouds.[250] In contrast, under cloud-free conditions, the satellite data were closer to the ground-based measurements, but they cannot distinguish between mountain and valley sites due to the large variability in altitude within a short horizontal distance, smaller than the size of a pixel. The main deficiencies in the satellite retrieval algorithm arose from the incorrect determination of the effective surface altitude and albedo due to the complex topography.

Such deficiencies have been taken into consideration in the Semi-Analytical Cloud Retrieval Algorithm (SACURA) in which the background spectral albedo is properly specified and cloud parameters are derived from the infrared sensors of the satellite.[177] Comparisons of estimates based on satellite data and radiative transfer modelling with observations at two locations in Belgium revealed a good agreement with correlation coefficients 0.88 and 0.91 for UV-B and UV-A irradiance respectively.

Variations of UV radiation in time and space

UV radiation at the Earth's surface varies with season, time of day, latitude, and altitude. It is also affected by the absorption and scattering processes from atmospheric constituents, as discussed above.

Latitudinal variations in annual doses of UV-B and UV-A have been assessed with high-resolution measurements from ground-based spectroradiometers that comply with the quality standards of the Network for the Detection of Atmospheric Composition Change (NDACC)[154] (Fig. 4). For all sites, the annual averages were derived from at least 10 years over periods where trends in irradiance were small. As expected, doses of UV-B and UV-A are generally largest close to the equator and smallest at high latitudes. Doses at high-altitude sites (South Pole, Mauna Loa, Boulder and Summit) are larger than for sites located at similar latitudes but at sea level.[263] This is most obvious when comparing data from Barrow (71.3°N; 8 m altitude) and Summit (72.6°N; 3202 m altitude), where the annual doses of UV-B and UV-A at the latter site are about 58% and 83% larger due to higher elevation and different surface reflectivity, respectively. Surface reflectivity in the order of 0.98 also contributes to the relatively large doses at the South Pole and Summit, while attenuation of UV radiation by aerosols is responsible for the relatively low dose at Tokyo. Latitudinal gradients are stronger in the UV-B than the UV-A region, partly because photons travel a longer path through the atmosphere for the lower solar elevations prevailing at higher latitudes, allowing greater absorption of UV-B radiation by ozone. Another factor contributing to the differences in gradients of UV-B and UV-A is the relatively small ozone column in the tropics. As a consequence, the ratio of annual dose of UV-B/UV-A is roughly 0.03 close to the equator, 0.02 at mid-latitude sites and less than 0.02 at high latitudes (Fig, 4, lower panel). It is interesting to note that the UV-B/UV-A ratios are not very different in polluted locations, such as Tokyo, compared with clean-air sites, suggesting that the optical depth of aerosols in the UV-B is not very different from that in the UV-A region, and/or that the wavelength dependence of the single scattering albedo throughout the UV region is small (see Fig. 3).

It has long been known that mid-latitude UV levels in summer are larger in the southern than in the northern hemisphere.[209] Factors contributing to this disparity include the smaller Sun-Earth distance during the southern-hemisphere summer, plus smaller ozone columns and less attenuation by aerosols at southern latitudes. However, for annual doses, the hemispherical differences are relatively small (Fig. 4, upper panel).

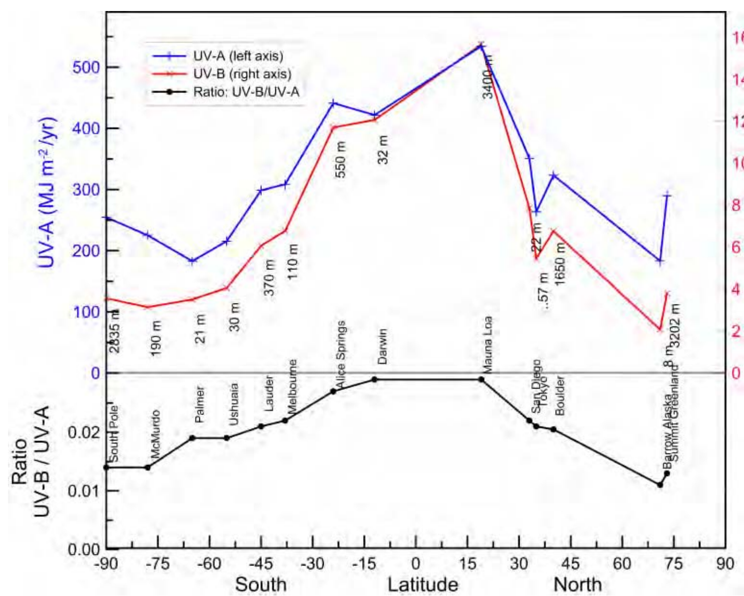

Fig. 4 Latitudinal variation of UV-A (315-400 nm) and UV-B (280-315 nm) annual dose (top) and the ratio of UV-B/UV-A dose (bottom).

Satellite observations indicate that the greatest UV levels at the surface of the Earth occur in the Altiplano region of Peru, Bolivia, Chile, and Argentina, where the UVI in summer may exceed 20.[269] The large UV levels in this region can be attributed to small SZA, overhead Sun, small total ozone, high elevation (hence less aerosol and unrestricted horizon), and minimum Earth-Sun separation in the austral summer. These findings have recently been confirmed by ground-based spectroradiometric measurements at the Chajnantor Plateau (23°S, 67°W; 5100 m altitude) of the Atacama Desert in Northern Chile.[48] The measured UVI peaked at a value of 20 under broken cloud conditions and was 18 for clear skies. Very high UVI values were reported for locations in Tibet in 2008-2010.[170] The measured monthly mean UVI in July was 14.5 in Tingri (28.7°N; 4335 m altitude) and 12.9 in Lhasa (29.7°N; 3683 m altitude), with a peak value of 20.6 in Tingri. Extremely high UV levels (UVI of up to 19 for clear sky and up to 22 under broken cloud conditions) were also measured at sea-level in the tropical Pacific (3.6°S, 85°W), when total ozone was 234 DU.[71] These values are more than double those that are common at northern mid-latitudes in summer.[70] More recently, UVI values higher than 40 have been reported at Licancabur, Bolivia (5916 m altitude).[29] However, these data are inconsistent with the satellite-derived ozone columns. Further work is needed to verify the result.

During the Arctic spring of 2011, when total ozone was extremely small, greatly increased levels of UV radiation were recorded at thirteen Arctic and sub-Arctic ground stations. Measurements of the noontime UVI during the low-ozone episode exceeded the climatological mean by up to 77% at locations in Alaska, Canada, and Greenland, and by up to 161% in Scandinavia.[20] The cumulative UV dose integrated over the duration of the low-ozone period increased by 40-50% at several sites in the Arctic and Scandinavia, and exceeded the climatological mean by more than 3σ at seven sites and by more than 4σ at two sites. Despite these large relative enhancements, absolute UV anomalies remained small (less than 0.5 UVI units at the western-hemisphere sites) or moderate (1.0 and 2.2 UVI units at the Scandinavian sites) because the low-ozone episode occurred at a time when the Sun was still low in the sky. In Alaska, Canada, and Greenland, the UV increases can be explained by low ozone, but at the Scandinavian sites, they were caused by a combination of low ozone and the absence of clouds. Despite the low absolute levels of UV radiation at northern polar latitudes, biological systems during this Arctic event may have been exposed to greater UV than usually experienced.

The small ozone values observed in 2011 in the Arctic propagated to midlatitudes and, as a consequence, ozone columns over Western Europe were 15-25% below the long-term mean between late March and late April 2011.[183] Model assessments suggest that noontime erythemal doses on clear-sky days were larger than usual by about 25% during the affected period. However, such increases have not been confirmed by measurement, so far.

Furthermore, it was found from ground-based and satellite observations that the interannual variability in springtime ozone in the Arctic was correlated with ozone in the summer and explained 20–40% of the summer UV variability at some locations.[121] Particularly for spring 2011, it was estimated that the massive ozone depletion in the Arctic increased the March–August cumulative erythemal clear–sky UV dose in the northern hemisphere outside the tropics by 3–4% compared to the climatological mean, with about 75% of the increase accumulated after the breakup of the polar vortex.

Unusually large UV levels were observed between 11 and 30 November 2009 over the southern tip of South America (~55°S) when the center of the Antarctic vortex became stagnant just south of South America for a three-week period, leading to ozone columns continuously more than 2σ below average. Ground-based measurements for three stations located in this region showed UVI values of 10 to 14, which, for clear-skies, typically only occur at latitudes lower than 40°in the northern hemisphere.[56] Analysis of 30 years of satellite observations revealed that this event was unique for the latitude belt of 52°to 56°S.

In August 2011, southern Australia was affected by ozone-poor air originating from tropical latitudes, resulting in measured UVERY levels of up to 40% greater than normal.[87] This is an example where meteorological factors have produced anomalous reduction of ozone on an almost continental scale and longer duration than previously observed.

The combined effect of all the factors discussed previously may result in very high levels of UV radiation at mid and low latitudes, primarily at high-altitude locations. These high-UV episodes will continue to occur in the future during low-ozone periods, irrespective of the recovery of ozone.

Observed long-term changes in UV radiation

In view of the expected rebound of stratospheric ozone depletion and recovery to levels before the 1980s, an important question is whether this change is reflected in the trends of UV radiation measurements. At most locations, any trends are currently still below the detection threshold imposed by instrument uncertainties and variabilities due to factors other than ozone, such as changes in aerosols, clouds and surface reflectivity. For example, over the period of the peak ozone depletion between the 1980s and 1990s, ozone and cloud effects contributed equally to the UVI increases over populated areas of the northern mid-latitudes.[143]

Long-term changes in UV radiation can be estimated both from space and the ground. Satellite observations have large uncertainties as discussed above. Changes in UV radiation at different spectral bands over the period 1979 to 2008 have been derived from a series of polar orbiting satellite instruments for the latitude range of 55°S to 55°N,[99] and results were summarized in the last assessment.[157, 243] A similar study for the time period 1997-2010 based on measurements of three satellites (TOMS/Nimbus 7, TOMS/Earth Probe and OMI)[108] has qualitatively confirmed the earlier work by Herman.[99] Over this later time period, the derived linear trends in erythemal irradiance (same for UVI) ranged between 0 and +5% per decade between 50°S and 50°N. These positive trends are significant at the 95% level with the exception of the equatorial zone and winter months of both hemispheres. Largest increases were observed during spring and summer at mid-latitudes of the Southern Hemisphere where the largest decrease of ozone was observed (Fig. 5). However, most of the UVERY changes due to ozone have occurred during the 1980s and the early 1990s; therefore, the calculated linear trends do not necessarily reflect a tendency in ozone that would continue into the future. At high-latitudes, satellite-based estimates of surface UV radiation can be too low by up to 50%, when high albedo from snow and ice cover is misinterpreted as clouds.[235] These systematic errors can also affect UV trend assessments. For example, it is difficult to quantify changes in UV radiation from space measurements over high-latitude locations that are affected by sea-ice variability.[99] For these reasons the trends discussed above were derived only for latitudes lower than 55°.

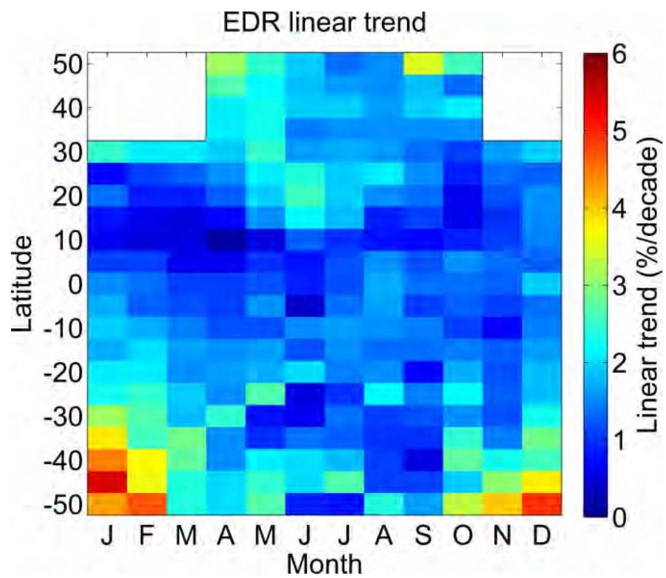

Fig. 5 Monthly linear trends (%/decade) of erythemal irradiance derived from TOMS and OMI data from 1979 to 2010 according to Ialongo et al.[108] All trends are positive. The data are zonally averaged for every 5° of latitude from 50° S to 50° N and represent mostly changes that have occurred in the first half of this period, when ozone depletion was progressing. Adapted from Ialongo et al.[108]

The combined effect of the surface reflectivity (RS), clouds, water haze, and aerosols on UV-A radiation, which is not affected by ozone, can be inferred by the, so-called, "Lambertian equivalent reflectivity" (LER), which represents the equivalent scene reflectivity as seen from space after removal of Rayleigh scattering effects.[137] The atmospheric transparency T is approximately T = (100−LER)/(100 - RS), where LER and RS are expressed in percent. Because the reflectivity of most surfaces is small (typically 2–4 % over land), a decrease of LER will lead to an increase in T by approximately the same amount. The LER at 340 nm during the past 33 years (1979–2011) has recently been analyzed globally[100] and changes in surface irradiance at 340 nm, but without accounting for effects of local air pollution sources, can be inferred from this study. Between 1979 and

2011, most of the decreases in LER (resulting in an increase of surface radiation) occurred over land, with the largest wide-spread decreases taking place over the US (0.97% per decade), Brazil (0.9 % per decade), and Europe (1.4 - 1.9 % per decade). Over India, southern China, and Indochina, LER has increased by 1-1.5 % per decade (Fig. 6). A trend that is twice as large was observed on the west coast of South America, but there was almost no change over most of Australia. These trends can be translated into downward trends in UV-A radiation, caused only by changes in cloudiness and partly in aerosols. In the ocean region near the Antarctic Peninsula (160°W - 50°W), LER has decreased strongly (>2% per decade), probably due to changes in clouds and sea-ice. Neither of these studies took account the effects of absorbing aerosols in the estimates of irradiance. Therefore, these trend estimates may not accurately reflect changes for regions where concentrations of absorbing aerosols and air pollutants have changed over time, such as in urban areas.

The variability of solar UV irradiance at 305 and 325 nm between 1990 and 2011 has been assessed from ground-based measurements at twelve sites in Canada, Europe, and Japan (latitudes between 25°N to 60°N).[272] For these sites at least, this period can be divided into three sub-periods that are characterized by different physical processes. UV radiation decreased during the first period (1991–1994), greatly affected by stratospheric aerosols from the Pinatubo volcanic eruption in 1991. The volcanic stratospheric aerosol layer had two effects: it induced destruction of ozone through heterogeneous chemical reactions[249] and reduced the path-length of UV-B solar radiation through the ozone layer for small solar elevations due to increased scattering by the aerosols.[16] Both mechanisms led to an increase in UV-B at the surface after the eruption in1991, which became smaller in the next years as the aerosol effect decayed. The second period (1995–2006) was characterized by a 1.4% per decade increase in total ozone, coinciding with a significant decline of the aerosol optical depth over the regions of study. This “brightening” effect (increase of the atmospheric transparency T) more than offset the effect of the increase in ozone, resulting in positive UV trends of 9.4% per decade at 305 nm and 8.8% per decade at 325 nm. The third period (2007–2011) showed statistically significant evidence of a slowdown or turning point in the upward trends in UV-B radiation over Canada, Europe, and Japan. These results are consistent with the decrease in LER seen from satellites (Fig. 6) and observations of surface shortwave (300-3000 nm) solar irradiance, which indicate that the brightening effect — which started in the late 1980s and is mostly attributed to changes in cloudiness and aerosols — has slowed down during the last few years or is no longer progressing.[10, 110, 185, 205] However, since some of the sites discussed above[272] are located in urban areas affected by air pollution, results cannot be simply applied to a global scale or to sites located at higher altitudes, where aerosols may evolve differently or remain constant.[172]

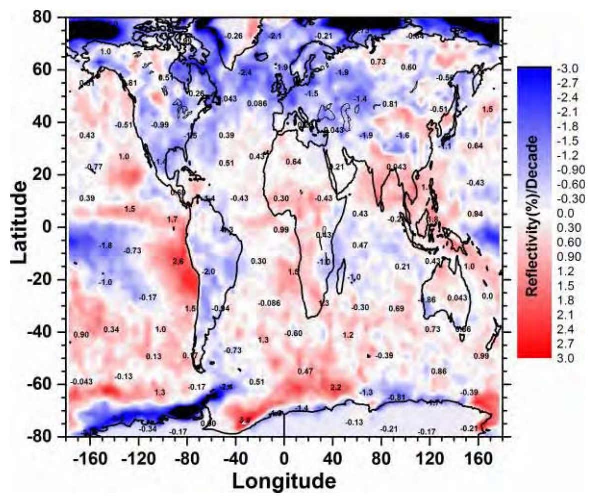

Fig. 6 Trends in LER (combined reflectivity from clouds, aerosols, and the surface) as seen from space. Trends in LER smaller than 0.3% per decade are not statistically significant from zero. Negative trends in LER lead to positive trends in UV-A by approximately the same amount. Trends in LER outside Polar Regions are caused by clouds and not aerosols. Adapted from Herman et al.[100]

Several recent studies reported positive trends in UV at European sites caused by reduction in cloud cover are consistent with satellite observations (Fig. 6). A statistically significant increasing trend of 6.6% per decade in daily maximum UVI from 1993 to 2008 was found for Reading, United Kingdom, presumably caused by reduction in midday clouds, since ozone remained constant.[226] Increases in erythemal dose of 5.5±1.0% (1σ) per decade were found for April-October in the period 1976-2008 from ground-based UV measurement at Belsk, Poland (51°N).[131] At both locations, the total ozone levels had stopped declining in the mid-1990s, and the observed increases in UV were attributed to decreasing attenuation by clouds. In such locations, which are dominated by cloudy weather, any effects from changing aerosols cannot be detected as the optical depth of clouds is much greater than that of aerosols. Similarly, the trend of increasing spectral UV irradiance at Hoher Sonnblick (Austrian Alps, 3106 m altitude) was also attributed to decreasing attenuation by clouds (5.8% per decade during summer), confirmed by synoptic observations of clouds and measurements of duration of sunshine. Spectral irradiance at 315 nm was found to increase between 1997 and 2011 from 9.3% per decade at SZA=45°(spring-summer) to 14.2% per decade at SZA=65°(whole year).[75] Because ozone has been increasing by 1.9±1.3 % per decade over this period, the increase of irradiance at 305 nm was smaller (between 5.1% and 7.9%) and not statistically significant.

Trends in monthly average UVI at Barrow, Alaska (71.3°N), calculated from spectral UV measurements between 1991 and 2011 were not statistically significant, except for October (-14% per decade).[18] This large trend was attributed to decreasing surface reflectivity as the onset of snow cover in autumn has been delayed at this site with a statistically significant trend of 13.6 days per decade. This study emphasizes the importance of climate factors on long-term changes in UV radiation.

After removing the annual variability, UV irradiance at 305 nm was found to decrease with an average rate of 3.9% per decade for 1991-2011 over four northern hemisphere high-latitude stations (Barrow, Sodankylä, Jokioinen, and Churchill), whereas no significant change was found for irradiance at 325 nm, which is only slightly affected by ozone.[65] For the three southern stations examined (Ushuaia, Palmer, and Syowa) no significant changes for either wavelength were found.

The above studies indicate that factors other than ozone have dominated changes in UV radiation during the last two decades at many sites. They also indicate that UV-B irradiance has stopped increasing at mid-latitude locations in response to the slowdown of the decline of ozone.

Simulations of historic changes in UV radiation

As mentioned in our previous assessment,[157, 243] changes in UV radiation over timescales of centuries to a few decades can be estimated using various proxies or simulated variations of factors that may directly or indirectly affect the solar UV radiation at the Earth's surface (see also Chapter 3). Although such estimates have large uncertainties, they are useful in assessing qualitatively the causes of the variations in UV radiation that may have occurred in the past.

A modelling study[255] suggests that levels of UV-B radiation in year 2000 were 2-8% lower than in 1850 over the northern hemisphere and the tropics, and higher by 4% and 30%, respectively, over the mid- and high-latitudes of the southern hemisphere. At most locations outside the tropics, the UV-B changes were caused by changes in tropospheric ozone, except for the northern hemisphere mid-latitudes where changes in tropospheric ozone and aerosols are equally important. These increases in tropospheric ozone in the northern midlatitudes counteracted the increases of UV-B due to stratospheric ozone depletion in the 1900s.

Artificial neural networks trained with measured erythemal irradiance, duration of sunshine, and a combination of measured and modeled total column ozone, were used to reconstruct the daily erythemal dose for Potsdam, Germany from 1901 to 1999 (Fig. 7).[116] A positive, statistically significant trend was found for the first half of the 20th century, in line with the observed negative trend in cloud cover. Since 1950, the trend in annual UVERY was negative until the mid-1980s, when it turned positive again. However, for both these latter periods, the trends were not statistically significant. These estimates do not include potential effects from aerosols, which have decreased substantially in the second part of the 20th century (as discussed above), and would likely result in further increasing of UVERY in the 1980s and 1990s. Furthermore, the uncertainty in the ozone data before 1949, and implicitly in UVERY, is higher because it has been obtained by a CCM.

In a study for Australia, the UVI under cloud-free conditions was calculated with a radiative transfer model over a 50-year period (1959–2009) based on measured meteorological parameters.[145] After the 1990s, an overall increase in annual mean UVI of 2-6% relative to the 1970–1980 levels was reported for all latitudes in that country.

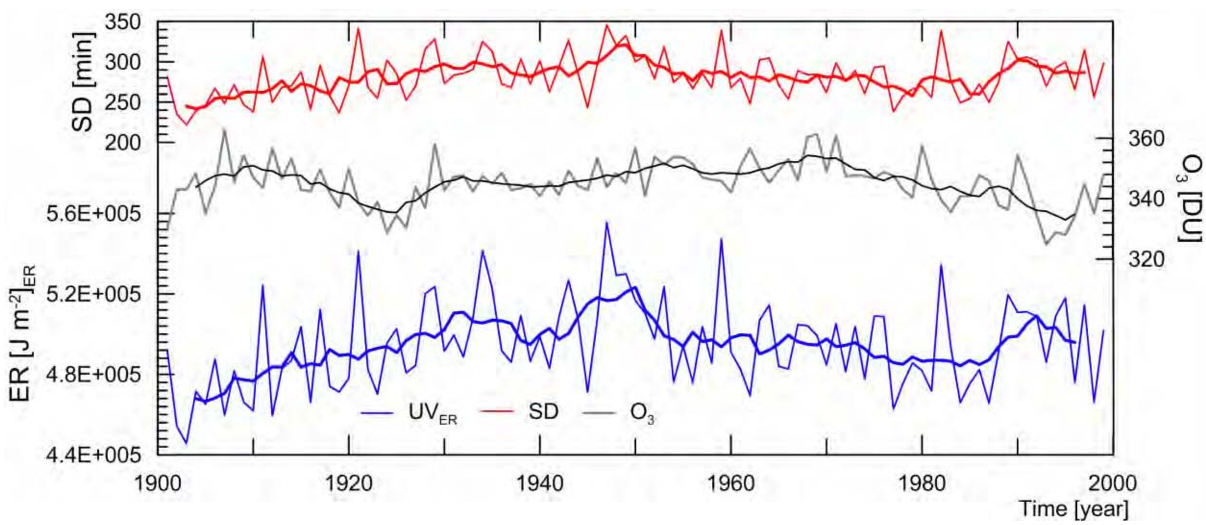

Fig. 7 Reconstructed annual total of UV_{ERY} time series (blue line, left-hand scale, lower graph, “ER”), mean annual total ozone in DU (gray line, right-hand scale) and mean annual sunshine duration (SD) in minutes per day (red line, left-hand scale, upper graph) for Potsdam, Germany, 1901 until 1999 (thin lines, annual values, thick lines 7-year running averages). Adapted from Junk et al.[116]

UV radiation under the water

The amount of UV radiation under the water surface of the ocean, lakes, and rivers depend on the available radiation field reaching the water surface and additionally on the transparency of the water body. The first is determined by the absorption and scattering processes of solar radiation in the atmosphere, as discussed above, and, at high latitudes, on the amount of ice over the water and the amount of snow over the ice. The transparency of water depends on the concentrations of dissolved and particulate material in the water, with chromophoric dissolved organic matter (CDOM) being the dominant attenuator of solar UV radiation[178, 270] and Chapter 5. The attenuation of solar UV radiation penetrating into the water column (quantified with the diffuse attenuation coefficient Kd, m-1) can be measured directly by radiometers or spectroradiometers, but such monitoring programs are sparse.[13, 270] Recently, measurements of the spectral shape of surface reflectance from the MODIS satellite have been used successfully to derive globally the diffuse attenuation of coastal waters.[13]

In some areas, the penetration depth of solar radiation into the water is large, such as in the South Pacific Gyre, where irradiances at 305, 325, 340 and 380 nm were reduced to 10% of their initial value at 28, 42, 59 and 110 m of depth, respectively.[237] These constitute the greatest depths of penetration ever reported for oceanic waters and are comparable with those measured in the clearest fresh waters.[80] In contrast, large attenuation of solar irradiance was measured in 2004 in the Mackenzie Delta Lakes, Canada, with different gradients in renewal rate of water, concentration of dissolved organic carbon (DOC), and composition of dissolved organic matter (DOM). However, because these lakes are shallow, UV-B and UV-A radiation is still able to penetrate the top 19% and 31% of water columns, respectively.[84] Thus, climate change effects on composition of DOM may significantly alter the UV radiation environment in such circumpolar delta lakes. The influence of inputs of DOM from rivers into the Arctic Ocean can now be inferred from analysis of satellite data (see Chapter 5).

In Polar Regions, sea-ice prevents a large fraction of UV radiation from reaching the (liquid) ocean surface, while a few centimeters of snow over ice almost completely blocks the transmission of UV-B radiation.[144, 180] Solar radiation under “first-year” ice in the upper ocean is spatially heterogeneous and depends on wavelength, thickness of ice, and the area and geometric distribution of melt ponds and bare ice surfaces.[79] Although there is an exponential decay in transmission or radiation through the ice sheet, it was reported that the transmission of radiation in the water under the ice can increase with depth when bare and ponded sea-ice surfaces are interspersed close to the observation site. [79] Projections based on earth-system models and radiative transfer calculations suggest that, compared to the 1950s, up to 10 times more UV-B radiation will enter large parts of the Arctic Ocean by 2100, mainly because of the partial disappearance of sea-ice.[77]

The future evolution of sea-ice and its snow cover is linked to changes in climate and will likely lead to increases in UV-B radiation reaching the ocean surface beneath the ice. The complex radiation field beneath the first-year sea-ice during the melt-season has significant implications for biological production, biogeochemical processes, and the heat balance of sea-ice and under-ice ocean waters. Effects of UV penetration into the water column, as well as the modification of the ratio UV-B/UV-A by CDOM in the water column, are discussed further in Chapter 5.

Projections of UV radiation: Causes and health effects

Projected changes back to the 1960s and out to the 2090s relative to the present

Surface UV radiation in the future will be influenced by: increases in stratospheric ozone due to reduction in ODSs; changes in ozone and cloudiness induced by increasing concentrations of GHGs; changes in tropospheric UV-absorbing aerosols; and decreases in surface reflectivity at high latitudes and high altitudes. Simulations of these UV radiation levels are usually derived from radiative transfer model calculations that use input parameters estimated by climate models.

In our previous assessment,[157, 243] we reported estimates from model projections[9] suggesting that, by about 2050, the UVERY would decrease relative to 1980 by 2-10% at mid-latitudes, and by up to 20% at northern and 50% at southern high latitudes, mainly due to the recovery of stratospheric ozone and to changes in cloudiness. In the tropics, UVERY was projected to be higher by less than 2%. We also compared model projections between 2100 and 1960 to estimate the effects of climate change on surface

UV, because the ozone depletion started after 1960 and ozone recovery would have been completed by 2100. By the end of the 21st century UVERY was projected to: a) remain below 1960 levels due to changes in clouds and GHG-induced transport of ozone at mid-latitudes, b) decrease at high latitudes (particularly in the Arctic) by 5-10% due to changes in clouds, and c) increase in the tropics by 3-8% due to decreases in clouds and ozone, induced by GHGs.

However, these projections did not consider changes in aerosols and surface reflectivity. Similar results were reported by another simulation[64] that accounted also for the effects of changing albedo and cloud cover. By assuming typical aerosol optical depth and single scattering albedo values over Europe, in addition to projections of ozone, small reductions in erythemal and the vitamin D-effective daily doses were predicted for 2006–2100,[52] and were attributed to the recovery of stratospheric ozone and partially to reduction in the optical depth of aerosols. A recent modelling study focussing on the Arctic Ocean[77] projected reductions in UV-B irradiance by the end of the 21st century relative to the levels in the 1950s over a large fraction of the area. Under clear skies, UV-A irradiance is projected to decrease on average by 4–7% (depending on scenario and season), entirely driven by decreases in surface reflectivity, while UV-B is projected to decrease on average by 10–18%, mainly due to the projected ozone recovery. Under all skies, these effects are modulated by clouds, leading to changes in the monthly mean noontime UVI from +15% to -38%, depending on the location and season. Increases in irradiance were found only during August for the latitude band 55-65°N, caused by the projected decrease in cloudiness.

In this assessment, we provide updated estimates of the projections of the previous assessment,[243] taking into consideration effects from most factors affecting the UV radiation at the Earth's surface. This analysis is based on recent projections of cloudiness, ozone, surface reflectivity, and aerosols for the period 1955-2100 by different Earth-System models that were included in the fifth phase of the Climate Model Intercomparison Project (CMIP-5),[236] and for the Representative Concentration Pathways (RCP) emissions scenario 4.5. For the ozone projections, the ensemble mean of the CESM1(WACCM) model,[68, 85] which includes interactive chemistry, was used. These projections have also been used in the fifth IPCC Assessment Report.[110] Changes in annually averaged noon UVI due to changes in these factors are shown separately in Fig. 8 between the past (1955-1965 mean) and the present (2010-2020 mean) and between the present and the future (2085-2095 mean).

Separating the effects of changes in surface reflectivity, aerosols and clouds on UV radiation is potentially challenging because of the interactive influence of these factors on irradiance. Despite these inter-connected effects, the largest changes in reflectivity are projected for high and polar latitudes due to melting of ice or snow, while the largest changes in aerosols are projected for mid-latitudes and the tropics, particularly over regions with strong anthropogenic activities.

Effects of changes in aerosols. The future evolution of aerosols and their radiative effects depend on emissions scenarios which may differ from the actual development, both in terms of amount and composition of aerosols. Current trends in air pollution (hence in aerosols) show large regional differences;[102] at some regions decreasing (Europe and North America) and at others increasing (Asia). For all emissions scenarios associated with the (RCP), aerosols are expected to decrease significantly in the second half of the 21st century globally,[138] and particularly over Asia as a result of measures for improvement of air quality,[14, 228] even though the air pollution there is presently increasing.[102]

However, even if these scenarios were realistic, there would still be large uncertainties in the simulations of UV radiation due to poor knowledge of the spectral absorption efficiency of aerosols (i.e., of SSA) and its wavelength dependence. Most climate models use input parameters that are appropriate for less absorbing aerosols, which result in underestimation of their effect on UV radiation. The UVI

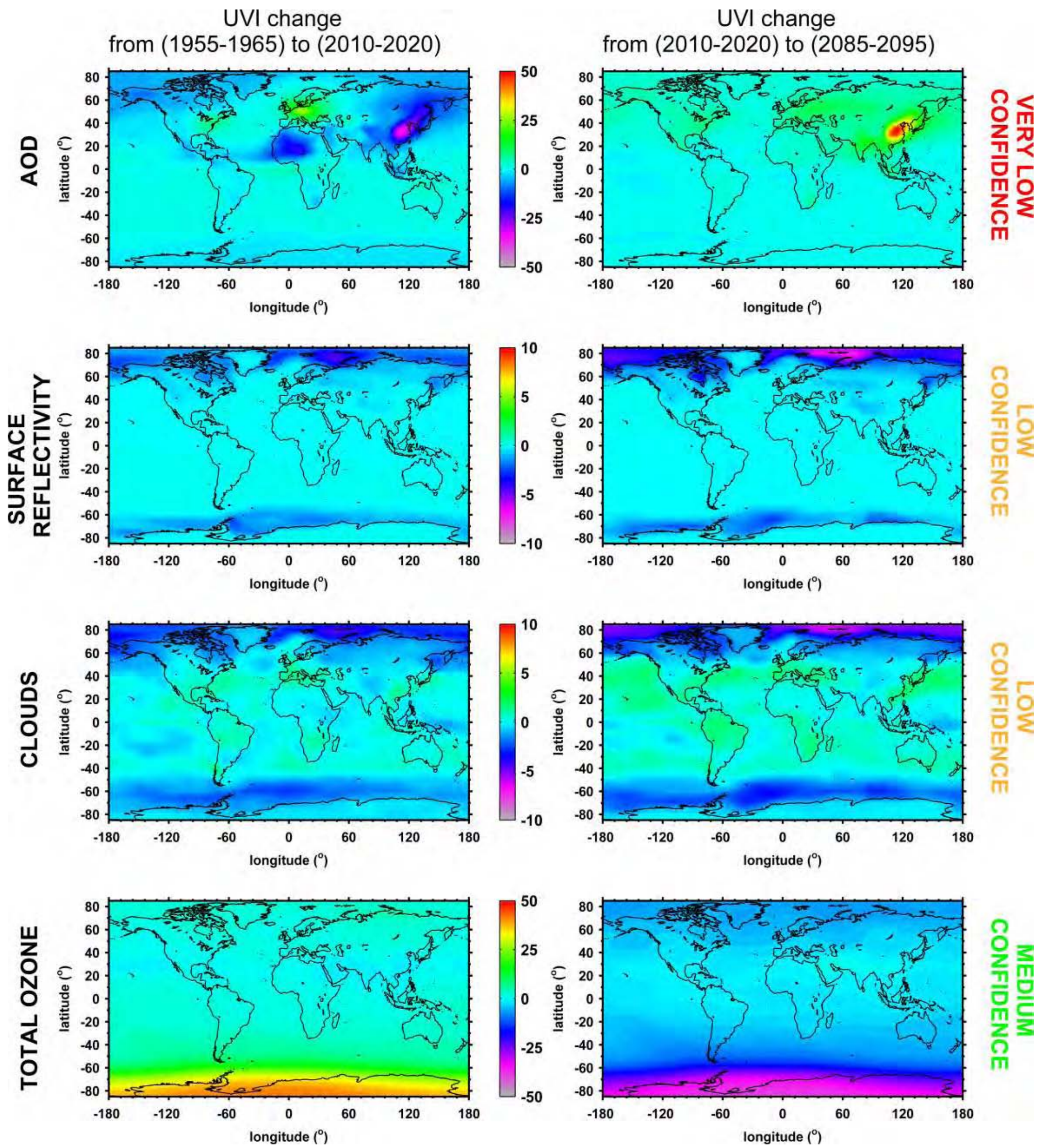

Fig. 8 Simulated annually averaged percentage changes in noontime UVI (or erythemally-weighted UV irradiance) relative to the "present" (i.e., 2010-2020). The left column shows simulated changes since 1955-1965. The right column shows the simulated changes expected from the present to the period 2085-2095. Effects of aerosols, surface reflectivity, cloudiness and total ozone on UVI are shown in each row, with our assessment of the confidence in UVI projections. Note the two different color-scales.

simulations shown here are based on projected aerosol optical depth values from the earth-system models. Because of the lack of specific SSA predictions, climatological values for SSA[126] were used, assuming no change with time, which may also be unrealistic. Finally, over areas dominated by clouds, the projected effects on UVI from changes in aerosols are more uncertain, particularly for large SZAs, for highly absorbing aerosols, and for highly reflective surfaces.

High levels of air pollution in the 1950s and 1960s over some urban areas in Eastern Europe should have resulted in less UV radiation at that time; the simulations show that estimated improvement of air quality since then[35] yielded increases in the UVI of up to 40% in the 2010s. Unfortunately, no high-quality direct measurements of UV radiation exist for that period, and neither have the reconstructed data series (see previous discussion) been forced with aerosol data to show this effect. However, measurements in Moscow revealed a ~4% increase in UV-A radiation from 1981 to 2003 due to reduction of aerosols.[263] In contrast to central Europe, UV radiation may have decreased in eastern Asia (by ~25%), due to increases in air pollution.[253] The decreases in UV (by ~15%) over north-west Africa are not statistically significant and are probably caused by the large differences among the model projections. By the end of the 21st century, the improvement of air-quality over most populated areas of the northern hemisphere may result into small increases in UVI compared to 2010s by 10-20%, except over China where much larger increases are projected. The projected aerosol effect in the

southern hemisphere is generally very small, because sources of aerosols are weaker compared to the northern hemisphere, and aerosols originate mostly from the ocean, while the fraction of land with important anthropogenic activities is very small. Consequently, the assumed changes in aerosol amount with time are generally very small there.[35]

In our assessment, estimates of the characteristics of aerosols in the past and understanding the effects of changes of aerosols in the future are highly uncertain at present. Although we have tools to carry out the UV calculations, knowledge of the input parameters to the RT models, and a complete understanding of interactions between the various effects is still lacking. Therefore, the simulated changes in UV radiation shown in Fig. 8 are associated with significant uncertainties, and particularly for the potential aerosol effects, are only illustrative. Despite the uncertainties, it is likely that, outside the polar regions, changes in aerosols and their properties in the future will be more important for the levels of UV at the surface than those from changes in ozone.

Effects of changes in surface reflectivity. As discussed previously, surface reflectivity is projected to decrease between the 1960s and the end of the 21st century over areas that were covered by sea-ice and snow earlier in this period, whereas in other areas the expected effects, mainly from changes in land-use, would be much smaller. Projected effects on UV radiation are therefore significant only over high and polar latitudes.

Over the Arctic, large reductions in reflectivity due to sea-ice melting have already occurred; hence the simulated UVI is ~5% lower than in the 1960s, over and close to areas covered by sea-ice. These effects are most pronounced in the summer and autumn, when the sea-ice disappears over large areas. This phenomenon is projected to continue through the end of the 21st century,[181] resulting to decreases in UVI with respect to the present by up to ~10%. In Antarctica, ice cover has generally increased slightly (as discussed above), while a small fraction of sea-ice has been lost in localized regions (mainly over the Weddell Sea), leading to small decreases in annual average UVI of less than ~2%. Small decreases are projected also for the future since Antarctica will be still covered by snow and ice by the end of the 21st century. However, other factors (e.g., ozone, clouds, and aerosols) that might be different from present would likely modulate the reflectivity effect.

Effects of changes in clouds. Effects of clouds on climate are significant and complex; and their representation in climate models continues to be a challenge. Many cloud processes, including aerosol-cloud processes, occur at scales smaller than those resolved in large-scale climate models. Therefore, general circulation models typically use parameterisations to represent a range of cloud properties. A recent assessment reports considerable improvements in the ability of models to account for effects from clouds.[192]

For the UV projections presented here, the effect of clouds on UVI was estimated through the CMF calculated from projections of all-sky and clear-sky total solar radiation by the Earth system models. Extrapolation of the CMF from visible to ultraviolet wavelengths is based on empirical relationships. Changes in the CMF between the two periods shown are directly translated into changes in UVI due to clouds. The modification of solar radiation by clouds depends on aerosols in the underlying layers and on surface reflectivity, as both lead to increasing multiple scattering of radiation. These factors are implicitly taken into account in the total radiation projections, but their effect on the derived CMF is small.

The projected changes in noontime UVI due to clouds are mostly negative. Cloudiness is projected to increase over the Arctic Ocean due to increased evaporation as sea-ice declines. Therefore, the highest decreases in UVI are simulated for latitudes north of 60°N, and are up to 4% from the 1960s to the 2010s, and about double this between the 2010s and the 2090s. Pole-ward of ~60°S, reductions of up to 3% in the UVI have been projected for both periods, mainly over the ocean. At all other latitudes the projected changes are very small, ranging between -2% and +2%.

Effects of changes in ozone. Depletion of ozone has led to increases in UV-B radiation during the 1980s and 1990s, and recovery of ozone will likely lead to reductions of UV-B relative to present levels. According to state-of-the-art simulations by CCMs, it is likely that, by the early-2030s, total ozone columns at mid-latitudes will exceed 1980 values.[265] The projected increases in total ozone are due to declining concentrations of ODSs and increases in the concentration of greenhouse and other source gases. Declining ODSs, stratospheric cooling, the possible strengthening of the Brewer-Dobson circulation and other factors are likely to result in a “super-recovery” of mid-latitude ozone columns, after 2040 to 2060, i.e., to levels greater than observed in the 1960s, leading to smaller levels of UV-B.

The future levels of ozone will greatly depend on future emissions of GHGs into the atmosphere, but also on influences from possible volcanic eruptions. Simulations indicate that the differences between GHG scenarios become important only in the latter half of the 21st century, and are largest in the northern mid-latitudes.[265] Improved understanding of the effects of Mt. Pinatubo eruption on stratospheric ozone suggests that a major volcanic eruption in the near future (while atmospheric chlorine levels from ODSs remain elevated) would result in lower levels of stratospheric ozone over much of the globe that would persist for several years.[5] In the Arctic, the evolution of springtime ozone in the future is uncertain because it is still debated whether changes in ozone will be driven by increases in PSCs from stratospheric cooling or by decreases in PCSs from stratospheric warming due to increases in planetary wave activity.[141]

Despite these open issues, the simulations and predictions of total ozone are more certain than the evolution of the other factors discussed above. Compared to the levels in the 1960s the UVI levels in the 2010s are higher only at southern high and polar latitudes where the ozone hole continues to form during the austral spring, and forces the annually averaged UVI to be up to 70% higher. Increases in UVI everywhere else are very small or close to zero. The pattern for the future is a near-complete reversal, as

UVI is projected to decrease over Antarctica in the 2090s by up to 40% compared to the 2010s. Decreases in the UVI are projected for the rest of the mid-latitude areas ranging between 5% and 10%. In the tropics, the changes are very small (±2-4%).

Overall effects. From the above discussion of individual factors that will affect the levels of UV radiation by 2100, it appears that the ozone will continue to be the dominant factor over Antarctica, while clouds and surface reflectivity will dominate the changes over the Arctic. The effects of the aerosols, although highly uncertain, are potentially very important, and will probably dominate future changes in both the UV-B and UV-A radiation in highly populated regions. Because the largest potential effects are also the most uncertain, we do not attempt to combine the four panels to show an overall effect.

In our last assessment, it was projected, on the basis of models available at that time, that there would be increases in UV at low latitudes by 2100 (where the UV is already high). The present assessment does not support that general statement. Fig. 8 shows a more complex picture and any projected increases (due mainly to reductions in cloud) are smaller than provisionally projected.

Effect of the Montreal Protocol on UV radiation

The amended and adjusted Montreal Protocol continues to be successful in reducing emissions and atmospheric abundances of most controlled ODSs, and has been hailed as the most effective environmental treaty ever. As a result of its success, the concentrations of most of the man-made chemicals that led to ozone depletion are declining, and ozone is judged to be on a path towards recovery.[265] Despite their long atmospheric lifetimes, by 2012, the total combined abundance of anthropogenic ODSs in the troposphere had decreased by nearly 10% from the peak value in 1993. New estimates of the contributions of specific substances or groups of substances to the decline in tropospheric chlorine and bromine are now available.[265]

Several attempts have been made to quantify the success of the amended and adjusted Montreal Protocol by comparing the environmental implications of ozone differences in the future "world expected" with those in the future "world avoided" by its successful implementation. A recent model simulation, that included the effects of coupling with the deep ocean,[83] showed that without the Montreal Protocol, ozone concentrations would have continued to decline, with an acceleration of that decline in the latter part of this century. In 2070, the stratospheric ozone layer would have collapsed to less than 100 DU worldwide and the peak UVI would have reached values greater than 35 in the tropics; at the sunlit northern polar cap UVI values would have been in the range 5–15, which are similar to or larger than the values found in the subtropics and tropics in 2000. Such an enhancement of UV irradiance at the surface is beyond anything that modern ecosystems have presumably experienced.

Another simulation[64] that accounted also for the effects of climate change (e.g., changing albedo and cloud cover), reported the geographical distribution of changes in UVERY that would occur without the implementation of the Montreal Protocol. For the no-Montreal Protocol simulation, dramatic increases in erythemal irradiance between the 1970s and 2100 were calculated, with 5-fold increases over populated areas, corresponding to summer UVI in excess of 50.

An early attempt to quantify the health effects concluded that the implementation of the Montreal Protocol has been hugely beneficial to avoid the health risks, such as skin cancer, which are associated with high UV, while there is only a small increase in health risks, such as vitamin D deficiency, that are associated with low UV.[168] Fig. 9 shows the projected changes in ozone and UVI that would have occurred in the "world avoided" case.[167, 168] The plots compare only latitudes 50°N and 50°S, but similar patterns are seen for other latitudes. The rate of ozone decline would have accelerated markedly after 2040, reaching minimum values of approximately 100 DU, similar to the lowest values seen during the most severe Antarctic ozone hole, by 2070. By that time, peak UVI values at mid latitudes would have been approximately 3 times as high as in the period prior to the onset of ozone depletion. The present differences in peak UVI values between the northern and southern hemispheres would have persisted and amplified by the 2060s. Summer-winter contrasts in UVI would have been amplified in absolute terms (differences), but reduced in relative terms (ratios), which may have had important implications for vitamin D production.

The effects on projected skin cancer rates were further estimated in a later study that also included the effects of projected future changes in cloud cover.[246] The study showed that, due to the decreases in ozone over the latter part of the 20th century, the incidence of skin cancer would rise by approximately 4% around the mid-21st century, but with large geographical differences. Of the regions tested, the largest increases (170-200 cases per million) were projected for the Australian region, but since the skin cancer models used as inputs were developed for the Netherlands and did not take account of behavioral changes in sun-exposure, their relevance to other regions is questionable.

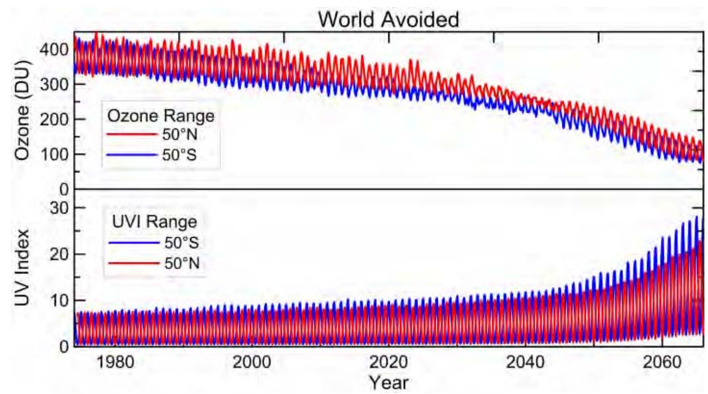

Fig. 9 Simulations of the “world avoided” total ozone (top panel) and UVI (bottom panel) between 1974 and 2075 for latitudes 50°N and 50°S.

Van Dijk et al.[246] predicted that, without the Montreal Protocol, there would have been much larger increases in rates of skin cancer. Even by as early as year 2030, 2 million cases of skin-cancer would have been prevented yearly, which is 14% fewer skin-cancer cases per year (see Chapter 2 for further details). This assumes no changes in human behavior with regard to sun-exposure. However, because there is a time delay of several decades between peak UV and subsequent diagnosis, the increase in year 2030 is attributable mainly to the relatively small ozone depletion that was present around the turn of the century (see Fig. 9). Further studies investigating the health effects early in the 22nd century would give a more realistic assessment of the true benefits of the Montreal Protocol.

Biological effects of UV radiation

The damaging or beneficial biological effects of UV radiation have a unique dependence on wavelength, which is quantified by weighting functions, also called “action spectra”.[157, 208] Action spectra typically increase by several orders of magnitude towards shorter wavelengths in the UV-B region (see examples in Fig. 10). Because of this wavelength sensitivity, biological effects depend strongly on the spectrum of the incident radiation. The shape of the spectrum depends on the amount of atmospheric ozone and the path of solar radiation through the ozone, which is a strong function of SZA. To quantify a biological effect, the solar irradiance spectrum at the Earth’s surface is multiplied with the action spectrum for this effect, and the result is integrated over wavelength to derive the biologically effective UV irradiance (UVEFF).

Sensitivity of biologically effective UV radiation to changes of ozone

The sensitivity of UV radiation to changes of ozone depends greatly on wavelength. Because every biological effect has a unique dependence on wavelength, to quantify the changes in biologically effective UV radiation due to changes in ozone, these wavelength dependencies should be taken into account. The relationship between change in total ozone column (TOC) and change in biologically effective UV irradiance can be quantified in terms of the Radiation Amplification Factor (RAF). For small (<10%) changes in ozone the RAF is simply the relative fractional change in effective UV irradiance with fractional change in total column ozone:

$$RAF = -(\Delta UV_{EFF} / UV_{EFF}) / (\Delta TOC / TOC) ,$$

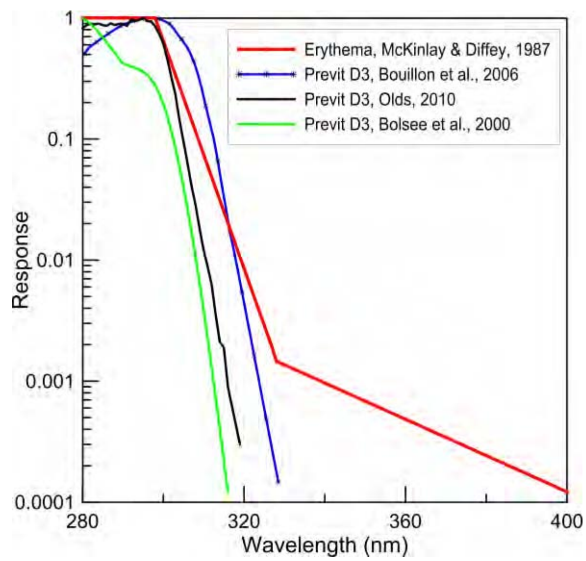

Fig. 10 Biological action spectra for erythema and production of previtamin D3

where ΔUV_{EFF} and ΔTOC are the respective changes in UV_{EFF} and TOC. For example, RAF=1.5 means that a 1% decrease in ozone will lead to a 1.5% increase in biologically effective UV radiation. For larger (>10%) changes in ozone, the power form[165] is more appropriate:

$$UV_{EFF+} / UV_{EFF-} = (TOC_{-} / TOC_{+})^{RAF} ,$$

where the subscripts (+ and -) refer to the cases with larger or smaller values of ozone, respectively.

Biological effects that are dominated by UV-B wavelengths have larger RAFs than effects where the contribution from the longer wavelengths is significant. As an example, we illustrate this for the case of vitamin D production by UV radiation, because this topic has received prominence in recent years, and the action spectrum for previtamin D3 production is controversial.[171] Table 1 shows the RAFs for three suggested action spectra for previtamin D3 production (Fig. 10) compared with the RAF for erythema for typical conditions in January and July. The previtamin D3-related action spectra are for illustrative purposes only and although the accuracy of the currently-accepted spectrum[24] has been called into question,[171] we are not in a position to advocate any change to it. A comprehensive list of RAFs and action spectra for a large variety of biological effects was included in the previous assessment report.[243]

Table 1 RAFs for action spectra calculated on the basis of daily integrals for latitude 30°N. This is an update of Table 1 from McKenzie et al.[157]

Effect	RAF Jan (290 DU)	RAF July (305 DU)	Reference
Erythema (CIE, standard reference)	1.1	1.2	CIE;[40] McKinley and Diffey;[160] Webb et al.[259]
Previtamin D3 (CIE)	1.7	1.4	Bouillon et al.[24]
Previtamin D3 (CIE truncated to 315 nm)	1.8	1.5	Bouillon et al.[24]
Previtamin D3	1.7	1.4	Olds [173]
Previtamin D3	2.6	2.2	Bolsee et al.[22]

RAFs also depend to some degree on factors other than SZA and ozone that alter the shape of the solar spectrum, such as extinction by aerosols or the vertical distribution of ozone in the atmosphere.[248] Limitations of the RAF and its application to other action spectra have been discussed in more detail elsewhere.[165]

New numerical parameterizations have recently been developed to calculate biologically effective irradiance as a function of TOC and solar elevation angle for commonly used action spectra.[99] Furthermore, a new method has been devised to calculate RAFs from measurements of UVERY and TOC during times when UVERY is also affected by clouds and aerosols.[182]

While the basic understanding of the sensitivity of UV radiation to changes in ozone has not changed since the last assessment, additional studies are now available that corroborate the magnitude of this sensitivity and allow refinement of the values of action spectra.

The action spectrum for erythema

There have been slight variations in the definition of the action spectrum for erythema since it was first introduced.[160] Their action spectrum for erythema was standardized by the Commission Internationale de l'Éclairage (CIE) in 1987[39] and updated in 1998.[40] Deviations in erythemal irradiance resulting from the two versions of the action spectrum are less than 0.5% for SZAs <40°and increase to around 2% at 85°SZA[259] and the RAF changes by less than 0.02 (Fig. 11). Even though the differences are small, this change is important due to the large number of studies and time series that have been based on the CIE 1987 action spectrum. In accordance with Webb et al,[259] we recommend that the standard action spectrum for erythema recommended by CIE[40] should be used in the future.

Measurements of personal exposure to UV radiation

To date, the most widely used method for personal UV exposure studies is to equip volunteers with small dosimeters attached to various parts of the body. Dosimeters may be based on photoresponsive films, which change their transmission upon exposure to UV radiation,[27, 219, 242] DNA molecules in cultures of immobilized spores with a spectral response corresponding to erythema,[71, 216, 217] and photodetectors that convert UV radiation into signals of voltage or current.[206, 207, 260] The ability to convert doses absorbed by polysulphone (PS) badges into biologically effective solar UV exposure was assessed,[221] taking as example two relevant effects for human skin: induction of erythema and production of previtamin D3. Comparisons of doses derived from PS badges positioned horizontally

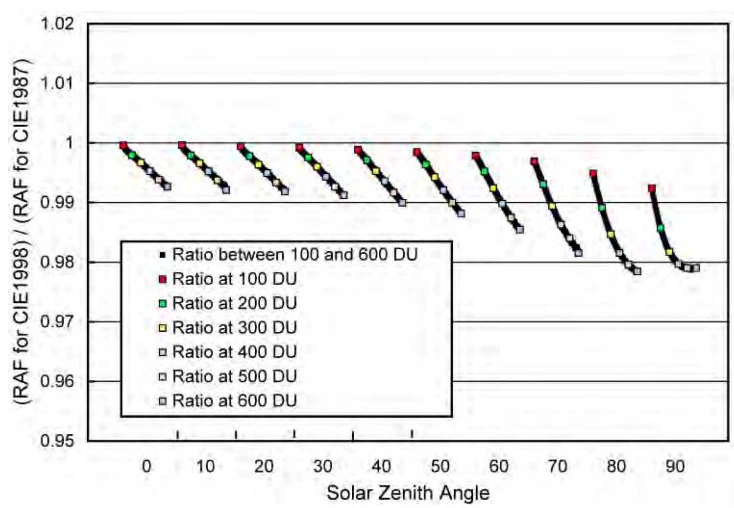

Fig. 11 Ratio of radiation amplification factors (RAF) calculated for the CIE 1998 and CIE 1987 erythema action spectra. The figure is based on model spectra that were calculated for different solar zenith angles and total column ozone[210] and subsequently weighted with either the CIE 1998 or the CIE 1987 erythema action spectrum.

and at different inclination angles (to simulate various anatomic sites of the human body), revealed larger deviations at large solar zenith angles and/or for high reflectivity surfaces.[31]

More recently, electronic dosimeters have become available, and their use is becoming more widespread.[55, 159, 213] The accuracy of measurements of two types of personal dosimeters, namely PS films and electronic ultraviolet (EUV) dosimeters using an aluminum gallium nitride ($Al_{27}Ga_{73}N$) photodetector, have recently been assessed.[213] PS dosimeters showed mean absolute deviations of 26% relative to a reference spectroradiometer, with a maximum deviation of 44%. Since the PS doses were derived using a single calibration curve, further experimental investigation of these dosimeters is needed to better assess their accuracy. The calibrated EUV dosimeters showed mean absolute deviations of 15% (maximum 33%), which were partly caused by small, but significant sensitivities to visible radiation (i.e., stray light). It was concluded that calibrating UV sensors by direct comparison with a reference instrument leads to reliable results and that these simple devices are useful to estimate personal UV exposures. They should not be used, however, as an inexpensive replacement for meteorological grade instruments.

Inexpensive, non-scientific instruments for UVI measurements have recently become available. These sensors are part of watches, portable weather stations, and handheld UV meters. The accuracy of several of these devices has been assessed.[51] While the measurements of some test devices agreed with those of a reference spectroradiometer to within 20%, some instruments overestimated the UVI by up to a factor of three and hence did not provide trustworthy results.

Health-related exposure to UV radiation

Exposure to sunlight, specifically the UV radiation, has both positive and negative health effects, as discussed in Chapter 2. Despite the positive effects, it is excessive sun-exposure which has been of greater concern, because of its adverse effects to humans, terrestrial and aquatic ecosystems, materials, and air quality (see all Chapters of this report). Quantification of exposure of humans to UV radiation is complex as many factors are involved, including the natural variations of radiation, the orientation of the exposed parts in conjunction with the time and location, behavioral aspects, clothing, as well as effects of reflections on the surroundings.[242]

This complexity is confirmed by recent exposure studies using personal dosimeters which include: seafarers of merchant vessels,[71] farmers at a mid-latitude site,[206] urban dwellers engaging in typical outdoor activities such as shopping, walking, cycling, and sightseeing,[207] professional cyclists,[216] young (age 9-12) skiers,[217] vineyard workers,[219] and people engaged in activities such as walking, sitting, and lying.[260] From measurements with personal electronic UV dosimeters in New Zealand over a few weeks (outside the peak summer period),[158, 159] it was shown that cumulative doses received by dosimeters worn on the wrist were typically less than 2% of the available ambient doses, and that the equivalent full body exposure is less than 1% of the ambient. This implies that the people wearing the dosimeters were probably indoors for about 95% of the time. These studies suggest that personal UV exposure is better approximated by dosimeters and diaries than by measurements of the ambient UV irradiance. Furthermore, the translation of traditional global-horizontal irradiance measurements into exposure levels relevant to humans therefore depends critically on information on behavior and location.

Maximizing the benefits while minimizing the damage is a multifaceted problem in which many of the elements are important and need to be quantified.[258] A recent attempt has been made to quantify the available ambient UV doses each month, including both beneficial and detrimental effects, in Northern Eurasia.[37]

As discussed above, problems arise when one uses UV measurements on a horizontal surface to perform risk-benefit assessments because they do not yield the actual doses people get while they are outdoors as different parts of the body are exposed at different angles. More realistic UV doses for people who are outdoors engaged in a variety of different activities can be estimated from simple geometrical parameterizations.[190]

As part of further refinements, the importance of including the effects of clouds and aerosols in parameterizations to derive vitamin D-effective irradiance from erythemal irradiance was highlighted by Feister et al.[70] They showed from 4 years of measurements in Germany that optically thick clouds can strongly modify the ratio between erythemal and vitamin D-effective irradiance, suggesting that the parameterizations derived for cloud-free conditions are not always applicable.

Similarly, the role of shade has been emphasized by Turnbull and Parisi[241] who measured the spectral dependence of the ratio of diffuse to global UV radiation, and showed that under clear skies this ratio decreases with wavelength throughout most of the UV region for wavelengths greater than 300 nm. For example, for unpolluted conditions at SZA=40°, the diffuse to global ratio decreases from ~0.6 at 300 nm to ~0.3 at 400 nm. This means that in the UV-B region, the protection offered is less than one would estimate from our perception of the visible solar radiation. To get protection sufficient for most purposes (e.g., Solar Protection Factor >30) from UV-B radiation in the shade, it is important to ensure most of the diffuse sky radiation is also blocked. Interestingly, because the wavelengths for previtamin D production are slightly shorter than for erythema, this implies that exposure to diffuse light, such as in the shade of trees or buildings, may slightly favor the production of vitamin D while minimizing the risk of erythema in non-covered skin.

The field of atmospheric UV research is plagued with difficulties in nomenclature. A recent report[41] highlights some of the issues, taking vitamin-D synthesis, a beneficial effect, as a specific example. Terminologies for the standard vitamin-D dose (SDD) and the minimum vitamin-D dose - for daily sufficiency - (MDD) are proposed, analogous to the standard erythema dose (SED) and minimal erythema dose (MED) that are in common use for erythema. Note that the quantitative value of the MDD is not yet known; nor is there agreement on the recommended minimum levels of the status of vitamin-D (see Chapter 2). In the present literature, the SDD has confusingly been defined in terms of a physiological response. In recognition of the fact that currently accepted action spectra may be revised if new data become available, continuation of spectrally resolved irradiance measurements will allow reprocessing of biologically effective irradiances and doses in the future.

Effects of geoengineering on ozone and UV radiation

Geoengineering –or "climate engineering"– refers to a broad set of methods and technologies that could be used to deliberately alter the climate system in order to alleviate the impacts of climate change. Solar Radiation Management (SRM) has been suggested as a means to counteract the warming from increasing GHG by reducing the amount of solar radiation absorbed by the Earth's surface. Carbon Dioxide Reduction (CDR) aims at reducing the future concentrations of CO_2 by accelerating the natural removal of atmospheric CO_2 or increasing the storage of carbon in reservoirs.[110]

Of those two geoengineering methods, only the SRM would directly influence the amount of UV radiation received at the Earth's surface. Space reflectors, injection of aerosols in the stratosphere, or seeding of marine clouds would reduce the amount of UV radiation reaching the surface. In contrast, increasing of surface reflectivity by creating micro bubbles at the ocean surface, growing more reflective crops, or painting roofs and other built structures in light colors may lead to increased surface UV radiation through scattering of reflected radiation towards the ground.

The injection of sulfur dioxide into the stratosphere[53] is one of the methods suggested to reduce the amount of solar radiation reaching the Earth's surface, through increased scattering of solar radiation to space. However, it is known that stratospheric sulfate aerosols from volcanic eruptions and natural emissions deplete the stratospheric ozone, and similar effects should be expected from stratospheric aerosols introduced for SRM, leading ultimately to increases in the amount of UV-B radiation reaching the surface, which are larger than the reduction achieved from the SRM.

This is further supported by recent modelling studies[98, 189, 239] suggesting that such interventions would lead to a general decrease in stratospheric ozone concentrations mainly via changes in photolysis rates, tropical upwelling of ozone-poor air, and an increase in available surfaces for heterogeneous chemistry. Considering the role of very short-lived halogens in the stratosphere (e.g., Bry and Cly) increases in annual average UVERY of up to 5% in mid and high latitudes were simulated for the 2040s due to the impact of stratospheric sulfur on ozone.[239] Recently, it was projected that the increase in UV-B radiation at the surface due to ozone depletion could be offset in the 2040s by the screening due to the SRM aerosols in the tropics and mid-latitudes, while in polar regions the UV-B radiation would increase by 5% on average, with 12% peak increases during springtime.[186]

Other potential UV-related impacts of geoengineering have been investigated with models, revealing effects on cloud cover[132] and rainfall patterns,[73] both of which ultimately lead to changes in UV radiation at the Earth's surface. Model simulations showed that SRM to counteract a 1% annual rise in atmospheric CO_2 suppresses the increases in precipitation that would otherwise accompany the rising GHG, had geoengineering never been used. However, in some of these sensitivity studies extreme and perhaps unlikely scenarios[73] have been assumed. For example, the effect of geoengineering with sulfate aerosols was investigated in a world with a different climate by first setting global CO_2 levels at an extremely large level of 1,120 parts per million (ppm) or four times the pre-industrial level.[240] They found that global precipitation rates would increase by approximately 7% compared with pre-industrial times, but with high spatial and temporal variability. However, when they re-ran the models, with SRM geoengineering included, they found a 4.5% reduction in global precipitation. Again, there was a high degree of variability, but notably, decreases in precipitation rates on land and in oceans were much more similar.

The interactions and feedbacks of the suggested geoengineering methods with the natural variability of the atmospheric and surface reflectivity are not yet fully explored. The atmosphere is a complex system and any deliberate interventions should be treated with great care as they may have unanticipated adverse effects. Moreover, with the current observing systems, it would not be feasible to assess whether the small intended changes in solar radiation at the Earth's surface from the implementation of geo-engineering would have actually occurred.

Gaps in knowledge

Simulations of surface UV radiation for the future are limited in accuracy due to difficulties in assessing the combined effects of clouds and aerosols that are expected to change. Over ice- and or snow-covered areas, these effects are even more complicated. Additional uncertainties for UV projections arise from the scenarios describing the evolution of the atmosphere in the future.

Significant changes in aerosol concentrations are expected in the future (both positive and negative, depending on the region). The effect of these aerosols on surface UV irradiance will depend strongly on their single scattering albedo. However, even for the aerosols that are present in the current atmosphere, this parameter is not well quantified in the UV-B region because of confounding effects of ozone absorption. Better quantification of the SSA in the UV-B region over a wide range of aerosol types (possibly involving laboratory studies to avoid the effect of ozone) would increase our ability to model the effects of aerosol on UV radiation at the Earth's surface.

To our current understanding, variations in solar activity lead to decreases in total ozone of up to 3% between the maximum and the minimum of the 11-year solar cycle. However, the relative contributions of solar activity-induced radiative and dynamical effects on ozone are not yet fully resolved. Moreover, there are still uncertainties in the measurements of solar spectral irradiance outside the Earth's atmosphere.

Improvement in the understanding of these processes and the availability of higher quality information of the UV-related factors would strengthen our ability to effectively interpret ongoing changes and predict future changes in UV radiation.

Instruments at the ground measure UV irradiance directly and the results are therefore more accurate than the inversion results from satellite data, but the spatial coverage of surface observations is sparse and vast regions of the Earth (e.g., Africa, Siberia, the global oceans, particularly in the southern hemisphere) are not being monitored from the ground. In light of these limitations, robust assessments of long term changes in UV radiation must be based both on observations from space and from the ground.

Assessment of the long-term benefits of the Montreal Protocol requires inputs from both the atmospheric sciences and the health communities. To date, the health costs of non–implementation of the Montreal Protocol have been calculated only up to year 2030. Because of the lag between UV exposure and onset of diseases this is representative only of the changes due to ozone depletion up to year 2000. This severely underestimates the true benefits of the Montreal Protocol because ozone changes would have become much larger in the latter half of the 21st century (see Fig. 9).

There is incomplete characterization of many action spectra of interest. Examples are the action spectrum for the formation of previtamin D3 from sunlight and the action spectrum for melanoma in human skin. These are required for quantitative assessments of the environmental effects of future changes in UV radiation, particularly those due to changes in ozone.

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References

1 Abreu JA, Beer J, Steinhilber F, Tobias SM, Weiss NO, 2008, For how long will the current grand maximum of solar activity persist?, *Geophys. Res. Lett.*, **35**, L20109.

2 Anet JG, Rozanov EV, Muthers S, Peter T, Brönnimann S, Arfeuille F, Beer J, Shapiro AI, Raible CC, Steinhilber F, Schmutz WK, 2013, Impact of a potential 21st century "grand solar minimum" on surface temperatures and stratospheric ozone, *Geophys. Res. Lett.*, **40**, 4420-4425.

3 Antón M, Cachorro VE, Vilaplana JM, Toledano C, Krotkov NA, Arola A, Serrano A, de la Morena B, 2010, Comparison of UV irradiances from Aura/Ozone Monitoring Instrument (OMI) with Brewer measurements at El Arenosillo (Spain) – Part 1: Analysis of parameter influence, *Atmos. Chem. Phys.*, **10**, 5979-5989.

4 Antón M, Alados-Arboledas L, Guerrero-Rascado JL, Costa MJ, C Chiu J, Olmo FJ, 2012, Experimental and modeled UV erythemal irradiance under overcast conditions: the role of cloud optical depth, *Atmos. Chem. Phys.*, **12**, 11723-11732.

5 Aquila V, Oman LD, Stolarski R, Douglass AR, Newman PA, 2012, The response of ozone and nitrogen dioxide to the eruption of Mt. Pinatubo at southern and northern midlatitudes, *J. Atmos. Sci.*, **70**, 894-900.

6 Arblaster JM, Meehl GA, Karoly DJ, 2011, Future climate change in the Southern Hemisphere: Competing effects of ozone and greenhouse gases, *Geophys. Res. Lett.*, **38**, L02701.

7 Arola A, Kazadzis S, Lindfors A, Krotkov N, Kujanpää J, Tamminen J, Bais A, Sarra Ad, Villaplana JM, Brogniez C, Siani AM, Janouch M, Weihs P, Webb A, Koskela T, Kouremeti N, Meloni D, Buchard V, Auriol F, Ialongo I, Staneck M, Simic S, Smedley A, Kinne S, 2009, A new approach to correct for absorbing aerosols in OMI UV, *Geophys. Res. Lett.*, **36**, L22805.

8 Bais AF, Kazantzidis A, Kazadzis S, Balis DS, Zerefos CS, Meleti C, 2005, Deriving an effective aerosol single scattering albedo from spectral surface UV irradiance measurements, *Atmos. Environ.*, **39**, 1093-1102.

9 Bais AF, Tourpali K, Kazantzidis A, Akiyoshi H, Bekki S, Braesicke P, Chipperfield MP, Dameris M, Eyring V, Garny H, Iachetti D, Jöckel P, Kubin A, Langematz U, Mancini E, Michou M, Morgenstern O, Nakamura T, Newman PA, Pitari G, Plummer DA, Rozanov E, Shepherd TG, Shibata K, Tian W, Yamashita Y, 2011, Projections of UV radiation changes in the 21st century: impact of ozone recovery and cloud effects, *Atmos. Chem. Phys.*, **11**, 7533-7545.

10 Bais AF, Drosoglou T, Meleti C, Tourpali K, Kouremeti N, 2013, Changes in surface shortwave solar irradiance from 1993 to 2011 at Thessaloniki (Greece), *Int. J Climatol.*, **33**, 2871–2876.

11 Balis D, Isaksen ISA, Zerefos C, Zyrichidou I, Eleftheratos K, Tourpali K, Bojkov R, Rognerud B, Stordal F, Søvde OA, Orsolini Y, 2011, Observed and modelled record ozone decline over the Arctic during winter/spring 2011, *Geophys. Res. Lett.*, **38**, L23801.

12 Barnard JC, Volkamer R, Kassianov EI, 2008, Estimation of the mass absorption cross section of the organic carbon component of aerosols in the Mexico City Metropolitan Area, *Atmos. Chem. Phys.*, **8**, 6665-6679.

13 Barnes BB, Hu C, Cannizzaro JP, Craig SE, Hallock P, Jones DL, Lehrter JC, Melo N, Schaeffer BA, Zepp R, 2014, Estimation of diffuse attenuation of ultraviolet light in optically shallow Florida Keys waters from MODIS measurements, *Rem. Sens. Environ.*, **140**, 519-532.

14 Bellouin N, Rae J, Jones A, Johnson C, Haywood J, Boucher O, 2011, Aerosol forcing in the Climate Model Intercomparison Project (CMIP5) simulations by HadGEM2-ES and the role of ammonium nitrate, *J. Geophys. Res. Atmos.*, **116**, D20206.

15 Berger DS, Urbach F, 1982, A climatology of sunburning ultraviolet radiation *Photochem. Photobiol.*, **35**, 187-192.

16 Bernhard G, Booth CR, Ehramjian JC, Stone R, Dutton EG, 2007, Ultraviolet and visible radiation at Barrow, Alaska: Climatology and influencing factors on the basis of version 2 National Science Foundation network data, *J. Geophys. Res. Atmos.*, **112**, D09101.

17 Bernhard G, Booth C, Ehramjian J, 2010, Climatology of Ultraviolet Radiation at High Latitudes Derived from Measurements of the National Science Foundation's Ultraviolet Spectral Irradiance Monitoring Network, in *UV Radiation in Global Climate Change* eds.: Gao W, Slusser J, Schmoldt D, Springer Berlin Heidelberg, pp. 48-72.

18 Bernhard G, 2011, Trends of solar ultraviolet irradiance at Barrow, Alaska, and the effect of measurement uncertainties on trend detection, *Atmos. Chem. Phys.*, **11**, 13029-13045.

19 Bernhard G, Manney G, Fioletov V, Grooß J-U, Heikkilä A, Johnsen B, Koskela T, Lakkala K, Müller R, Myhre CL, Rex M, 2012, Ozone and UV radiation, in: State of the Climate in 2011, *Bull. Amer. Meteorolog. Soc.*, **93**, S129-S132.

20 Bernhard G, Dahlback A, Fioletov V, Heikkilä A, Johnsen B, Koskela T, Lakkala K, Svendby T, 2013, High levels of ultraviolet radiation observed by ground-based instruments below the 2011 Arctic ozone hole, *Atmos. Chem. Phys.*, **13**, 10573-10590.

21 Blunden J, Arndt DS, 2014, State of the Climate in 2013, *Bull. Amer. Meteorolog. Soc.*, **95**, S1-S257.

22 Bolsee D, Webb AR, Gillotay D, Dorschel B, Knuschke P, Krins A, Terenetskaya I, 2000, Laboratory facilities and recommendations for the characterization of biological ultraviolet dosimeters, *Appl. Optic.*, **39**, 2813-2822.

23 Bones DL, Henricksen DK, Mang SA, Gonsior M, Bateman AP, Nguyen TB, Cooper WJ, Nizkorodov SA, 2010, Appearance of strong absorbers and fluorophores in limonene-O3 secondary organic aerosol due to NH4+-mediated chemical aging over long time scales, *J. Geophys. Res. Atmos.*, **115**, D05203.

24 Bouillon R, Eisman J, Garabedian M, Holick M, Kleinschmidt J, Suda T, Terenetskaya I, Webb A, 2006, *Action Spectrum for the Production of Previtamin D3 in Human Skin, CIE Report No 174,* **Vol. 174:2006**, Commission Internationale de L'Eclairage, Vienna.

25 Buchard V, Brogniez C, Auriol F, Bonnel B, 2011, Aerosol single scattering albedo retrieved from ground-based measurements in the UV and visible region, *Atmos. Meas. Tech.*, **4**, 1-7.

26 Buntoung S, Webb AR, 2010, Comparison of erythemal UV irradiances from Ozone Monitoring Instrument (OMI) and ground-based data at four Thai stations, *J. Geophys. Res. Atmos.*, **115**, D18215.

27 Butson ET, Cheung T, Yu PKN, Butson MJ, 2010, Measuring solar UV radiation with EBT radiochromic film, *Phys. Med. Biol.*, **55**, N487-N493.

28 Cabrera S, Ipiña A, Damiani A, Cordero RR, Piacentini RD, 2012, UV index values and trends in Santiago, Chile (33.5°S) based on ground and satellite data, *J. Photochem. Photobiol. B.*, **115**, 73-84.

29 Cabrol NA, Feister U, Häder D-P, Piazena H, Grin EA, Klein A, 2014, Record solar UV irradiance in the tropical Andes, *Front. Environ. Sci.*, **2**, DOI: 10.3389/fenvs.2014.00019.

30 Cachorro VE, Berjón A, Toledano C, Mogo S, Prats N, de Frutos AM, Vilaplana JM, Sorribas M, De La Morena BA, Gröbner J, Laulainen N, 2009, Detailed Aerosol Optical Depth Intercomparison between Brewer and Li-Cor 1800 Spectroradiometers and a Cimel Sun Photometer, *J. Atmos. Ocean. Technol.*, **26**, 1558-1571.

31 Casale GR, Siani AM, Diémoz H, Kimlin MG, Colosimo A, 2012, Applicability of the Polysulphone Horizontal Calibration to Differently Inclined Dosimeters, *Photochem. Photobiol.*, **88**, 207-214.

32 Cazorla A, Bahadur R, Suski KJ, Cahill JF, Chand D, Schmid B, Ramanathan V, Prather KA, 2013, Relating aerosol absorption due to soot, organic carbon, and dust to emission sources determined from in-situ chemical measurements, *Atmos. Chem. Phys.*, **13**, 9337-9350.

33 Chehade W, Weber M, Burrows JP, 2014, Total ozone trends and variability during 1979–2012 from merged data sets of various satellites, *Atmos. Chem. Phys.*, **14**, 7059-7074.

34 Chen Y, Xie S, 2012, Temporal and spatial visibility trends in the Sichuan Basin, China, 1973 to 2010, *Atmos. Res.*, **112**, 25-34.

35 Chin M, Diehl T, Tan Q, Prospero JM, Kahn RA, Remer LA, Yu H, Sayer AM, Bian H, Geogdzhayev IV, Holben BN, Howell SG, Huebert BJ, Hsu NC, Kim D, Kucsera TL, Levy RC, Mishchenko MI, Pan X, Quinn PK, Schuster GL, Streets DG, Strode SA, Torres O, Zhao XP, 2014, Multi-decadal aerosol variations from 1980 to 2009: a perspective from observations and a global model, *Atmos. Chem. Phys.*, **14**, 3657-3690.

36 Chubarova N, Nezval Y, Sviridenkov I, Smirnov A, Slutsker I, 2012, Smoke aerosol and its radiative effects during extreme fire event over Central Russia in summer 2010, *Atmos. Meas. Tech.*, **5**, 557-568.

37 Chubarova N, Zhdanova Y, 2013, Ultraviolet resources over Northern Eurasia, *J. Photochem. Photobiol. B.*, **127**, 38-51.

38 Chubarova NY, Nezval YI, 2000, Thirty year variability of UV irradiance in Moscow, *J. Geophys. Res. Atmos.*, **105**, 12529-12539.

39 CIE, 1987, *A Reference Action Spectrum for Ultraviolet Induced Erythemal in Human Skin,* **Vol. 6(1)**, Commission Internationale de l'Eclairage, Vienna, Austria.

40 CIE, 1998, *Erythema Reference Action Spectrum and Standard Erythema Dose, CIE DS 007.1/E-1998*, Commission Internationale de l'Eclairage, Vienna, Austria.

41 CIE, 2014, *Rationalizing Nomenclature for UV Doses and Effects on Humans, CIE 209:2014 / WMO/GAW report No. 211*, Commission Internationale de l'Eclairage, Vienna, Austria.

42 Coldewey-Egbers M, Loyola R DG, Braesicke P, Dameris M, van Roozendael M, Lerot C, Zimmer W, 2014, A new health check of the ozone layer at global and regional scales, *Geophys. Res. Lett.*, **41**, 4363–4372.

43 Collaud Coen M, Andrews E, Asmi A, Baltensperger U, Bukowiecki N, Day D, Fiebig M, Fjaeraa AM, Flentje H, Hyvärinen A, Jefferson A, Jennings SG, Kouvarakis G, Lihavainen H, Lund Myhre C, Malm WC, Mihapopoulos N, Molenar JV, O'Dowd C, Ogren JA, Schichtel BA, Sheridan P, Virkkula A,

Weingartner E, Weller R, Laj P, 2013, Aerosol decadal trends – Part 1: In-situ optical measurements at GAW and IMPROVE stations, *Atmos. Chem. Phys.*, **13**, 869-894.

44 Comiso JC, Parkinson CL, Gersten R, Stock L, 2008, Accelerated decline in the Arctic sea ice cover, *Geophys. Res. Lett.*, **35**, L01703.

45 Cordero RR, Seckmeyer G, Riechelmann S, Damiani A, Labbe F, 2012, Monte Carlo-based uncertainty analysis of UV array spectroradiometers, *Metrologia*, **49**, 745.

46 Cordero RR, Seckmeyer G, Damiani A, Labbe F, Laroze D, 2013, Monte Carlo-based uncertainties of surface UV estimates from models and from spectroradiometers, *Metrologia*, **50**, DOI:10.1088/0026-1394/50/5/L1.

47 Cordero RR, Seckmeyer G, Damiani A, Jorquera J, Carrasco J, Muñoz R, Da Silva L, Labbe F, Laroze D, 2014, Aerosol effects on the UV irradiance in Santiago de Chile, *Atmos. Res.*, **149**, 282-291.

48 Cordero RR, Seckmeyer G, Damiani A, Riechelmann S, Rayas J, Labbe F, Laroze D, 2014, The world's highest levels of surface UV, *Photochem. Photobiol. Sci.*, **13**, 70-81.

49 Corr CA, Krotkov N, Madronich S, Slusser JR, Holben B, Gao W, Flynn J, Lefer B, Kreidenweis SM, 2009, Retrieval of aerosol single scattering albedo at ultraviolet wavelengths at the T1 site during MILAGRO, *Atmos. Chem. Phys.*, **9**, 5813-5827.

50 Corr CA, Hall SR, Ullmann K, Anderson BE, Beyersdorf AJ, Thornhill KL, Cubison MJ, Jimenez JL, Wisthaler A, Dibb JE, 2012, Spectral absorption of biomass burning aerosol determined from retrieved single scattering albedo during ARCTAS, *Atmos. Chem. Phys.*, **12**, 10505-10518.

51 Correa MdP, Godin-Beekmann S, Haeffelin M, Brogniez C, Verschaeve F, Saiag P, Pazmino A, Mahe E, 2010, Comparison between UV index measurements performed by research-grade and consumer-products instruments, *Photochem. Photobiol. Sci.*, **9**, 459-463.

52 Correa MdP, Godin-Beekmann S, Haeffelin M, Bekki S, Saiag P, Badosa J, Jegou F, Pazmino A, Mahe E, 2013, Projected changes in clear-sky erythemal and vitamin D effective UV doses for Europe over the period 2006 to 2100, *Photochem. Photobiol. Sci.*, **12**, 1053-1064.

53 Crutzen PJ, 2006, Albedo enhancement by stratospheric sulfur injections: A contribution to resolve a policy dilemma?, *Clim.Change*, **77**, 211-220.

54 Damiani A, Cabrera S, Muñoz RC, Cordero RR, Labbe F, 2013, Satellite-derived UV irradiance for a region with complex morphology and meteorology: comparison against ground measurements in Santiago de Chile, *Int. J. Remote Sens.*, **34**, 5812-5833.

55 Datta P, Bogh MK, Olsen P, Eriksen P, Schmedes AV, Grage MM-L, Philipsen PA, Wulf HC, 2012, Increase in serum 25-hydroxyvitamin-D3 in humans after solar exposure under natural conditions compared to artificial UVB exposure of hands and face, *Photochem. Photobiol. Sci.*, **11**, 1817-1824.

56 de Laat ATJ, van der A RJ, Allaart MAF, van Weele M, Benitez GC, Casiccia C, Paes Leme NM, Quel E, Salvador J, Wolfram E, 2010, Extreme sunbathing: Three weeks of small total O_3 columns and high UV radiation over the southern tip of South America during the 2009 Antarctic O_3 hole season, *Geophys. Res. Lett.*, **37**, L14805.

57 de Miguel A, Román R, Bilbao J, Mateos D, 2011, Evolution of erythemal and total shortwave solar radiation in Valladolid, Spain: Effects of atmospheric factors, *J. Atmos. Sol-Terr. Phys.*, **73**, 578-586.

58 den Outer PN, Slaper H, Kaurola J, Lindfors A, Kazantzidis A, Bais AF, Feister U, Junk J, Janouch M, Josefsson W, 2010, Reconstructing of erythemal ultraviolet radiation levels in Europe for the past 4 decades, *J. Geophys. Res. Atmos.*, **115**, D10102.

59 Desyaterik Y, Sun Y, Shen X, Lee T, Wang X, Wang T, Collett JL, 2013, Speciation of “brown” carbon in cloud water impacted by agricultural biomass burning in eastern China, *J. Geophys. Res. Atmos.*, **118**, 7389-7399.

60 Diaz S, Vernet M, Paladini A, Fuenzalida H, Deferrari G, Booth CR, Cabrera S, Casiccia C, Dieguez M, Lovengreen C, Pedroni J, Rosales A, Vrsalovic J, 2011, Availability of vitamin D photoconversion weighted UV radiation in southern South America, *Photochem. Photobiol. Sci.*, **10**, 1854-1867.

61 Dickerson RR, Ondragunta SK, Stenchikov G, Civerolo KL, Doddridge BG, Holben BN, 1997, The impact of aerosols on solar ultraviolet radiation and photochemical smog, *Science.*, **278**, 827-830.

62 Doyle M, Dorling S, 2002, Visibility trends in the UK 1950–1997, *Atmos. Environ.*, **36**, 3161-3172.

63 Eck TF, Holben BN, Sinyuk A, Pinker RT, Goloub P, Chen H, Chatenet B, Li Z, Singh RP, Tripathi SN, Reid JS, Giles DM, Dubovik O, O'Neill NT, Smirnov A, Wang P, Xia X, 2010, Climatological aspects of the optical properties of fine/coarse mode aerosol mixtures, *J. Geophys. Res. Atmos.*, **115**, D19205.

64 Egorova T, Rozanov E, Gröbner J, Hauser M, Schmutz W, 2013, Montreal Protocol Benefits simulated with CCM SOCOL, *Atmos. Chem. Phys.*, **13**, 3811-3823.

65 Eleftheratos K, Kazadzis S, Zerefos CS, Tourpali K, Meleti C, Balis D, Zyrichidou I, Lakkala K, Feister U, Koskela T, Heikkilä A, Karhu JM, 2014, Ozone and spectroradiometric UV changes in the past 20 years over high latitudes, *Atmos-Ocean*, DOI: 10.1080/07055900.2014.919897.

66 Epstein SA, Tapavicza E, Furche F, Nizkorodov SA, 2013, Direct photolysis of carbonyl compounds dissolved in cloud and fog-droplets, *Atmos. Chem. Phys.*, **13**, 9461-9477.

67 Ermolli I, Matthes K, Dudok de Wit T, Krivova NA, Tourpali K, Weber M, Unruh YC, Gray L, Langematz U, Pilewskie P, Rozanov E, Schmutz W, Shapiro A, Solanki SK, Woods TN, 2013, Recent variability of the solar spectral irradiance and its impact on climate modelling, *Atmos. Chem. Phys.*, **13**, 3945-3977.

68 Eyring V, Arblaster JM, Cionni I, Sedláček J, Perlwitz J, Young PJ, Bekki S, Bergmann D, Cameron-Smith P, Collins WJ, Faluvegi G, Gottschaldt KD, Horowitz LW, Kinnison DE, Lamarque JF, Marsh DR, Saint-Martin D, Shindell DT, Sudo K, Szopa S, Watanabe S, 2013, Long-term ozone changes and associated climate impacts in CMIP5 simulations, *J. Geophys. Res. Atmos.*, **118**, 5029-5060.

69 Farman JC, Gardiner BG, Shanklin JD, 1985, Large losses of total ozone in Antarctica reveal seasonal ClOx/NOx interaction, *Nature*, **315**, 207-210.

70 Feister U, Laschewski G, Grewe R-D, 2011, UV index forecasts and measurements of health-effective radiation, *J. Photochem. Photobiol. B.*, **102**, 55-68.

71 Feister U, Meyer G, Kirst U, 2013, Solar UV exposure of seafarers along subtropical and tropical shipping routes, *Photochem. Photobiol.*, **89**, 1497-1506.

72 Feng Y, Ramanathan V, Kotamarthi VR, 2013, Brown carbon: a significant atmospheric absorber of solar radiation?, *Atmos. Chem. Phys.*, **13**, 8607-8621.

73 Ferraro AJ, Highwood EJ, Charlton-Perez AJ, 2014, Weakened tropical circulation and reduced precipitation in response to geoengineering, *Environ. Res. Lett.*, **9**, DOI:10.1088/1748-9326/9/1/014001.

74 Fioletov VE, McArthur LJ, Mathews TW, Marrett L, 2010, Estimated ultraviolet exposure levels for a sufficient vitamin D status in North America, *J. Photochem. Photobiol. B.*, **100**, 57-66.

75 Fitzka M, Simic S, Hadzimustafic J, 2012, Trends in spectral UV radiation from long-term measurements at Hoher Sonnblick, Austria, *Theotet. Appl. Climatol.*, **110**, 585–593.

76 Fitzka M, Hadzimustafic J, Simic S, 2014, Total ozone and Umkehr observations at Hoher Sonnblick 1994–2011: Climatology and extreme events, *J. Geophys. Res. Atmos.*, **119**, 739-752.

77 Fountoulakis I, Bais AF, Tourpali K, Fragkos K, Misios S, 2014, Projected changes in solar UV radiation in the Arctic and sub-Arctic Ocean: Effects from changes in reflectivity, ice transmittance, clouds, and ozone, *J. Geophys. Res. Atmos.*, **119**, 8073–8090.

78 Frederick JE, Hodge AL, 2011, Solar irradiance at the earth's surface: long-term behavior observed at the South Pole, *Atmos. Chem. Phys.*, **11**, 1177-1189.

79 Frey KE, Perovich DK, Light B, 2011, The spatial distribution of solar radiation under a melting Arctic sea ice cover, *Geophys. Res. Lett.*, **38**, L22501.

80 Gall MP, Davies-Colley RJ, Merrilees RA, 2013, Exceptional visual clarity and optical purity in a sub-alpine lake, *Limnol. Oceanogr.*, **58**, 443–451.

81 Gao Z, Chang N-B, Gao W, 2010, Comparative analyses of the ultraviolet-B flux over the continental United State based on the NASA total ozone mapping spectrometer data and USDA ground-based measurements, *J. Appl. Remote Sens.*, **4**, 043547-043547-18.

82 Garcia RR, 2011, Atmospheric science: An Arctic ozone hole?, *Nature*, **478**, 462-463.

83 Garcia RR, Kinnison DE, Marsh DR, 2012, "World avoided" simulations with the Whole Atmosphere Community Climate Model, *J. Geophys. Res.*, **117**, D23303.

84 Gareis JAL, Lesack LFW, Bothwell ML, 2010, Attenuation of in situ UV radiation in Mackenzie Delta lakes with varying dissolved organic matter compositions, *Water Resource. Res.*, **46**, W09516.

85 Gent PR, Danabasoglu G, Donner LJ, Holland MM, Hunke EC, Jayne SR, Lawrence DM, Neale RB, Rasch PJ, Vertenstein M, Worley PH, Yang Z-L, Zhang M, 2011, The Community Climate System Model Version 4, *J. Climate*, **24**, 4973-4991.

86 Gerasopoulos E, Amiridis V, Kazadzis S, Kokkalis P, Eleftheratos K, Andreae MO, Andreae TW, El-Askary H, Zerefos CS, 2011, Three-year ground based measurements of aerosol optical depth over the Eastern Mediterranean: the urban environment of Athens, *Atmos. Chem. Phys.*, **11**, 2145-2159.

87 Gies P, Klekociuk A, Tully M, Henderson S, Javorniczky J, King K, Lemus-Deschamps L, Makin J, 2013, Low Ozone Over Southern Australia in August 2011 and its Impact on Solar Ultraviolet Radiation Levels, *Photochem. Photobiol.*, **89**, 984-994.

88 Giles DM, Holben BN, Eck TF, Sinyuk A, Smirnov A, Slutsker I, Dickerson RR, Thompson AM, Schafer JS, 2012, An analysis of AERONET aerosol absorption properties and classifications representative of aerosol source regions, *J. Geophys. Res. Atmos.*, **117**, D17203.
89 Goering CD, L'Ecuyer TS, Stephens GL, Slusser JR, Scott G, Davis J, Barnard JC, Madronich S, 2005, Simultaneous retrievals of column ozone and aerosol optical properties from direct and diffuse solar irradiance measurements, *J. Geophys. Res. Atmos.*, **110**, D05204.
90 Gyawali M, Arnott WP, Zaveri RA, Song C, Moosmüller H, Liu L, Mishchenko MI, Chen LWA, Green MC, Watson JG, Chow JC, 2012, Photoacoustic optical properties at UV, VIS, and near IR wavelengths for laboratory generated and winter time ambient urban aerosols, *Atmos. Chem. Phys.*, **12**, 2587-2601.
91 Haigh JD, Winning AR, Toumi R, Harder JW, 2010, An influence of solar spectral variations on radiative forcing of climate, *Nature*, **467**, 696-699.
92 Harder JW, Fontenla JM, Pilewskie P, Richard EC, Woods TN, 2009, Trends in solar spectral irradiance variability in the visible and infrared, *Geophys. Res. Lett.*, **36**, L07801.
93 Hartmann DL, Tank AMGK, Rusticucci M, Alexander LV, Brönnimann S, Charabi Y, Dentener FJ, Dlugokencky EJ, Easterling DR, Kaplan A, Soden BJ, Thorne PW, Wild M, Zhai PM, 2013, Observations: Atmosphere and Surface, in *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change* eds.: Stocker TF, Qin D, Plattner G-K, Tignor M, Allen SK, Boschung J, Nauels A, Xia Y, Bex V, Midgley PM, Cambridge University Press, Cambridge, United Kingdom and New York, NY, U.S.A.
94 Hassler B, Bodeker GE, Solomon S, Young PJ, 2011, Changes in the polar vortex: Effects on Antarctic total ozone observations at various stations, *Geophys. Res. Lett.*, **38**, L01805.
95 Hassler B, Daniel JS, Johnson BJ, Solomon S, Oltmans SJ, 2011, An assessment of changing ozone loss rates at South Pole: Twenty-five years of ozonesonde measurements, *J. Geophys. Res.*, **116**, D22301.
96 He H, Fioletov VE, Tarasick DW, Mathews TW, Long C, 2013, Validation of Environment Canada and NOAA UV Index Forecasts with Brewer Measurements from Canada, *J. Appl. Meteorol. Climatol.*, **52**, 1477-1489.
97 Heald CL, Coe H, Jimenez JL, Weber RJ, Bahreini R, Middlebrook AM, Russell LM, Jolleys M, Fu TM, Allan JD, Bower KN, Capes G, Crosier J, Morgan WT, Robinson NH, Williams PI, Cubison MJ, DeCarlo PF, Dunlea EJ, 2011, Exploring the vertical profile of atmospheric organic aerosol: comparing 17 aircraft field campaigns with a global model, *Atmos. Chem. Phys.*, **11**, 12673-12696.
98 Heckendorn P, Weisenstein D, Fueglistaler S, Luo BP, Rozanov E, Schraner M, Thomason LW, Peter T, 2009, The impact of geoengineering aerosols on stratospheric temperature and ozone, *Environ. Res. Lett.*, **4**, 045108.
99 Herman JR, 2010, Use of an improved radiation amplification factor to estimate the effect of total ozone changes on action spectrum weighted irradiances and an instrument response function, *J. Geophys. Res. Atmos.*, **115**, D23119.
100 Herman JR, DeLand MT, Huang LK, Labow G, Larko D, Lloyd SA, Mao J, Qin W, Weaver C, 2013, A net decrease in the Earth's cloud, aerosol, and surface 340 nm reflectivity during the past 33 yr (1979–2011), *Atmos. Chem. Phys.*, **13**, 8505-8524.
101 Hezel PJ, Zhang X, Bitz CM, Kelly BP, Massonnet F, 2012, Projected decline in spring snow depth on Arctic sea ice caused by progressively later autumn open ocean freeze-up this century, *Geophys. Res. Lett.*, **39**, L17505.
102 Hilboll A, Richter A, Burrows JP, 2013, Long-term changes of tropospheric NO_2 over megacities derived from multiple satellite instruments, *Atmos. Chem. Phys.*, **13**, 4145-4169.
103 Hoffer A, Gelencsér A, Guyon P, Kiss G, Schmid O, Frank GP, Artaxo P, Andreae MO, 2006, Optical properties of humic-like substances (HULIS) in biomass-burning aerosols, *Atmos. Chem. Phys.*, **6**, 3563-3570.
104 Hood LL, Soukharev BE, 2012, The Lower-Stratospheric Response to 11-Yr Solar Forcing: Coupling to the Troposphere–Ocean Response, *J. Atmos. Sci.*, **69**, 1841-1864.
105 Hu B, Wang YS, 2013, Ultraviolet radiation in the background region over Northeast China, *J. Atmos. Chem.*, **70**, 283-296.
106 Hudson RD, 2012, Measurements of the movement of the jet streams at mid-latitudes, in the Northern and Southern Hemispheres, 1979 to 2010, *Atmos. Chem. Phys.*, **12**, 7797-7808.
107 Ialongo I, Buchard V, Brogniez C, Casale GR, Siani AM, 2010, Aerosol single scattering albedo retrieval in the UV range: an application to OMI satellite validation, *Atmos. Chem. Phys.*, **10**, 331-340.

108 Ialongo I, Arola A, Kujanpää J, Tamminen J, 2011, Use of satellite erythemal UV products in analysing the global UV changes, *Atmos. Chem. Phys.*, **11**, 9649-9658.

109 IPCC, 2007, *(Intergovernmental Panel on Climate Change): Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, Cambridge, UK, and New York, NY.

110 IPCC, 2013, *(Intergovernmental Panel on Climate Change): Working Group I Contribution to the IPCC Fifth Assessment Report Climate Change 2013: The Physical Science Basis* Cambridge University Press, Cambridge, United Kingdom and New York, NY, U.S.A., Cambridge, UK, and New York, NY.

111 Isaksen ISA, Zerefos C, Wang WC, Balis D, Eleftheratos K, Rognerud B, Stordal F, Berntsen TK, LaCasce JH, Søvde OA, Olivié D, Orsolini YJ, Zyrichidou I, Prather M, Tuinder ONE, 2012, Attribution of the Arctic ozone column deficit in March 2011, *Geophys. Res. Lett.*, **39**, L24810.

112 Janjai S, Wisitsirikun S, Buntoung S, Pattarapanitchai S, Wattan R, Masiri I, Bhattarai BK, 2013, Comparison of UV index from Ozone Monitoring Instrument (OMI) with multi-channel filter radiometers at four sites in the tropics: effects of aerosols and clouds, *Int. J Climatol.*, **34**, 453-461.

113 Jégou F, Godin-Beekman S, Corrêa MP, Brogniez C, Auriol F, Peuch VH, Haeffelin M, Pazmino A, Saiag P, Goutail F, Mahé E, 2011, Validity of satellite measurements used for the monitoring of UV radiation risk on health, *Atmos. Chem. Phys.*, **11**, 13377-13394.

114 Jimenez JL, Canagaratna MR, Donahue NM, Prevot ASH, Zhang Q, Kroll JH, DeCarlo PF, Allan JD, Coe H, Ng NL, Aiken AC, Docherty KS, Ulbrich IM, Grieshop AP, Robinson AL, Duplissy J, Smith JD, Wilson KR, Lanz VA, Hueglin C, Sun YL, Tian J, Laaksonen A, Raatikainen T, Rautiainen J, Vaattovaara P, Ehn M, Kulmala M, Tomlinson JM, Collins DR, Cubison MJ, E., Dunlea J, Huffman JA, Onasch TB, Alfarra MR, Williams PI, Bower K, Kondo Y, Schneider J, Drewnick F, Borrmann S, Weimer S, Demerjian K, Salcedo D, Cottrell L, Griffin R, Takami A, Miyoshi T, Hatakeyama S, Shimono A, Sun JY, Zhang YM, Dzepina K, Kimmel JR, Sueper D, Jayne JT, Herndon SC, Trimborn AM, Williams LR, Wood EC, Middlebrook AM, Kolb CE, Baltensperger U, Worsnop DR, 2009, Evolution of organic aerosols in the atmosphere, *Science.*, **326**, 1525-1529.

115 Joughin I, Smith BE, Medley B, 2014, Marine ice sheet collapse potentially under way for the Thwaites Glacier Basin, West Antarctica, *Science.*, **344**, 735-738.

116 Junk J, Feister U, Helbig A, Görgen K, Rozanov E, Krzy, cin JW, Hoffmann L, 2012, The benefit of modeled ozone data for the reconstruction of a 99-year UV radiation time series, *J. Geophys. Res.*, **117**, D16102.

117 Kahn RA, Nelson DL, Garay MJ, Levy RC, Bull MA, Diner DJ, Martonchik JV, Paradise SR, Hansen EG, Remer LA, 2009, MISR aerosol product attributes and statistical comparisons with MODIS, *Geosci. Remote Sens. IEEE Transact.*, **47**, 4095-4114.

118 Kang SM, Polvani LM, Fyfe JC, Sigmond M, 2011, Impact of polar ozone depletion on subtropical precipitation, *Science.*, **332**, 951-954.

119 Kang SM, Polvani LM, Fyfe JC, Son SW, Sigmond M, P. Correa GJ, 2013, Modeling evidence that ozone depletion has impacted extreme precipitation in the austral summer, *Geophys. Res. Lett.*, **40**, 4054-4059.

120 Karpechko AY, Gillett NP, Gray LJ, Dall'Amico M, 2010, Influence of ozone recovery and greenhouse gas increases on Southern Hemisphere circulation, *J. Geophys. Res. Atmos.*, **115**, D22117.

121 Karpechko AY, Backman L, Thölix L, Ialongo I, Andersson M, Fioletov V, Heikkilä A, Johnsen B, Koskela T, Kyrölä E, Lakkala K, Myhre CL, Rex M, Sofieva VF, Tamminen J, Wohltmann I, 2013, The link between springtime total ozone and summer UV radiation in Northern Hemisphere extratropics, *J. Geophys. Res. Atmos.*, **118**, 8649-8661.

122 Kazadzis S, Kouremeti N, Bais A, Kazantzidis A, Meleti C, 2009, Aerosol forcing efficiency in the UVA region from spectral solar irradiance measurements at an urban environment, *Ann. Geophys.*, **27**, 2515-2522.

123 Kazadzis S, Amiridis V, Kouremeti N, 2012, The Effect of Aerosol Absorption in Solar Radiation, in *Advances in Meteorology, Climatology and Atmospheric Physics* eds.: Helmis CG, Nastos PT, Springer-Verlag, Berlin, pp. 1041-1048.

124 Kazantzidis A, Eleftheratos K, Zerefos CS, 2011, Effects of cirrus cloudiness on solar irradiance in four spectral bands, *Atmos. Res.*, **102**, 452-459.

125 Kimlin MG, Schallhorn KA, Meltzer RS, Slusser JR, Lantz K, 2005, Comparison of ultraviolet data from colocated instruments from the U.S. EPA Brewer Spectrophotometer Network and the U.S. Department of Agriculture UV-B Monitoring and Research Program, *Optic. Eng.*, **44**, 1-8.

126 Kinne S, O'Donnel D, Stier P, Kloster S, Zhang K, Schmidt H, Rast S, Giorgetta M, Eck TF, Stevens B, 2013, MAC-v1: A new global aerosol climatology for climate studies, *J. Adv. Model. Earth Syst.*, **5**, 704-740.

127 Kirchstetter TW, Thatcher TL, 2012, Contribution of organic carbon to wood smoke particulate matter absorption of solar radiation, *Atmos. Chem. Phys.*, **12**, 6067-6072.

128 Kreuter A, Blumthaler M, Webb AR, Bais AF, Kift R, Kouremeti N, 2013, Effects of Albedo on Solar Irradiance, in *Advances in Meteorology, Climatology and Atmospheric Physics*, Springer, Berlin Heidelberg, Germany, pp. 1089-1095.

129 Kreuter A, Buras R, Mayer B, Webb A, Kift R, Bais A, Kouremeti N, Blumthaler M, 2014, Solar irradiance in the heterogeneous albedo environment of the Arctic coast: measurements and a 3-D model study, *Atmos. Chem. Phys.*, **14**, 5989-6002.

130 Krotkov N, Bhartia PK, Herman J, Slusser J, Scott G, Labow G, Vasilkov AP, Eck TF, Dubovik O, Holben BN, 2005, Aerosol ultraviolet absorption experiment (2002 to 2004), part 2: Absorption optical thickness, refractive index, and single scattering albedo, *Optic. Eng.*, **44**, 041005.

131 Krzyścin JW, Sobolewski PS, Jarosławski J, Podgórski J, Rajewska-Więch B, 2011, Erythemal UV observations at Belsk, Poland, in the period 1976–2008: Data homogenization, climatology, and trends, *Acta Geophysica*, **59**, 155-182.

132 Kuebbeler M, Lohmann U, Feichter J, 2012, Effects of stratospheric sulfate aerosol geo-engineering on cirrus clouds, *Geophys. Res. Lett.*, **39**, L23803.

133 Kumharn W, Rimmer JS, Smedley ARD, Ying TY, Webb AR, 2012, Aerosol optical depth and the global Brewer network: A study using U.K.- and Malaysia-based Brewer spectrophotometers, *J. Atmos. Ocean. Technol.*, **29**, 857-866.

134 Kuttippurath J, Godin-Beekmann S, Lefèvre F, Nikulin G, Santee ML, Froidevaux L, 2012, Record-breaking ozone loss in the Arctic winter 2010/2011: comparison with 1996/1997, *Atmos. Chem. Phys.*, **12**, 7073-7085.

135 Kuttippurath J, Lefèvre F, Pommereau JP, Roscoe HK, Goutail F, Pazmiño A, Shanklin JD, 2013, Antarctic ozone loss in 1979-2010: first sign of ozone recovery, *Atmos. Chem. Phys.*, **13**, 1625-1635.

136 Kwok R, Rothrock DA, 2009, Decline in Arctic sea ice thickness from submarine and ICESat records: 1958–2008, *Geophys. Res. Lett.*, **36**, L15501.

137 Labow GJ, Herman JR, Huang L-K, Lloyd SA, DeLand MT, Qin W, Mao J, Larko DE, 2011, Diurnal variation of 340 nm Lambertian equivalent reflectivity due to clouds and aerosols over land and oceans, *J. Geophys. Res.*, **116**, D11202.

138 Lamarque J-F, Kyle GP, Meinshausen M, Riahi K, Smith SJ, van Vuuren DP, Conley AJ, Vitt F, 2011, Global and regional evolution of short-lived radiatively-active gases and aerosols in the Representative Concentration Pathways, *Clim.Change*, **109**, 191-212.

139 Lamarque JF, Bond TC, Eyring V, Granier C, Heil A, Klimont Z, Lee D, Liousse C, Mieville A, Owen B, Schultz MG, Shindell D, Smith SJ, Stehfest E, Van Aardenne J, Cooper OR, Kainuma M, Mahowald N, McConnell JR, Naik V, Riahi K, van Vuuren DP, 2010, Historical (1850–2000) gridded anthropogenic and biomass burning emissions of reactive gases and aerosols: methodology and application, *Atmos. Chem. Phys.*, **10**, 7017-7039.

140 Lambe AT, Cappa CD, Massoli P, Onasch TB, Forestieri SD, Martin AT, Cummings MJ, Croasdale DR, Brune WH, Worsnop DR, Davidovits P, 2013, Relationship between Oxidation Level and Optical Properties of Secondary Organic Aerosol, *Environ. Sci. Technol.*, **47**, 6349-6357.

141 Langematz U, Meul S, Grunow K, Romanowsky E, Oberländer S, Abalichin J, Kubin A, 2014, Future arctic temperature and ozone: The role of stratospheric composition changes, *J. Geophys. Res. Atmos.*, **119**, 2092-2112.

142 Laskin A, Laskin J, Nizkorodov SA, 2012, Mass spectrometric approaches for chemical characterisation of atmospheric aerosols: critical review of the most recent advances, *Environ. Chem.*, **9**, 163-189.

143 Lee-Taylor J, Madronich S, Fischer C, Mayer B, 2010, A Climatology of UV Radiation, 1979–2000, 65S–65N, in *UV Radiation in Global Climate Change* eds.: Gao W, Slusser J, Schmoldt D, Springer Berlin Heidelberg, pp. 1-20.

144 Lei R, Zhang Z, Matero I, Cheng B, Li Q, Huang W, 2012, Reflection and transmission of irradiance by snow and sea ice in the central Arctic Ocean in summer 2010, *Polar Res.*, **31**, 17325.

145 Lemus-Deschamps L, Makin JK, 2012, Fifty years of changes in UV Index and implications for skin cancer in Australia, *Int. J. Biometeorol.*, **56**, 727-35.

146 Liley JB, Forgan BW, 2009, Aerosol optical depth over Lauder, New Zealand, *Geophys. Res. Lett.*, **36**, L07811.
147 Lindfors A, Tanskanen A, Arola A, van der A R, Bais A, Feister U, Janouch M, Josefsson W, Koskela T, Lakkala K, den Outer PN, Smedley ARD, Slaper H, Webb AR, 2009, The PROMOTE UV record: Toward a global satellite-based climatology of surface ultraviolet irradiance, *IEEE J. Select. Top. Appl. Earth Obs. Remote Sens.*, **2**, 207-212.
148 Liu Y, Key JR, Liu Z, Wang X, Vavrus SJ, 2012, A cloudier Arctic expected with diminishing sea ice, *Geophys. Res. Lett.*, **39**, L05705.
149 Lockwood M, Rouillard AP, Finch ID, 2009, The rise and fall of open solar flux during the current grand solar maximum, *Astrophys. J.*, **700**, 937.
150 Lockwood M, Bell C, Woollings T, Harrison RG, Gray LJ, Haigh JD, 2010, Top-down solar modulation of climate: evidence for centennial-scale change, *Environ. Res. Lett.*, **5**, 034008.
151 Lockwood M, Owens MJ, Barnard L, Davis CJ, Steinhilber F, 2011, The persistence of solar activity indicators and the descent of the Sun into Maunder Minimum conditions, *Geophys. Res. Lett.*, **38**, L22105.
152 Manney GL, Santee ML, Rex M, Livesey NJ, Pitts MC, Veefkind P, Nash ER, Wohltmann I, Lehmann R, Froidevaux L, Poole LR, Schoeberl MR, Haffner DP, Davies J, Dorokhov V, Gernandt H, Johnson B, Kivi R, Kyro E, Larsen N, Levelt PF, Makshtas A, McElroy CT, Nakajima H, Parrondo MC, Tarasick DW, von der Gathen P, Walker KA, Zinoviev NS, 2011, Unprecedented Arctic ozone loss in 2011, *Nature*, **478**, 469-475.
153 Markus T, Stroeve JC, Miller J, 2009, Recent changes in Arctic sea ice melt onset, freezeup, and melt season length, *J. Geophys. Res. Oceans*, **114**, C12024.
154 McKenzie RL, Johnston PV, Seckmeyer G, 1997, UV spectro-radiometry in the network for the detection of stratospheric change (NDSC), in *Solar Ultraviolet Radiation. Modelling, Measurements and Effects,* **Vol. 1.52** (Eds.: Zerefos CS, Bais AF), Springer-Verlag, Berlin, pp. 279-287.
155 McKenzie RL, Weinreis C, Johnston PV, Liley B, Shiona H, Kotkamp M, Smale D, Takegawa N, Kondo Y, 2008, Effects of urban pollution on UV spectral irradiances, *Atmos. Chem. Phys.*, **8**, 5683–5697.
156 McKenzie RL, Liley JB, Björn LO, 2009, UV Radiation: Balancing Risks and Benefits, *Photochem. Photobiol.*, **85**, 88-98.
157 McKenzie RL, Aucamp PJ, Bais AF, Björn LO, Ilyas M, Madronich S, 2011, Ozone depletion and climate change: Impacts on UV radiation, *Photochem. Photobiol. Sci.*, **10**, 182-198.
158 McKenzie RL, Scragg R, Liley B, Johnston P, Wishart J, Stewart A, Prematunga R, 2012, Serum 25-hydroxyvitamin-D responses to multiple UV exposures from solaria: inferences for exposure to sunlight, *Photochem Photobiol Sci*, **11**, 1174-85.
159 McKenzie RL, Liley B, Johnston P, Scragg R, Stewart A, Reeder AI, Allen MW, 2013, Small doses from artificial UV sources elucidate the photo-production of vitamin D, *Photochem. Photobiol. Sci.*, **12**, 1726-1737.
160 McKinlay AF, Diffey BL, 1987, A Reference Action Spectrum for Ultraviolet Induced Erythema in Human Skin, in *Human Exposure to Ultraviolet Radiation: Risks and Regulations* eds.: Passchier WF, Bosnajakovic BFM, Elsevier, Amsterdam, pp. 83-87.
161 McLandress C, Shepherd TG, Scinocca JF, Plummer DA, Sigmond M, Jonsson AI, Reader MC, 2011, Separating the Dynamical Effects of Climate Change and Ozone Depletion. Part II: Southern Hemisphere Troposphere, *J. Climate*, **24**, 1850-1868.
162 Medina R, Fitzgerald RM, Min Q, 2012, Retrieval of the single scattering albedo in the El Paso-Juarez Airshed using the TUV model and a UV-MFRSR radiometer, *Atmos. Environ.*, **46**, 430-440.
163 Meinander O, Kazadzis S, Arola A, Riihelä A, Räisänen P, Kivi R, Kontu A, Kouznetsov R, Sofiev M, Svensson J, Suokanerva H, Aaltonen V, Manninen T, Roujean JL, Hautecoeur O, 2013, Spectral albedo of seasonal snow during intensive melt period at Sodankylä, beyond the Arctic Circle, *Atmos. Chem. Phys.*, **13**, 3793-3810.
164 Meleti C, Bais AF, Kazadzis S, Kouremeti N, Garane K, Zerefos C, 2009, Factors affecting solar ultraviolet irradiance measured since 1990 at Thessaloniki, Greece, *Int. J. Remote Sens.*, **30**, 4167-4179.
165 Micheletti MI, Piacentini RD, Madronich S, 2003, Sensitivity of biologically active UV radiation to stratospheric ozone changes: Effects of action spectrum shape and wavelength range, *Photochem. Photobiol.*, **78**, 456-461.
166 NARSTO, 2004, *Particulate Matter Science for Policy Makers: A NARSTO Assessment*, Cambridge, England.

167 Newman PA, Oman LD, Douglass AR, Fleming EL, Frith SM, Hurwitz MM, Kawa SR, Jackman CH, Krotkov NA, Nash ER, Nielsen JE, Pawson S, Stolarski RS, Velders GJM, 2009, What would have happened to the ozone layer if chlorofluorocarbons (CFCs) had not been regulated?, *Atmos. Chem. Phys.*, **9**, 2113-2128.

168 Newman PA, McKenzie RL, 2011, UV impacts avoided by the Montreal Protocol, *Photochem. Photobiol. Sci.*, **10**, 1152-1160.

169 Nikitidou E, Kazantzidis A, Bock VD, Backer HD, 2013, The aerosol forcing efficiency in the UV region and the estimation of single scattering albed at a typical West European site, *Atmos. Environ.*, **69**, 313-320.

170 Norsang G, Chen Y-C, Pingcuo N, Dahlback A, Frette Ø, Kjeldstad B, Hamre B, Stamnes K, Stamnes JJ, 2014, Comparison of ground-based measurements of solar UV radiation at four sites on the Tibetan Plateau, *Appl. Optic.*, **53**, 736-747.

171 Norval M, Björn LO, Gruijl FRd, 2009, Is the action spectrum for the UV-induced production of previtamin D3 in human skin correct?, *Photochem. Photobiol. Sci.*, **9**, 11-17.

172 Nyeki S, Halios CH, Baum W, Eleftheriadis K, Flentje H, Gröbner J, Vuilleumier L, Wehrli C, 2012, Ground-based aerosol optical depth trends at three high-altitude sites in Switzerland and southern Germany from 1995 to 2010, *J. Geophys. Res.*, **117**, D18202.

173 Olds W, 2010, *Elucidating the Links Between UV Radiation and Vitamin D Synthesis:Using an In Vitro Model, PhD Thesis*, Queensland University of Technology (Brisbane)

174 Omar AH, Winker DM, Vaughan MA, Hu Y, Trepte CR, Ferrare RA, Lee K-P, Hostetler CA, Kittaka C, Rogers RR, Kuehn RE, Liu Z, 2009, The CALIPSO Automated Aerosol Classification and Lidar Ratio Selection Algorithm, *J. Atmos. Ocean. Technol.*, **26**, 1994-2014.

175 Owens MJ, Lockwood M, Barnard L, Davis CJ, 2011, Solar cycle 24: Implications for energetic particles and long-term space climate change, *Geophys. Res. Lett.*, **38**, L19106.

176 Palancar GG, Lefer BL, Hall SR, Shaw WJ, Corr CA, Herndon SC, Slusser JR, Madronich S, 2013, Effect of aerosols and NO2 concentration on ultraviolet actinic flux near Mexico City during MILAGRO: measurements and model calculations, *Atmos. Chem. Phys.*, **13**, 1011-1022.

177 Pandey P, De Ridder K, Gillotay D, van Lipzig NPM, 2012, Estimating cloud optical thickness and associated surface UV irradiance from SEVIRI by implementing a semi-analytical cloud retrieval algorithm, *Atmos. Chem. Phys.*, **12**, 7961-7975.

178 Para J, Charrière B, Matsuoka A, Miller WL, Rontani JF, Sempéré R, 2013, UV/PAR radiation and DOM properties in surface coastal waters of the Canadian shelf of the Beaufort Sea during summer 2009, *Biogeosci.*, **10**, 2761-2774.

179 Parkinson CL, Cavalieri DJ, 2012, Antarctic sea ice variability and trends, 1979-2010, *The Cryosphere*, **6**, 871-880.

180 Perovich DK, 2006, The interaction of ultraviolet light with Arctic sea ice during SHEBA, *Annal. Glaciol.*, **44**, 47-52.

181 Perovich DK, Polashenski C, 2012, Albedo evolution of seasonal Arctic sea ice, *Geophys. Res. Lett.*, **39**, L08501.

182 Petkov B, Vitale V, Gröbner J, Hülsen G, De Simone S, Gallo V, Tomasi C, Busetto M, Barth VL, Lanconelli C, Mazzola M, 2012, Short-term variations in surface UV-B irradiance and total ozone column at Ny-Ålesund during the QAARC campaign, *Atmos. Res.*, **108**, 9-18.

183 Petkov B, Vitale V, Tomasi C, Siani AM, Seckmeyer G, Webb A, Smedley ARD, Casale GR, Werner R, Lanconelli C, Mazzola M, Lupi A, Busetto M, Diémoz H, Goutail F, Köhler U, Mendeva BT, Josefsson W, Moore D, Bartolomé ML, Moreta González JR, Mišaga O, Dahlback A, Tóth Z, Varghese S, De Backer H, Stübi R, Vaníček K, 2014, Response of the ozone column over Europe to the 2011 Arctic ozone depletion event according to ground-based observations and assessment of the consequent variations in surface UV irradiance, *Atmos. Environ.*, **85**, 169-178.

184 Petters JL, Saxena VK, Slusser JR, Wenny BN, Madronich S, 2003, Aerosol single scattering albedo retrieved from measurements of surface UV irradiance and a radiative transfer model, *J. Geophys. Res. Atmos.*, **108**, 4288.

185 Philipona R, Behrens K, Ruckstuhl C, 2009, How declining aerosols and rising greenhouse gases forced rapid warming in Europe since the 1980s, *Geophys. Res. Lett.*, **36**, L02806.

186 Pitari G, Aquila V, Kravitz B, Robock A, Watanabe S, Cionni I, Luca ND, Genova GD, Mancini E, Tilmes S, 2014, Stratospheric ozone response to sulfate geoengineering: Results from the Geoengineering Model Intercomparison Project (GeoMIP), *J. Geophys. Res. Atmos.*, **119**, 2629–2653.

187 Polvani LM, Previdi M, Deser C, 2011, Large cancellation, due to ozone recovery, of future Southern Hemisphere atmospheric circulation trends, *Geophys. Res. Lett.*, **38**, L04707.

188 Pommereau JP, Goutail F, Lefèvre F, Pazmino A, Adams C, Dorokhov V, Eriksen P, Kivi R, Stebel K, Zhao X, van Roozendael M, 2013, Why unprecedented ozone loss in the Arctic in 2011? Is it related to climate change?, *Atmos. Chem. Phys.*, **13**, 5299-5308.

189 Pope FD, Braesicke P, Grainger RG, Kalberer M, Watson IM, Davidson PJ, Cox RA, 2012, Stratospheric aerosol particles and solar-radiation management, *Nature Clim. Change*, **2**, 713-719.

190 Pope SJ, Godar DE, 2010, Solar UV Geometric Conversion Factors: Horizontal Plane to Cylinder Model dagger, *Photochem. Photobiol.*, **86**, 457-466.

191 Portmann RW, Daniel JS, Ravishankara AR, 2012, Stratospheric ozone depletion due to nitrous oxide: influences of other gases, *Philos. Trans. Roy. Soc. Lond. B.*, **367**, 1256-1264.

192 Randall DA, 2013, Beyond deadlock, *Geophys. Res. Lett.*, **40**, 5970-5976.

193 Reader MC, Plummer DA, Scinocca JF, Shepherd TG, 2013, Contributions to twentieth century total column ozone change from halocarbons, tropospheric ozone precursors, and climate change, *Geophys. Res. Lett.*, **40**, 6276-6281.

194 Remer LA, Mattoo S, Levy RC, Munchak LA, 2013, MODIS 3 km aerosol product: algorithm and global perspective, *Atmos. Meas. Tech.*, **6**, 1829-1844.

195 Riechelmann S, Schrempf M, Seckmeyer G, 2013, Simultaneous measurement of spectral sky radiance by a non-scanning multidirectional spectroradiometer (MUDIS), *Measure. Sci. Technol.*, **24**, 125501.

196 Rieder HE, Staehelin J, Maeder JA, Peter T, Ribatet M, Davison AC, Stübi R, Weihs P, Holawe F, 2010, Extreme events in total ozone over Arosa - Part 2: Fingerprints of atmospheric dynamics and chemistry and effects on mean values and long-term changes, *Atmos. Chem. Phys.*, **10**, 10033-10045.

197 Rieder HE, Staehelin J, Maeder JA, Peter T, Ribatet M, Davison AC, Stübi R, Weihs P, Holawe F, 2010, Extreme events in total ozone over Arosa - Part 1: Application of extreme value theory, *Atmos. Chem. Phys.*, **10**, 10021-10031.

198 Rignot E, Mouginot J, Morlighem M, Seroussi H, Scheuchl B, 2014, Widespread, rapid grounding line retreat of Pine Island, Thwaites, Smith, and Kohler glaciers, West Antarctica, from 1992 to 2011, *Geophys. Res. Lett.*, **41**, 3502-3509.

199 Rincón AG, Guzmán MI, Hoffmann MR, Colussi AJ, 2009, Thermochromism of Model Organic Aerosol Matter, *J. Phys. Chem. Lett.*, **1**, 368-373.

200 Robinson SA, Erickson III DJ, 2014, Not just about sunburn – the ozone hole's profound effect on climate has significant implications for Southern Hemisphere ecosystems, *Glob. Change Biol.*, in press.

201 Ruckstuhl C, Philipona R, Behrens K, Collaud Coen M, Dürr B, Heimo A, Mätzler C, Nyeki S, Ohmura A, Vuilleumier L, Weller M, Wehrli C, Zelenka A, 2008, Aerosol and cloud effects on solar brightening and the recent rapid warming, *Geophys. Res. Lett.*, **35**, L12708.

202 Sabetghadam S, Ahmadi-Givi F, Golestani Y, 2012, Visibility trends in Tehran during 1958–2008, *Atmos. Environ.*, **62**, 512-520.

203 Salby M, Titova E, Deschamps L, 2011, Rebound of Antarctic ozone, *Geophys. Res. Lett.*, **38**, L09702.

204 Salby M, Titova EA, Deschamps L, 2012, Changes of the Antarctic ozone hole: Controlling mechanisms, seasonal predictability, and evolution, *J. Geophys. Res.*, **117**, D10111.

205 Sanchez-Lorenzo A, Calbó J, Wild M, 2013, Global and diffuse solar radiation in Spain: Building a homogeneous dataset and assessing their trends, *Glob. Planet. Change*, **100**, 343-352.

206 Schmalwieser AW, Cabaj A, Schauberger G, Rohn H, Maier B, Maier H, 2010, Facial solar UV exposure of Austrian farmers during occupation, *Photochem Photobiol*, **86**, 1404-13.

207 Schmalwieser AW, Enzi C, Wallisch S, Holawe F, Maier B, Weihs P, 2010, UV exposition during typical lifestyle behavior in an urban environment, *Photochem Photobiol*, **86**, 711-5.

208 Schmalwieser AW, Wallisch S, Diffey B, 2012, A library of action spectra for erythema and pigmentation, *Photochem. Photobiol. Sci.*, **11**, 251-268.

209 Seckmeyer G, McKenzie RL, 1992, Increased ultraviolet-radiation in New-Zealand (45-degrees-S) relative to Germany (48-degrees-N), *Nature*, **359**, 135-137.

210 Seckmeyer G, Bais A, Bernhard G, Blumthaler M, Booth CR, Lantz K, McKenzie RL, 2005, *Instruments to measure solar ultraviolet irradiance. Part 2: Broadband instruments measuring erythemally weighted solar irradiance, World Meteorological Organisation, Global Atmospheric Watch, Report No. 164*, Geneva.

211 Seckmeyer G, Pissulla D, Glandorf M, Henriques D, Johnsen B, Webb A, Siani AM, Bais A, Kjeldstad B, Brogniez C, Lenoble J, Gardiner B, Kirsch P, Koskela T, Kaurola J, Uhlmann B, Slaper H, den Outer P,

Janouch M, Werle P, Grobner J, Mayer B, de la Casiniere A, Simic S, Carvalho F, 2008, Variability of UV irradiance in Europe, *Photochem. Photobiol.*, **84**, 172-179.

212 Seckmeyer G, Bais A, Bernhard G, Blumthaler M, Drüke S, Kiedron P, K.Lantz, McKenzie RL, Riechelmann S, 2010, Instruments to Measure Solar Ultraviolet Radiation Part 4: Array Spectroradiometers, World Meteorological Organization, Global Atmospheric Watch, Report No. 191, Geneva, p. 43

213 Seckmeyer G, Klingebiel M, Riechelmann S, Lohse I, McKenzie RL, Ben Liley J, Allen MW, Siani A-M, Casale GR, 2012, A critical assessment of two types of personal UV dosimeters, *Photochem. Photobiol.*, **88**, 215-222.

214 Seckmeyer G, Schrempf M, Wieczorek A, Riechelmann S, Graw K, Seckmeyer S, Zankl M, 2013, A novel method to calculate solar UV exposure relevant to vitamin D production in humans, *Photochem. Photobiol.*, **89**, 974-983.

215 Seidel DJ, Gillett NP, Lanzante JR, Shine KP, Thorne PW, 2011, Stratospheric temperature trends: our evolving understanding, *Wiley. Interdiscip. Rev. Climate Change*, **2**, 592-616.

216 Serrano M-A, Canada J, Moreno JC, 2010, Erythemal ultraviolet exposure of cyclists in Valencia, Spain, *Photochem Photobiol*, **86**, 716-21.

217 Serrano M-A, Canada J, Moreno JC, Members of the Valencia Solar Radiation Research Group, 2013, Erythemal ultraviolet solar radiation doses received by young skiers, *Photochem. Photobiol. Sci.*, **12**, 1976-1983.

218 Sharma NP, Bhattarai BK, Sapkota B, Kjeldstad B, 2013, Satellite estimation and ground measurements of solar UV index and influence of aerosol in ground based UV data in Kathmandu, Nepal, *Int. J. Environ. Sci.*, **3**, 1362-1372.

219 Siani AM, Casale GR, Sisto R, Colosimo A, Lang CA, Kimlin MG, 2011, Occupational Exposures to Solar Ultraviolet Radiation of Vineyard Workers in Tuscany (Italy), *Photochem. Photobiol.*, **87**, 925-934.

220 Siani AM, Modesti S, Casale GR, Diemoz H, Colosimo A, 2013, Biologically effective surface UV climatology at Rome and Aosta, Italy, *AIP Conference Proceedings*, **1531**, 903-906.

221 Siani AM, Casale GR, Modesti S, Parisi AV, Colosimo A, 2014, Investigation on the capability of polysulphone for measuring biologically effective solar UV exposures, *Photochem. Photobiol. Sci.*, **13**, 521-530.

222 Sigmond M, Reader MC, Fyfe JC, Gillett NP, 2011, Drivers of past and future Southern Ocean change: Stratospheric ozone versus greenhouse gas impacts, *Geophys. Res. Lett.*, **38**, L12601.

223 Silva AA, 2013, Erythemal dose rate under noon overcast skies, *Photochem. Photobiol. Sci.*, **12**, 777-786.

224 Simic S, Fitzka M, Schmalwieser A, Weihs P, Hadzimustafic J, 2011, Factors affecting UV irradiance at selected wavelengths at Hoher Sonnblick, *Atmos. Res.*, **101**, 869-878.

225 Sinnhuber BM, Stiller G, Ruhnke R, von Clarmann T, Kellmann S, Aschmann J, 2011, Arctic winter 2010/2011 at the brink of an ozone hole, *Geophys. Res. Lett.*, **38**, L24814.

226 Smedley ARD, Rimmer JS, Moore D, Toumi R, Webb AR, 2012, Total ozone and surface UV trends in the United Kingdom: 1979–2008, *Int. J Climatol.*, **32**, 338-346.

227 Smith KL, Polvani LM, Marsh DR, 2012, Mitigation of 21st century Antarctic sea ice loss by stratospheric ozone recovery, *Geophys. Res. Lett.*, **39**, L20701.

228 Smith SJ, Bond TC, 2014, Two hundred fifty years of aerosols and climate: the end of the age of aerosols, *Atmos. Chem. Phys.*, **14**, 537-549.

229 Son S-W, Gerber EP, Perlwitz J, Polvani LM, Gillett N, Seo K-H, Eyring V, Shepherd TG, Waugh D, Akiyoshi H, Austin J, Baumgaertner A, Bekki S, Braesicke P, Brühl C, Butchart N, Chipperfield M, Cugnet D, Dameris M, Dhomse S, Frith S, Garny H, Garcia R, Hardiman SC, Jöckel P, Lamarque J-F, Mancini E, Marchand M, Michou M, Nakamura T, Morgenstern O, Pitari G, Plummer DA, Pyle J, Rozanov E, Scinocca JF, Shibata K, Smale D, Teyssèdre H, Tian W, Yamashita Y, 2010, The impact of stratospheric ozone on the Southern Hemisphere circulation change: A multimodel assessment, *J. Geophys. Res. Atmos.*, **115**, D014271.

230 Steig EJ, Ding Q, Battisti DS, Jenkins A, 2012, Tropical forcing of Circumpolar Deep Water Inflow and outlet glacier thinning in the Amundsen Sea Embayment, West Antarctica, *Annal. Glaciol.*, **53**, 19-28.

231 Steinhilber F, Beer J, 2013, Prediction of solar activity for the next 500 years, *J. Geophys. Res. Space Phys.*, **118**, 1861-1867.

232 Stolarski RS, Douglass AR, Remsberg EE, Livesey NJ, Gille JC, 2012, Ozone temperature correlations in the upper stratosphere as a measure of chlorine content, *J. Geophys. Res.*, **117**, D10305.

233 Streets DG, Yan F, Chin M, Diehl T, Mahowald N, Schultz M, Wild M, Wu Y, Yu C, 2009, Anthropogenic and natural contributions to regional trends in aerosol optical depth, 1980–2006, *J. Geophys. Res. Atmos.*, **114**, D00D18.
234 Swartz WH, Stolarski RS, Oman LD, Fleming EL, Jackman CH, 2012, Middle atmosphere response to different descriptions of the 11-yr solar cycle in spectral irradiance in a chemistry-climate model, *Atmos. Chem. Phys.*, **12**, 5937-5948.
235 Tanskanen A, Lindfors A, Maatta A, Krotkov N, Herman J, Kaurola J, Koskela T, Lakkala K, Fioletov V, Bernhard G, McKenzie R, Kondo Y, O'Neill M, Slaper H, den Outer P, Bais AF, Tamminen J, 2007, Validation of daily erythemal doses from ozone monitoring instrument with ground-based UV measurement data, *J. Geophys. Res. Atmos.*, **112**, D24S44.
236 Taylor KE, Stouffer RJ, Meehl GA, 2011, An overview of CMIP5 and the experiment design, *Bull. Amer. Meteorolog. Soc.*, **93**, 485-498.
237 Tedetti M, Sempéré R, Vasilkov A, Charrière B, Nérini D, Miller WL, Kawamura K, Raimbault P, 2007, High penetration of ultraviolet radiation in the south east Pacific waters, *Geophys. Res. Lett.*, **34**, L12610.
238 Thompson DWJ, Seidel DJ, Randel WJ, Zou C-Z, Butler AH, Mears C, Osso A, Long C, Lin R, 2012, The mystery of recent stratospheric temperature trends, *Nature*, **491**, 692-697.
239 Tilmes S, Kinnison DE, Garcia RR, Salawitch R, Canty T, Lee-Taylor J, Madronich S, Chance K, 2012, Impact of very short-lived halogens on stratospheric ozone abundance and UV radiation in a geo-engineered atmosphere, *Atmos. Chem. Phys.*, **12**, 10945-10955.
240 Tilmes S, Fasullo J, Lamarque J-F, Marsh DR, Mills M, Alterskjær K, Muri H, Kristjánsson JE, Boucher O, Schulz M, Cole JNS, Curry CL, Jones A, Haywood J, Irvine PJ, Ji D, Moore JC, Karam DB, Kravitz B, Rasch PJ, Singh B, Yoon J-H, Niemeier U, Schmidt H, Robock A, Yang S, Watanabe S, 2013, The hydrological impact of geoengineering in the Geoengineering Model Intercomparison Project (GeoMIP), *J. Geophys. Res. Atmos.*, **118**, 11,036-11,058.
241 Turnbull DJ, Parisi AV, 2010, Latitudinal variations over Australia of the solar UV-radiation exposures for vitamin D(3) in shade compared to full sun, *Radiat. Res.*, **173**, 373-379.
242 Turner J, Parisi AV, 2013, Influence of reflected UV irradiance on occupational exposure from combinations of reflective wall surfaces, *Photochem. Photobiol. Sci.*, **12**, 1589-1595.
243 UNEP, 2010, *Environmental Effects of Ozone Depletion and its Interaction with Climate Change: 2010 Assessment*, United Nations Environment Programme (UNEP), Nairobi.
244 Updyke KM, Nguyen TB, Nizkorodov SA, 2012, Formation of brown carbon via reactions of ammonia with secondary organic aerosols from biogenic and anthropogenic precursors, *Atmos. Environ.*, **63**, 22-31.
245 Utrillas MP, Marín MJ, Esteve AR, Estellés V, Gandía S, Núnez JA, Martínez-Lozano JA, 2013, Ten years of measured UV Index from the Spanish UVB Radiometric Network, *J. Photochem. Photobiol. B.*, **125**, 1-7.
246 van Dijk A, Slaper H, Outer PNd, Morgenstern O, Braesicke P, Pyle JA, Garny H, Stenke A, Dameris M, Kazantzidis A, Tourpali K, Bais AF, 2013, Skin cancer risks avoided by the Montreal Protocol – worldwide modelling integrating coupled climate-chemistry models with a risk model for UV, *Photochem. Photobiol. Sci.*, **89**, 234-246.
247 Vernez D, Milon A, Vuilleumier L, Bulliard JL, 2012, Anatomical exposure patterns of skin to sunlight: relative contributions of direct, diffuse and reflected ultraviolet radiation, *Br. J. Dermatol.*, **167**, 383-390.
248 Vitale V, Petkov B, Goutail F, Lanconelli C, Lupi A, Mazzola M, Busetto M, Pazmino A, Schioppo R, Genoni L, Tomasi C, 2011, Variations of UV irradiance at Antarctic station Concordia during the springs of 2008 and 2009, *Antarctic. Sci.*, **23**, 389-398.
249 Vogelmann AM, Ackerman TP, Turco RP, 1992, Enhancements in biologically effective ultraviolet radiation following volcanic eruptions, *Nature*, **359**, 47.
250 Wagner JE, Angelini F, Arola A, Blumthaler M, Fitzka M, Gobbi GP, Kift R, Kreuter A, Rieder HE, Simic S, Webb ANN, Weihs P, 2010, Comparison of surface UV irradiance in mountainous regions derived from satellite observations and model calculations with ground-based measurements, *Metero. Zeits.*, **19**, 481-490.
251 Wang K, Dickinson RE, Liang S, 2009, Clear Sky Visibility Has Decreased over Land Globally from 1973 to 2007, *Science.*, **323**, 1468-1470.
252 Wang M, Overland JE, 2012, A sea ice free summer Arctic within 30 years: An update from CMIP5 models, *Geophys. Res. Lett.*, **39**, L18501.
253 Wang YW, Yang YH, 2014, China's dimming and brightening: evidence, causes and hydrological implications, *Ann. Geophys.*, **32**, 41-55.

254 Wang ZB, Hu M, Wu ZJ, Yue DL, He LY, Huang XF, Liu XG, Wiedensohler A, 2013, Long-term measurements of particle number size distributions and the relationships with air mass history and source apportionment in the summer of Beijing, *Atmos. Chem. Phys.*, **13**, 10159-10170.

255 Watanabe S, Takemura T, Sudo K, Yokohata T, Kawase H, 2012, Anthropogenic changes in the surface all-sky UV-B radiation through 1850–2005 simulated by an Earth system model, *Atmos. Chem. Phys.*, **12**, 5249-5257.

256 Waugh DW, Primeau F, DeVries T, Holzer M, 2013, Recent Changes in the Ventilation of the Southern Oceans, *Science.*, **339**, 568-570.

257 Webb A, Gardiner BG, Leszczynski K, Mohnen VA, Johnston P, Harrison N, Bigelow D, 2003, *Quality Assurance in Monitoring Solar Ultraviolet Radiation: The State of the Art, World Meteorological Organisation, Global Atmospheric Watch, Report No. 146*, Geneva.

258 Webb AR, Kift R, Berry JL, Rhodes LE, 2011, The vitamin D debate: Translating controlled experiments into reality for human sun exposure times, *Photochem. Photobiol.*, **87**, 741-745.

259 Webb AR, Slaper H, Koepke P, Schmalwieser AW, 2011, Know your standard: Clarifying the CIE erythema action spectrum, *Photochem. Photobiol.*, **87**, 483-486.

260 Weihs P, Schmalwieser A, Reinisch C, Meraner E, Walisch S, Harald M, 2013, Measurements of personal UV exposure on different parts of the body during various activities, *Photochem. Photobiol.*, **89**, 1004-1007.

261 Wenny BN, Schafer JS, DeLuisi JJ, Saxena VK, Barnard WF, Petropavlovskikh IV, Vergamini AJ, 1998, A study of regional aerosol radiative properties and effects on ultraviolet-B radiation, *J. Geophys. Res.*, **103**, 17083-17097.

262 Wetzel MA, Shaw GE, Slusser JR, Borys RD, Cahill CF, 2003, Physical, chemical, and ultraviolet radiative characteristics of aerosol in central Alaska, *J. Geophys. Res. Atmos.*, **108**, 4418.

263 WMO, 2007, (World Meteorological Organization): Scientific Assessment of Ozone Depletion: 2006, Global ozone Research and Monitoring Project, Report No. 50, Geneva, Switzerland p. 572

264 WMO, 2011, (World Meteorological Organization): Scientific Assessment of Ozone Depletion: 2010, Global Ozone Research and Monitoring Project, Report No. 52, Geneva, Switzerland p. 438

265 WMO, 2015, (World Meteorological Organization): Scientific Assessment of Ozone Depletion: 2014, Global Ozone Research and Monitoring Project, Report No. 55, Geneva, Switzerland

266 Wu J, Zhang X, Hu J, Zhao D, 2013, Probability of different visibility grades in China over a 50-year period, *Meteorol. Atmos. Phys.*, **122**, 115-123.

267 Xu M, Liang XZ, Gao W, Krotkov N, 2010, Comparison of TOMS retrievals and UVMRP measurements of surface spectral UV radiation in the United States, *Atmos. Chem. Phys.*, **10**, 8669-8683.

268 Yoon J, von Hoyningen-Huene W, Vountas M, Burrows JP, 2011, Analysis of linear long-term trend of aerosol optical thickness derived from SeaWiFS using BAER over Europe and South China, *Atmos. Chem. Phys.*, **11**, 12149-12167.

269 Zaratti F, Piacentini RD, Guillen HA, Cabrera S, Liley B, McKenzie R, 2014, Proposal for a modification of the UVI Risk Scale, *Photochem. Photobiol. Sci.*, **13**, 980-985.

270 Zepp RG, Shank GC, Stabenau E, Patterson KW, Cyterski M, Fisher W, Bartels E, Anderson SL, 2008, Spatial and temporal variability of solar ultraviolet exposure of coral assemblages in the Florida Keys: Importance of colored dissolved organic matter, *Limnol. Oceanogr.*, **53**, 1909-1922.

271 Zerefos CS, Eleftheratos K, Meleti C, Kazadzis S, Romanou A, Ichoku C, Tselioudis G, Bais A, 2009, Solar dimming and brightening over Thessaloniki, Greece, and Beijing, China, *Tellus Ser. B-Chem. Phys. Meteorol.*, **61**, 657-665.

272 Zerefos CS, Tourpali K, Eleftheratos K, Kazadzis S, Meleti C, Feister U, Koskela T, Heikkilä A, 2012, Evidence of a possible turning point in solar UV-B over Canada, Europe and Japan, *Atmos. Chem. Phys.*, **12**, 2469-2477.

273 Zhang J, Reid JS, 2010, A decadal regional and global trend analysis of the aerosol optical depth using a data-assimilation grade over-water MODIS and Level 2 MISR aerosol products, *Atmos. Chem. Phys.*, **10**, 10949-10963.

274 Zhang Q, Jimenez JL, Canagaratna MR, Allan JD, Coe H, Ulbrich I, Alfarra MR, Takami A, Middlebrook AM, Sun YL, Dzepina K, Dunlea E, Docherty K, DeCarlo PF, Salcedo D, Onasch T, Jayne JT, Miyoshi T, Shimono A, Hatakeyama S, Takegawa N, Kondo Y, Schneider J, Drewnick F, Borrmann S, Weimer S, Demerjian K, Williams P, Bower K, Bahreini R, Cottrell L, Griffin RJ, Rautiainen J, Sun JY, Zhang YM, 2007, Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically-influenced Northern Hemisphere midlatitudes, *Geophys. Res. Lett.*, **34**, L13801.

275 Zhang X, Lin Y-H, Surratt JD, Zotter P, Prévôt ASH, Weber RJ, 2011, Light-absorbing soluble organic aerosol in Los Angeles and Atlanta: A contrast in secondary organic aerosol, *Geophys. Res. Lett.*, **38**, L21810.

276 Ziemke JR, Chandra S, 2012, Development of a climate record of tropospheric and stratospheric column ozone from satellite remote sensing: evidence of an early recovery of global stratospheric ozone, *Atmos. Chem. Phys.*, **12**, 5737-5753.

Chapter 2. The consequences for human health of stratospheric ozone depletion in association with other environmental factors

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Summary

Due to the implementation of the Montreal Protocol, which has limited, and is now probably reversing, the depletion of the stratospheric ozone layer, only modest increases in solar UV-B radiation at the surface of the Earth have occurred. For many fair-skinned populations, changing behaviour with regard to exposure to the sun over the past half century – more time in the sun, less clothing cover (more skin exposed), and preference for a tan – has probably contributed more to greater levels of exposure to UV-B radiation than ozone depletion. Exposure to UV-B radiation has both adverse and beneficial effects on human health. This report focuses on an assessment of the evidence regarding these outcomes published since our previous report in 2010.

The skin and the eyes are the organs exposed to solar UV radiation. Excessive solar irradiation causes skin cancer, including cutaneous malignant melanoma and the non-melanoma skin cancers, basal cell carcinoma and squamous cell carcinoma, and contributes to the development of other rare skin cancers such as Merkel cell carcinoma. Although the incidence of melanoma continues to increase in many countries, in some locations, primarily those with strong sun protection programmes, incidence has stabilised or decreased over the past 5 years, particularly in younger age-groups. However the incidence of the non-melanoma skin cancers is still increasing in most locations. Exposure of the skin to the sun also induces systemic immune suppression that may have adverse effects on health, such as through the reactivation of latent viral infections, but also beneficial effects through suppression of autoimmune reactivity. Solar UV-B radiation damages the eyes, causing cataracts and pterygium.

UV-B irradiation of the skin is the main source of vitamin D in many geographic locations. Vitamin D plays a critical role in the maintenance of calcium homeostasis in the body; severe deficiency causes the bone diseases, rickets in children and osteomalacia in adults. Although many studies have implicated vitamin D deficiency in a wide range of diseases, such as cancer and cardiovascular disease, more recent evidence is less compelling, with meta-analyses of supplementation trials failing to show a beneficial effect on the health outcomes that have been tested. It continues to be difficult to provide public health messages to guide safe exposure to the sun that are accurate, simple, and can be used by people with different skin types, in different locations, and for different times of the year or day. There is increasing interest in relating sun protection messages to the UV Index. Current sun protection strategies are outlined and assessed.

Climatic factors affect the amount of UV radiation received by the skin and eyes, separately from the effect of ozone depletion. For example, cloud cover can decrease or increase the intensity of UV radiation at Earth's surface and warmer temperatures and changes in precipitation patterns may alter the amount of time people spend outdoors and their choice of clothing. The combination of changes in climate and UV radiation may affect the number of pathogenic microorganisms in surface waters, and could have an impact on food security through effects on plant and aquatic systems. It remains difficult to quantify these effects and their possible importance for human health.

Introduction

Stratospheric ozone limits the amount of biologically damaging UV radiation in the UV-B waveband that reaches the Earth's surface – a 1000-fold reduction in mutagenic UV radiation.[311] Depletion of the ozone layer results in greater potential exposure to UV-B radiation, while, for humans, actual exposure also depends on their behaviour, such as time spent outdoors, use of shade, and wearing of sun protective clothing. Global climate change is altering the recovery of the stratospheric ozone layer and, through effects on cloud cover, will modify the levels of UV radiation at Earth's surface (for detail, see Chapter 1). Loss of snow cover will decrease albedo in mountain regions, possibly reducing UV radiation incident on body surfaces. Changing climate may also alter human behaviour with regard to exposure to the sun. Warmer temperatures may accelerate the genesis of skin cancer and vitamin D production. In the following sections, we assess the health risks associated with ozone depletion, focussing on effects related to UV radiation in the UV-B wavelengths. In addition, the risks and benefits of changing personal exposure to UV radiation under the combined effects of ozone depletion and global climate change are considered.

Effects of solar UV radiation on the skin

Human skin comprises an outer thin epidermis of about 10 cell layers and typically <100 μm deep and an inner layer, the dermis, that consists mainly of connective tissue and gives skin its mechanical properties. Epidermal cells are mostly keratinocytes, with melanocytes in the basal layer producing melanin that determines pigmentation of the skin. UV radiation is absorbed in the skin by specific molecules called chromophores, with the ensuing chemical changes initiating multiple biological processes. UV-A radiation penetrates the skin to a greater depth (into the dermis) than UV-B radiation. Exposure to solar UV radiation may cause skin cancer and photo-ageing, but also initiates the synthesis of vitamin D which is critical for human health.

Skin cancer

Solar UV radiation is the major environmental risk factor for both melanoma and non-melanoma skin cancers (NMSCs).[394] Cutaneous malignant melanoma (CMM) is the least common of the skin cancers, but accounts for most deaths due to skin cancer. NMSCs include basal cell carcinoma (BCC), squamous cell carcinoma (SCC), and other rarer skin cancers. BCC occurs approximately 3-4 times more frequently than SCC. It has the lowest mortality rate but can cause significant ill-health due to extensive local invasion, particularly when it arises on the face.

It is difficult to assess whether, or to what level, alterations in ozone or climate have contributed to the rising incidence of skin cancer globally. Over the 20th century, increasing travel to sunny locations and changed styles of clothing, at least in some populations, have led to higher personal exposure to the sun. This has probably been a more important driver of the increasing incidence of skin cancer than changes in ozone or climate.[3] Changes in the diagnostic criteria for skin cancers, including the use of dermoscopy or epiluminescent microscopy and molecular classification,[97] a lack of accurate recording of lesions, and a more general growing awareness of skin cancer and conservatism (erring on the safe side) in diagnoses,[116] may also have introduced temporal biases in some instances.

Cutaneous malignant melanoma

Geographic variation and temporal trends in incidence and mortality. World-wide, it is estimated that there were around 230,000 new cases of CMM and 55,000 deaths in 2012.[174] The incidence varies widely from country to country (Table 1), with the highest age-standardised annual incidence rates (~35 per 100 000 population in 2012) in Australia and New Zealand.[174] CMM is rare in darker skinned populations, such as in South Asia.[201]

The incidence of CMM in fair-skinned populations has approximately doubled every 10-20 years since the 1960s and this trend is projected to continue for at least 20 more years[104] (Table 1).

Table 1 Illustrative examples of the change with time in the age-standardised (World Standard Population) incidence of CMM in men and women (per 100,000 population)

Men

Country	Year, incidence		Year, incidence		Year, projected incidence		Year, projected incidence	
Denmark[a]	1990	10.0	2007	16.0	2010	16.0	2015	18.0
England[a]	1990	4.6	2006	10.7	2010	12.2	2015	14.5
Spain[a]	1990	3.1	2004	8.1	2010	8.1	2015	9.3
Netherlands[a]	1989	7.4	2007	13.6	2010	15.1	2015	17.5
Australia[b]	1990	31.1	2000	38.3	2012	40.5		
New Zealand[c,d]			1998-2002	34.8	2012	39.2		
Canada[c,d]	1988-1992	7.7	1998-2002	10.9	2012	10.4		
USA[c,d]			1998-2002	15.1	2012	16.8		

Women

Country	Year, incidence		Year, incidence		Year, projected incidence		Year, projected incidence	
Denmark[a]	1990	12.8	2007	F 19.5	2010	21.1	2015	24.4
England[a]	1990	6.0	2006	F 12.3	2010	14.2	2015	16.9
Spain[a]	1990	3.6	2004	F 9.5	2010	9.5	2015	10.7
Netherlands[a]	1989	10.7	2007	F 17.3	2010	19.0	2015	21.9
Australia[b]	1990	25.0	2000	F28.8	2012	30.0		
New Zealand[c,d]			1998-2002	F 31.4	2012	33.1		
Canada[c,d]	1988-1992	6.9	1998-2002	9.3	2012	9.1		
USA[c,d]			1998-2002	11.4	2012	12.6		

[a]Data from[10]; [b]Data from www.aihw.gov.au; [c]Data from[174]; [d]Data from[110]

The rise in incidence of CMM has been attributed to changes in recreational behaviour leading to increased exposure to the sun.[266] The incidence rate has stabilised or is decreasing in younger age groups (<44 years) in some countries, such as Australia,[104] but continues to increase elsewhere.[49, 125] Public health campaigns to encourage protection from the sun , beginning in the 1980s, have probably contributed to the decrease in incidence in younger age groups in Australia.[19]

Although CMM accounts for only 4% of all skin cancer cases, it is responsible for about 80% of deaths from skin cancer.[104] Mortality due to CMM is increasing in Southern and Eastern Europe,[95, 342] particularly in elderly men who tend to have thicker lesions which are more invasive and less likely than the thinner lesions to respond to treatment.[365] Here, the increase in deaths is probably due to the rising incidence of CMM. Mortality due to CMM is stable or decreasing in Australia,[338] some parts of the USA,[125] and Western Europe,[184] with this decrease likely due to earlier detection of the tumours, possibly as a result of more self-awareness of risks of skin cancer in subgroups of the population.

Anatomical location. In fair-skinned populations, melanomas in older people occur predominantly on the head and neck and are associated with chronic cumulative exposure to the sun. In younger people, the lesions most frequently occur on the trunk and extremities, thought to be the result of high overall exposure to the sun, episodes of sunburn in childhood, and the presence of multiple or atypical naevi (moles).[75] The trunk is the site where the greatest increase in the number of cases in both sexes over the past 30 years has occurred,[118, 383] likely reflecting the increase in intermittent high dose exposure leading to sunburn as a result of wearing clothes with less coverage of the skin, and increased travel to sunny climates.[86]

Melanoma in deeply pigmented skin. There is a paucity of information about the incidence, or any change in incidence, in CMM in population groups with darker skin. The risk of CMM is estimated to be around 20-times lower in Black compared to White Americans.[320] A recent study in the North-East USA found no increase in the annual incidence of CMM in Hispanics and non-Hispanic Blacks since 1992, but a 4% increase in non-Hispanic Whites.[69] In contrast, there is evidence of increasing incidence of CMM in Hispanics from California between 1988 and 2001.[70] Darker-skinned people are more likely than those with fair skin to have advanced CMM at diagnosis in the USA[69] and in Brazil,[323] with a reduced chance of survival. The lower limb and/or hip is the commonest site for CMM in the dark-skinned populations of South Africa (around 70% of CMM) and Kenya (75%),[273] particularly the sole of the foot.[272, 273] As these body sites are not normally UV-irradiated, direct exposure to the sun is unlikely to be a risk factor although UV-induced systemic effects could be involved.[2]

Exposure to the sun as a causative factor in melanoma. Exposure to the sun is a key risk factor for CMM.[183, 211] Incidence is greater at locations closer to the Equator (more UV radiation) in fair-skinned populations.[104] For example, in 2012, the age-standardised incidence (World Standard Population, per 100,000) was 35.8 in New Zealand and 34.9 in Australia, compared to 14.6 in the UK and 9.6 in Canada.[174] Epidemiological studies have shown an increased risk of CMM in people who self-report higher levels of sunburn, and in those with phenotypic characteristics associated with greater sensitivity to UV radiation, including fair skin, light hair and eye colour, poor ability to tan, freckling, and having multiple naevi (moles). Childhood exposure to the sun may be particularly important; for example, migration from a high to a low latitude location before age 10 years[207] or 20 years[205] confers a greater risk of melanoma than migration at an older age.

Recent experimental studies indicate that both UV-A and UV-B radiation are involved in the development of CMM.[267] Initiation of melanoma following UV-A irradiation involves oxidative damage to DNA and requires the presence of melanin, whereas UV-B-induced melanoma is independent of melanin and involves direct UV-B-induced damage to DNA.[267] A two-hit model proposes that initiation of the tumour follows DNA damage induced by UV radiation, and then progression to melanoma depends on the host's genetic make-up (particularly for melanoma of the trunk) and/or tumour promotion by ongoing exposure to both UV-A and UV-B radiation.[247]

There is growing interest in the effects of exposures in early life on the risks of diseases that develop later in life. One indication that exposure early in life is important for melanoma comes from observations that, in predominantly fair-skinned populations, people with the disease are more likely to have been born in particular months of the year, compared with the general population. In two studies, young women (aged 15-24 years) with CMM from northern England[26] and Sweden[73] were significantly more likely to have been born in March (early Spring). The data are consistent with the two-hit model suggested in animal studies[247] - early exposure to UV radiation during the months soon after birth initiates the first event, then later exposure causes progression to CMM. It is interesting to note that, in the past, exposure of infants to sunlight was encouraged in some countries, a practice that has not continued in more recent years.[145, 146, 281, 307]

The higher incidence of small (<2 mm) melanomas during summer compared to winter in Northern Ireland (1984-2006) is consistent with exposure to UV radiation having a short-term promotional effect on melanocytes.[63]

Genetics of cutaneous melanoma. Susceptibility to CMM is partially determined by genetic factors (reviewed in Eggermont et al.[5] and Nikolaou & Stratigos[97, 266]). A family history of CMM confers a two-fold increase in risk.[278] Alternatively, in approximately 10% of people with CMM, there is a strong family history,[158] associated with specific mutations in genes involved in control of the cell cycle (e.g., *CDKN2A, CDK4*). Increased risk in association with polymorphisms in other genes, including those associated with fair-skin phenotype (*MC1R*)[158] and characteristic UV-induced cytosine to thymine (C>T) mutations in the tumour-control pathways,[163] provide strong evidence of a causal role for UV radiation in the development of CMM. Very recently, further experimental corroboration for the involvement of UV radiation in accelerated development of melanocytes has been obtained.[379] Most strikingly, recent studies show that melanomas (and cell lines thereof) have more mutations in their genomes than most other tumour types, e.g., more than 30,000 point mutations per cell, and hundreds of mutations in protein-coding genes. Tumours from sun-exposed skin have the greatest number of mutations, most of which are characteristic of those induced by exposure to UV radiation.[33, 193] It is difficult to distinguish driver from passenger mutations, but special intron-exon comparative analyses provide evidence of driver mutations that are related to UV radiation.[163]

Non-melanoma skin cancer

Geographic variation and temporal trends in incidence. BCC and SCC are the most frequently occurring cancers in fair-skinned populations. However, establishing accurate incidence data, and comparing incidence rates between countries or regions, or over time, is challenging for several reasons. First, these cancers may be treated using destructive therapies without prior biopsy, and such clinically-diagnosed lesions, particularly BCC, are often not included in estimates of incidence.[111] Differences in therapeutic approaches between countries or changes over time can therefore have a considerable influence on comparisons and trends. Secondly, there are very few regions that require mandatory reporting of NMSCs to cancer registries and population-based studies are rare. Thirdly, most reports are person-based rather than lesion-based so they do not account for the multiple lesions often observed in people living at lower latitudes; and lastly, variability in the population used to age-standardise incidence rates makes reported results difficult to compare.

Despite these difficulties, there is a strong association between intensity of ambient UV radiation and incidence of both BCC and SCC.[402] In a recent review, the highest annual incidence rates were in Australia (>1000 per 100 000 population for BCC) and the lowest in Africa (<1 per 100,000 population).[216] Data for the latter are sparse and the low incidence masks relatively high incidence in some sub-populations, for example among people with oculocutaneous albinism (OCA) [see section below], and in Caucasians in South Africa, where BCC and SCC are typically among the top 5 or 10 cancers reported (depending on year).[257]

There have been substantial increases in the incidence of NMSC over the past several decades. Across Europe, the annual incidence of BCC was estimated to be around 50 per 100,000 persons in 1980.[216] It has more than doubled since then in many parts of this region, and has quadrupled in the Netherlands.[112] The incidence of SCC was approximately 10 per 100,000 persons in Europe in 1980[216] with an increase to about 25 per 100,000 by 2000.[216] There are no estimates of SCC and BCC separately for the United States, but a study of data from national Medicare claims suggests that the age-adjusted rate of procedures for skin cancer increased by 77% between 1992 and 2006.[316]

A recent quantitative review of data published between 1979 and 2012 showed that, in fair-skinned populations worldwide, after adjustment for age, sex, and the levels of ambient UV radiation, the average annual increases in SCC and BCC incidence were 4% and 1%, respectively.[402] The incidence of SCC increased over time in both the older (≥60 years) and younger (<60 years) age groups, but only in the older age group for BCC.

Exposure to the sun as a risk factor for non-melanoma skin cancer. As the studies showing latitudinal variation suggest, exposure to solar UV radiation is the primary cause of BCC and SCC; almost 40% of the variability in incidence in SCC and BCC in populations of predominantly European ancestry could be explained by differences in the average daily levels of ambient UV radiation alone.[402] Nevertheless, evidence suggests that the timing and patterns of exposure to the sun that give rise to the two tumour types are different. SCC appears to be strongly associated with cumulative exposure to the sun. In fair-skinned people, SCC is rare on parts of the body that are not routinely exposed to the sun[114, 300, 344] and the presence of actinic keratoses, which are a marker of cumulative exposure to the sun, confers a 30-40-fold increase in the risk of SCC.[194] In contrast, BCC appears to be caused by intermittent exposure to the sun;[28, 83] up to 25% of BCCs occur on the trunk or lower limbs[344] and the association with actinic keratosis is considerably weaker than for SCC.[185] However, some studies have found no difference in the pattern of exposure in relation to the risk of BCC and SCC,[173] possibly because the risk factors for BCC vary according to the site and/or subtype of BCC. For example, chronic exposure to the sun may be more important for nodular BCC commonly found on the head and neck, and intermittent exposure to the sun more important for superficial BCCs that have a tendency to occur on the trunk.[260] It is of interest to note that there is a 3-fold increased risk of developing CMM after either SCC or BCC, even after adjustment for the self-reported reaction of the skin to chronic exposure to the sun.[305] This may indicate risk factors in common between the NMSCs and CMM, e.g., susceptibility of specific skin phototypes, and excessive (intermittent) exposure to the sun.

Non-melanoma skin cancer in more deeply pigmented skin. There have been few studies of incidence of NMSCs in dark-skinned populations.[216] Data collected by the National Cancer Registry of South Africa in the early 2000s indicated that the annual age-standardised incidence (per 100,000) of reported SCC was 4.6, 7.0, 41.5 and 101.3, and of reported BCC was 4.7, 13.0, 85.7 and 311.1 in the Black, Asian, Coloured and White population groups respectively.[272]

The epidemiology, clinical presentation, and prognosis of NMSC differ between people with fair skin and those with darker skin. For example, in several studies, SCC was more common than BCC in those with deeply pigmented skin[142, 273] and these tumours typically arose in sites of chronic inflammation or scarring, so that solar UV radiation may not be the major risk factor.[2] In contrast, the site-distribution of BCCs is similar in fair- and dark-skinned populations, occurring predominantly on the head or neck, suggesting that exposure to UV radiation is an important risk factor.

Over time, there has been little increase in the incidence of NMSC in Asian populations and almost none in dark-skinned populations (reviewed in Agbai et al.[31] and Gloster & Neal[2, 131]). However, mortality and morbidity from NMSC is disproportionately high in dark-skinned populations in comparison with incidence, due to diagnosis occurring at a more advanced stage, atypical presentation, lack of screening, and socioeconomic factors.[2] Public health education regarding protection against the sun and self-awareness, tailored appropriately for each population group, should be expanded to include people of all skin types.[408]

Genetics of non-melanoma skin cancer. Common variants in several genes influence the risk of BCC, including those in known pigmentation genes.[256, 341] In addition, there are rare genetic disorders in which NMSCs arise at a young age and incidence is dramatically increased. For example, incidence of skin cancer in people under the age of 20 years is increased 10,000-fold in patients with xeroderma pigmentosum, a disorder where the repair of UV-induced DNA damage is severely impaired.[88]

SCCs and BCCs are the cancers with the highest mutational loads (33 and 76 mutations per million DNA-bases, respectively), especially those from skin regularly exposed to the sun.[93, 181] The majority of these mutations bear the "UV signature" (cytosine to tyrosine transitions at cyclobutane pyrimidine dimers, CPD, Fig. 1). Both BCC and SCC show UV-signature mutations in tumour suppressor genes (*PTCH1* and *p53* respectively),[51, 181, 411] suggesting these are key abnormalities driving the development of these tumours.[102] These genetic studies clearly indicate the causal role of exposure to UV radiation in the development of NMSC.

Skin cancer in oculocutaneous albinism.
Oculocutaneous albinism (OCA) refers to a group of congenital developmental disorders in which there is either partial or complete lack of melanin in the skin, hair and eyes.[229] The number of melanocytes is not reduced, but there is decreased or absent production of melanin due to mutations in genes in the melanin biosynthetic pathway.[229] The four major types (OCA1, 2, 3 and 4) are present at different frequencies in various populations throughout the world; for example OCA2 is the most common type in sub-Saharan Africa.[229] Globally, about 1 in every 17,000 people have OCA (with about 1 in 70 people carrying the OCA gene),[78, 135] but this figure can be considerably higher, such as 1 in 3900 in South Africa.[195]

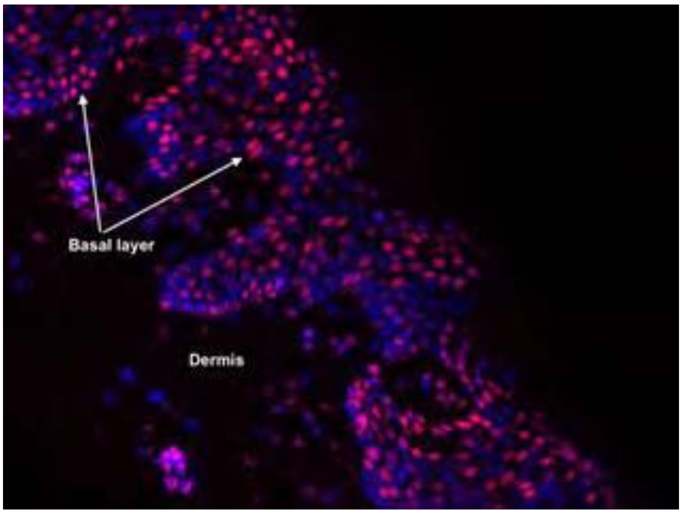

Fig. 1. Human skin shows cyclobutane pyrimidine dimers (CPD, red nuclei) when a biopsy is taken immediately after 4 standard erythema doses of simulated solar radiation. Note the presence of CPD in the epidermal basal layer that contains stem cells and that CPD are also present in the dermis. Photograph provided by Professor Antony Young, School of Medicine, Kings College, London, UK.

People with OCA experience visual impairment including photophobia (discomfort from exposure to light, leading to avoidance).[348] They are also highly susceptible to skin damage induced by solar UV radiation and it has been estimated that the risk of NMSC in people with OCA in Africa is one thousand times greater than that of the general population.[167] In most instances, the skin cancer occurs at 20-30 years of age, which is considerably younger than in those without OCA.[219] Cutaneous tumours in Africans with OCA are predominantly SCCs, with BCCs less frequent, and CMMs only occasionally seen,[189, 225] although the last may be under-reported as they are normally amelanotic (non-pigmented).[285] Most commonly, the skin cancers in Africans with OCA occur on the head and neck and tend to progress rapidly with metastasis to the cartilage, bone, and muscle, resulting in high mortality.[9, 219] The key role of exposure to the sun in the oncogenic process is emphasised by finding an increased frequency of skin tumours and lower life expectancy in people with OCA living in equatorial regions of sub-Saharan Africa than in parts further from the Equator.[219]

Viruses and skin cancer

There are two instances (see following sections) where an association between certain viruses and skin cancer has been demonstrated. In both cases, the tumours occur predominantly on body sites most exposed to the sun, suggesting that exposure to solar UV radiation is likely to play a crucial role in the carcinogenic process.

Merkel cell carcinoma and polyomavirus. Merkel cell carcinoma (MCC) is a rare, aggressive, neuroendocrine skin cancer with high rates of recurrence, metastasis, and mortality.[172] It mainly affects fair-skinned, elderly people (peak age around 75 years) or those who are immunosuppressed, particularly if they live in a sunny location.[172] The tumours occur most frequently on sun-damaged skin on the head and neck.[129] There is a positive correlation between ambient levels of UV radiation and age-adjusted incidence of MCC across the USA.[244] The incidence has risen in recent years, for example, from 0.15 cases to 0.44 cases per 100,000 between 1986 and 2001 in the USA.[162] This could be explained by increasing life expectancy, greater exposure to the sun and the rising number of immunosuppressed people in the general population as a result of an increasing number and range of organ transplants[399] and infection with HIV.[172]

Merkel cell polyomavirus is present in around 80% of MCCs. The viral DNA is integrated into the host DNA and is thought to cause cancer after genomic mutations that eliminate its ability to replicate but maintain its oncogenic function (reviewed in Arora et al.[11]). Exposure to UV radiation may play a role in the integration or mutagenic processes (for example, Demetriou et al.[95] and Mogha et al.[82, 250]) or in suppression of the immune response to the virus.[37]

Squamous cell carcinoma and papillomaviruses. Human papilloma viruses (HPVs) can infect the squamous epithelium of the skin and may play a causative role in the development of cutaneous SCC. Phylogenetic analysis of HPVs describes 120 different types across 5 genera.[34] Several studies have found that the presence in serum of antibodies to the beta or gamma HPV types is associated with an increased risk of SCC.[8, 108, 298] Furthermore, people with SCC have higher levels of beta HPV DNA in hair follicles of the eyebrow (used as a marker of infection) than controls without SCC.[261] The beta and gamma HPV types code for proteins that affect the normal controls of the cell cycle and may also subvert the normal immune response. The mechanism by which various types of HPV might influence the risk of cutaneous SCC is unclear, but is most likely through potentiating the effects of exposure to UV radiation.[48]

Photoageing

Chronic exposure to solar UV radiation results in photoaged skin, which is wrinkled, leathery, shows loss of elasticity, and is often associated with the development of SCC. Photoageing results from the UV-induced degradation of proteins such as collagen and elastin in the extracellular matrix of the dermis. UV-A radiation may be primarily responsible for chronic photoageing, given its greater depth of penetration.[218] In addition, a role for UV-B radiation is indicated. First, UV-B radiation can directly degrade some proteins, such as fibrillin and fibronectin, involved in maintaining the structure of the dermis.[259] Second, the action spectrum for the induction of matrix metalloproteinase (an enzyme that degrades collagen) in human skin is similar to that for erythema, suggesting that this is primarily an effect of exposure to UV-B radiation.[358] While not a risk to health per se, photoageing of the skin incurs considerable costs through the use of cosmetic and hydrating agents to improve the appearance and feel of the skin.

Melasma

Melasma appears as dark, macular, pigmented patches on the brow, cheek, upper lip and jaw, and is due to a localised increase in melanin production.[334] It can result in profound emotional and psychological stress, significantly reducing quality of life.[182] Melasma is particularly common in adult women living in tropical areas of the world and occurs more frequently in individuals with skin types of intermediate pigmentation (i.e. types III-V) than in those with fair (skin types I and II) or very dark skin (skin type VI).[143, 334] Its prevalence has been estimated as 3.4% in the general population in Beirut, Lebanon, 10.1% in Cuzco, Peru,[334] 34% in adult women in Botucatu, Brazil,[80] and 40% in adult women and 20% in adult men in South-East Asia.[335]

The precise pathophysiology of melasma is unclear, but is known to be complex. There is a genetic predisposition and several environmental triggers, one of which is exposure to sunlight. For example, a report from Tunisia indicated that 51% of patients recognised exposure to the sun as a triggering factor and 84% as an aggravating factor, with high lifetime exposure to the sun increasing the risk of severe melasma three-fold.[138] A case-control study in Brazil found that patients with melasma had a greater number of years of seaside or rural residence and greater exposure to the sun at work or during leisure than the controls; there was a lack of association with sunburn, implying that cumulative exposure to the sun may be more important than acute exposure.[143] Solar UV radiation can induce proliferation and migration of melanocytes[67] and the production of several cytokines that increase the production of melanin. In addition, inflammatory cells, especially mast cells, which produce a variety of potent pro-inflammatory substances, are likely to play key roles.[154]

Effects of solar UV radiation on the eye

The eye is partly protected from direct UV radiation by the brow ridges. This means that reflected radiation is likely to contribute more to the total UV radiation received than occurs for the skin. Higher intensity UV radiation induces the most damage, although less intense exposure over a long period also increases the risk of disease. Transmission of UV radiation through the eye (Fig. 2) generally decreases with increasing age, but there is wide inter-individual variability.[321] The cornea filters out wavelengths less than about 280 nm, although this is relevant for artificial sources only, as sunlight at the Earth's surface is confined to wavelengths >290 nm. There is further absorption in the aqueous humour (Fig. 2). The lens of a young child (e.g., <5 years) transmits close to 100% of the

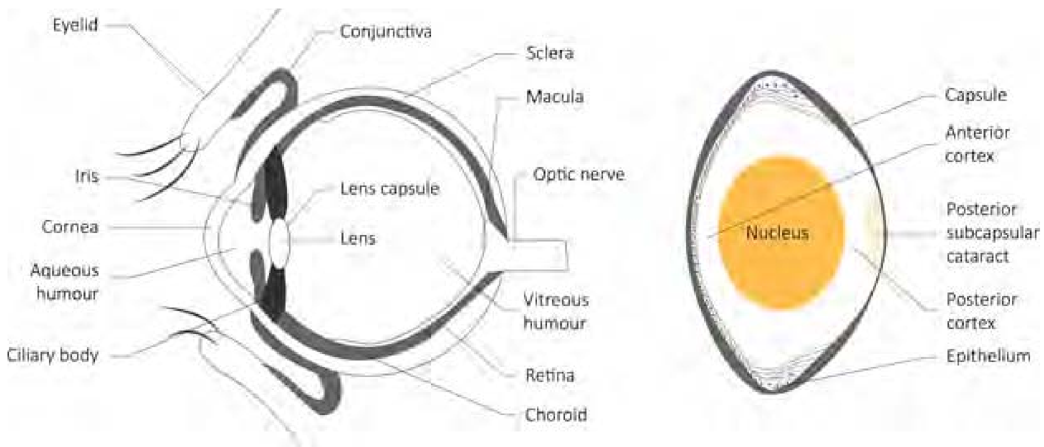

Fig. 2 A schematic drawing of a section through the human eye, with an enlarged schematic of the lens to the right

visible light spectrum (wavelength >400 nm), but absorbs UV radiation, except for a small window at 320 nm.[12] The lens of an older person (e.g., 60+ years) commonly filters out even some of the short blue visible light (400-500 nm) so that this, and UV radiation of shorter wavelengths, do not reach the retina.

Exposure to UV radiation increases the risk of a number of ocular conditions, with the strongest evidence of a specific effect of UV-B radiation for photokeratitis, pterygium, and cataract.

Photokeratitis and photoconjunctivitis

Exposure of the eye to high-dose UV radiation from the sun can result in inflammation of the cornea (photokeratitis) and/or conjunctiva (photoconjunctivitis) (Fig. 2). The maximum sensitivity is to the UV-B wavelengths.[74] The damage is probably caused by oxidative stress,[41, 61, 62] with the squamous cells of the epithelium of the cornea, the keratocytes of the stromal layer of the cornea, and the endothelial cells lining the back of the cornea, being affected.

Transmission of UV radiation decreases across the cornea from the centre to the periphery, due to scattering and absorption.[90] The centrally located endothelial cells receive a higher dose of UV radiation, and show evidence of higher oxidative stress than cells in the periphery. It is the damage to these central corneal endothelial cells that particularly causes corneal swelling and temporary loss of vision in UV-induced photokeratitis.[90]

Pterygium

Pterygium, a wing-shaped invasive growth of the conjunctiva (Fig. 3), is common in adults living in environments with high UV radiation. For example, it affects at least one eye in approximately 10% of: adults (≥15 years) on Norfolk Island, Australia;[332] south Indians (≥40 years) in Chennai, India;[16] and indigenous people (≥40 years) in Central Australia.[203] Some recent studies show that the prevalence of pterygium increases with increasing age and is more common in men than women,[16] but the increase with age is not consistently found.[332] Key risk factors for pterygium are greater time outdoors (including sports with high ocular exposure to UV radiation, such as surfing[353]), rural residence, having a skin type that tans[333] and non-use of spectacles.[16] Of note, the only study that has examined the risk of pterygium in association with wavelengths of solar radiation other than those in the UV range (using retrospectively reconstructed exposure behaviour during working hours) found a stronger association with visible light, and a weaker but still significant association with UV-B radiation.[355] Recent evidence suggests that a pterygium is not always benign: there is histological evidence of inflammatory and dysplastic changes in the epithelium and underlying connective tissue,[132] and of neoplasia in 2-10% of excised pterygia.[13, 274]

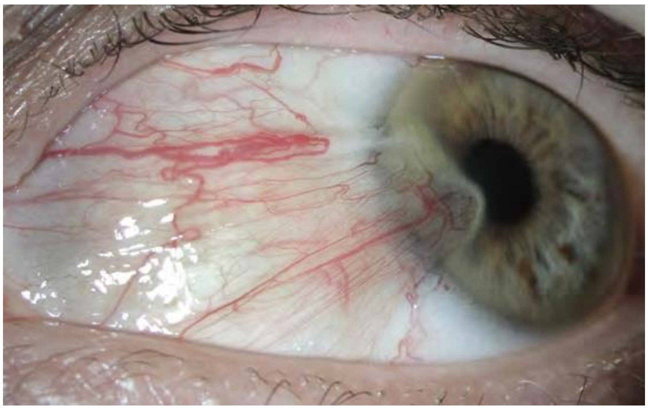

Fig. 3 Pterygium of the eye. Photograph provided by Dr David Mackey, University of Western Australia, Perth, Australia

Squamous cell carcinoma of the cornea and conjunctiva

Squamous cell carcinoma of the cornea and conjunctiva (SCCC) is rare; the annual incidence in the USA is estimated to be 0.84 per 100 000 population.[98] The incidence is higher in men, and in association with older age, residence at lower latitude, infection with HIV, and high exposure to UV radiation.[98] Infection with HPV and exposure to UV radiation may be common risk factors for pterygium and SCCC.[84]

Cataract

In 2010, cataract was the leading cause of blindness worldwide.[47] Of the three main types of age-related cataract – cortical, nuclear, and posterior subcapsular (Fig. 2) – UV radiation is primarily linked to an increased risk of cortical cataract.[354]

The action spectrum for acute/short term cataract development is relatively consistent across animal models, with UV-B radiation of shorter wavelengths being most damaging.[277] However, these models have limited relevance for cataract formation in humans because of wide inter-species variation in the dose of UV irradiation required,[249] and the typical use of a single very high dose, rather than repeated lower doses. Melanin in pigmented irises may absorb UV radiation, leading to fewer cataracts in those with more pigmented, than less pigmented, irises.[215] Lenses in older individuals may be more susceptible to UV-induced cataracts due to poorer defence against oxidative damage and decreased repair mechanisms.[177, 196, 409]

In the large Salisbury Eye Evaluation Study with participants aged 65-84 years, the incidence and progression of cortical cataract (but not nuclear cataract) were associated with higher levels of estimated exposure to UV-B radiation (calculated based on an empirical model incorporating self-reported time outdoors and use of protection from the sun).[346] In contrast, in the 15 year follow-up of participants in the Beaver Dam Eye Study,[190] there was no association between exposure to the sun (as measured by residential history) and cumulative incidence of any type of age-related cataract, after controlling for age and sex. However, the combined use of sun-sensitising medications and high exposure to the sun led to a significantly increased risk of cortical cataract.[190]

Ocular malignancies

There is strong evidence to support exposure to UV radiation as a risk factor for tumours of the eyelid and weaker evidence for ocular melanomas (reviewed in Yam and Kwok[403]). Over 90% of the malignancies of the eyelid are BCCs, particularly affecting the lower lid (50-65%), but also the medial canthus (inner corner of the eye, 25-30%), upper eyelid (15%) and lateral canthus (outer corner of the eye, 5%).[403] SCC accounts for most of the remainder of the periocular cutaneous tumours.[403]

Melanomas of the eye can involve the surface (i.e. the eyelid or conjunctiva), or occur at an intra-ocular location, affecting the elements of the uvea (i.e. the iris, ciliary body, and choroid; Fig. 2). Uveal melanoma is the most common primary intraocular malignancy (>90 %) and the leading cause of death from intraocular cancer.[115, 282] The reported annual incidence varies from 0.53 to 1.09 cases per 100,000 population, and is stable or decreasing.[115, 282] Uveal melanoma is primarily a disease of white populations; light-coloured irises, blond hair, and fair skin are risk factors.[228] There is mixed evidence implicating UV radiation as a risk factor for uveal melanoma: latitudinal variation in incidence is not consistently found;[282] occupational exposure to UV radiation may have a protective effect, but intermittent exposure may increase risk (reviewed in Mallet et al.[228]). People with the disease xeroderma pigmentosum, in which there is impaired ability to repair UV-induced DNA damage (see discussion above), have a 58-fold increased risk of uveal melanoma.[53, 228] Genetic studies show that the mutation patterns of the most frequently mutated genes in CMM and uveal melanoma (i.e. *BRAF* vs. *GNAQ, GNA11*) are similar,[228] and a mutation recently identified in CMM (*RAC1*) is also found in 20% of uveal melanoma cell lines.[228] Given the strong evidence supporting a role for UV radiation as a cause of CMM, these studies also provide some evidence that exposure to UV radiation is a risk factor for uveal melanoma.

Age-related macular degeneration

Age-related macular degeneration (AMD) was the cause of 7% of blindness worldwide in 2010,[47] and was the most frequent cause of blindness in older (50-75 years) white populations in Europe.[299] UV radiation had been discounted previously as a risk factor in AMD as it does not reach the retina. However, recognition of the considerable individual variability in the transmission of longer UV-B/shorter UV-A wavelengths (<320 nm) in older adults (60+ years) has led to reconsideration of a potential role of UV radiation. Possible mechanisms include: UV-induced oxidative damage to mitochondrial DNA, particularly in the macular region of the neural retina and the retinal pigment epithelium;[126] and/or upregulation of inflammatory cytokines (e.g., IL-6) and transcription factors (e.g., STAT3). Higher vitamin D status is associated with lower risk of AMD in women <75 years, but a higher risk in women ≥75.[242]

In a systematic review and meta-analysis of case-control and cross-sectional studies, higher exposure to the sun was associated with a 38% increase in the odds of having AMD.[347] However, blue light (400-500 nm) may be more important than UV radiation as a risk factor for AMD.[230, 391, 403]

Other possible effects on the eye

There is a well-established association between spending less time outdoors and an increased risk of developing myopia in childhood.[137, 140, 141, 331] While early hypotheses focused on the importance of variation in focal length with a mix of indoor and outdoor activities, more recent work suggests the importance of exposure to light, possibly through increased secretion of dopamine in the retina, with effects on the growth of the eye.[262] The wavelength dependence of this effect, and whether the pathways are mediated by vitamin D[405] or not,[331] are currently unknown.

Evidence from animal studies suggests that UV irradiation of the eye can cause systemic immunosuppression,[159, 160] but the relevance of these findings for human health is unclear at present.

Effects of solar UV radiation on immune function and consequences for disease

Mechanisms

UV photons penetrate the epidermis and upper dermis[359] and are absorbed by chromophores (Table 2), which then initiate a cascade leading to changes in immune responses.

Table 2 Cutaneous chromophores involved in the initiation of UV-induced changes in immune function (reviewed in[127]).

Chromophore	Change in structure following irradiation	Effect on immune function
DNA	Cyclobutane pyrimidine dimers and reactive oxygen species-induced base oxidation after exposure to radiation in both the UV-A and UV-B wavelengths	Oxidative stress; up-regulation of several immunosuppressive mediators and down-regulation of some immunostimulatory mediators
***Trans*-urocanic acid**	*Cis*-urocanic acid (peak effectiveness of isomerisation about 300 nm)	Oxidative damage; up-regulation of several immunosuppressive mediators; stimulation of neuropeptides; mast cell degranulation; cell growth arrest
Membrane phospholipids	Oxidative stress and lipid peroxidation	Clustering of receptors; activation of transcription factors; release of immune mediators
7-dehydro-cholesterol	Previtamin D after UV-B irradiation, leading to vitamin D, then 25-hydroxyvitamin D and finally the	Up-regulation of some antimicrobial responses and DNA repair; down-regulation of most acquired immune

Chromophore	Change in structure following irradiation	Effect on immune function
	active form, 1,25-dihydroxyvitamin D	responses
Tryptophan	Activation of the arylhydrocarbon receptor following exposure to UV-B radiation	Clustering and internalisation of growth factor receptors

While much of this information has been gathered from studies *in vitro* or in rodent models, less is known about humans. However, an action spectrum for the UV-induced suppression of the human immune response to a previously-encountered antigen (termed memory or recall immune responses) has been constructed: it has two peaks, one within the UV-B waveband at 300 nm and one at 370 nm in the UV-A waveband.[77, 232] There is also evidence from studies in both humans and mice that interactive and additive effects between wavebands can occur.[175, 292, 306]

Briefly, exposure to UV radiation causes up-regulation of some innate immune responses, and down-regulation of some acquired primary and memory immune responses, mainly through effects on T cell activity (reviewed in Gibbs & Norval,[163] Schwarz & Schwarz,[169] and Ullrich & Byrne[369]). The up-regulation includes the production of several antimicrobial peptides (AMPs) in the epidermis,[72, 130] possibly through a vitamin D pathway (see below). The AMPs provide immediate protection against a variety of pathogens (bacteria, fungi, and viruses having a viral envelope) and they are also involved in the promotion of cell growth, healing, and angiogenesis. In contrast to these stimulatory functions, exposure to UV radiation induces T regulatory cells (T_{regs}) and other cell types which contribute to immunosuppression and help to restore cutaneous homeostasis.[72, 258] Mediators such as platelet-activating factor, prostaglandin E_2, histamine, and tumour necrosis factor-α, are produced locally at the irradiated site. These alter the migration patterns and functions of various populations of immune cells. The end result is the generation of cell subsets with suppressive activity which are thought to remain for the life-time of the individual.[233, 264]

The UV-induced alterations in the normal immune response can be beneficial for some human diseases and detrimental for others. Vitamin D, synthesised following exposure of the skin to UV-B radiation, also has positive and negative effects on immune-related diseases. Indeed, it is difficult to distinguish between immunoregulation by vitamin D and other mediators induced by UV radiation,[20, 148, 245, 324, 375] since the downstream effects on immune parameters are similar. For clarity, the effects of UV radiation and those of vitamin D have been assessed separately in the sections below. We first focus on the effects of UV radiation on immunity, and address vitamin D-related effects on immune function in the section specifically on vitamin D.

Polymorphic light eruption

Polymorphic light eruption (PLE) is the commonest of the photodermatoses, with a prevalence of up to 20%.[330] PLE is manifest as an intermittent itchy red skin eruption which resolves without scarring after a few days to weeks. It occurs 2-3 times more frequently in women than in men, with onset typically in the first three decades of life,[330] and is found predominantly in those with fair skin, although all skin types can be affected.[330] A recent study of Indian patients with dark skin phototypes (IV and V) who suffered from various photodermatoses revealed that PLE was the commonest of these, affecting 60% of the group.[381] The lesions occur most often in the spring and early summer or during a sunny holiday, following the first exposure to a large dose of sunlight. After repeated exposures, the lesions are less likely to occur. This process, called photohardening, is used therapeutically with good results. Recent investigations indicate that key events in photohardening include a decrease in the number of Langerhans cells in the epidermis and recruitment of mast cells into the dermis,[398] together with changes in systemic cytokine levels.[397]

PLE is immunologically-mediated as a result of a failure to establish the normal suppression of immune responses following exposure to UV radiation. The antigen involved has not been identified but is likely to be novel, induced by the DNA damaging properties of UV radiation. Various abnormalities in the cutaneous immune response following UV radiation have been demonstrated in people with PLE compared with controls.[121, 136] This disease therefore illustrates the positive evolutionary advantage of UV-induced immunosuppression in individuals who are not susceptible to PLE and what can happen if it is absent.

Asthma

Asthma comprises a group of diseases that present as wheeze, chest tightness, or shortness of breath, occurring as a result of obstruction of the airways and restriction of airflow that is usually reversible. The level of severity, frequency of symptoms, age of onset, main inflammatory phenotypes, and triggers and pathways are variable. This heterogeneity may explain the current lack of consistency in results from studies examining the relationship between UV radiation and the risk of asthma.

There are anecdotal accounts that sunny holidays or living at high altitude decrease asthma symptoms. The prevalence of asthma was inversely associated with the intensity of UV radiation,[197] or past personal exposure to solar UV radiation.[170] However, in a study where different sub-types of asthma were considered, residence at latitudes closer to the equator (and with greater intensity of UV-B radiation) was associated with an increased risk of having asthma in atopic participants (with a history of allergic responses to specific antigens) but a decreased risk in those without atopy.[276] These findings highlight the importance of differentiating between subtypes of asthma in examining associations with exposure to UV radiation. Nevertheless, individual-level exposure to UV radiation was not measured (only latitude and ambient UV radiation), so that the results could reflect exposure to other latitude-associated factors such as temperature and indoor heating.

Infection and vaccination

Studies over the past 20 years have shown that exposure to solar UV radiation suppresses microbe-specific acquired immune responses in animal models of infection. This modulation can lead to an increased microbial load, reactivation from latency, and more severe symptoms, including death (reviewed in Norval et al.[268]). A recent study showed that spending 8 or more hours outdoors per week when the UV Index was ≥4 was associated with an increased risk of ocular recurrence of herpes simplex virus (HSV) infection resulting in eruptive lesions.[224] UV radiation prior to vaccination causes a less effective immune response in several mouse models (reviewed in Norval & Woods[271]), but whether exposure to UV radiation adversely affects the course of infections and the efficacy of vaccination in humans remains an open question.

Despite the paucity of new information, there remains the possibility that UV-induced immunosuppression could convert an asymptomatic infection into a symptomatic one, reactivate a range of persistent infections, increase the oncogenic potential of microbes, and reduce the memory immune response, for example after vaccination, so that it is no longer protective.

Autoimmune diseases

Many autoimmune diseases are considered to have both environmental and genetic risk factors. Evidence to support the importance of environmental exposures comes from geographical variation (changing incidence with changing latitude), temporal patterns (such as variations in incidence with season or season-of-birth) and results from observational epidemiological studies. Several studies show an inverse association between exposure to UV radiation and immune-mediated diseases, suggesting that the UV may be protective. In many cases, the assumed pathway has been through enhanced synthesis of vitamin D (see section on Vitamin D below). However this evidence is now being re-evaluated in light of possible alternative pathways, including UV-induced immune modulation and altered susceptibility to relevant viral infections, and non-UV pathways such as changes in the secretion of melatonin (reviewed in Hart et al.[147]). While there have been suggestions that exposure to UV radiation may be important for conditions such as inflammatory bowel disease (for example, Nerich et al.[263]), type 1 diabetes,[291] and rheumatic diseases (including rheumatoid arthritis, systemic lupus erythematosus, dermatomyositis, and others),[124] the strongest evidence is for multiple sclerosis.

Multiple sclerosis. Many studies (but not all) have shown that the prevalence, incidence, or mortality from multiple sclerosis (MS) increases with increasing latitude and decreasing altitude or intensity of ambient UV radiation, in predominantly fair-skinned populations (reviewed in Hewer et al.[155]). In the US Nurses Health Studies, a latitudinal gradient present in a cohort of female nurses born before 1946 was not apparent in a similar cohort born after 1946.[153] The findings reflected an increase in incidence in the south in the later cohort (rather than a decrease in the north). One explanation given to explain this change was that increasing sun-protective behaviours in the south had reduced the difference in personal dose of UV between the north and south.[14] Studies from the northern[395] and southern[343] hemispheres show that, compared to the general population, people with MS were more likely to have been born in late spring and less likely to have been born in late autumn. This timing would be consistent with a hypothesis that exposure of the mother to more UV radiation during the late first trimester, when the foetal nervous system is developing and maturing, is protective for the development of MS in later life.[343] Alternatively, it is also possible that exposures early in infancy, rather than in pregnancy, influence risk, or other factors that vary seasonally could be important. Animal studies suggest that UV-B irradiation can prevent the onset of experimental autoimmune encephalomyelitis, used as a model for MS,[30] and there is supportive evidence from recent studies in humans.[221, 413]

The role of UV-induced immune suppression in skin cancer

Cutaneous malignant melanoma. Evidence that the immune response is important for the development of CMM is clearly shown by the increase in incidence following organ transplantation that requires ongoing treatment with immunosuppressive medications.[377] UV radiation, particularly UV-B, can cause suppression of many aspects of cell-mediated immunity but, until recently, how it influenced the initiation of CMM was unknown. In a transgenic mouse model, the recruitment of macrophages to the skin following UV-B irradiation and their subsequent proliferation were shown to be critical in the survival of melanocytes, including those with UV-induced DNA damage.[144, 406, 407] In addition, inflammation induced by UV radiation increased metastasis of melanoma, with neutrophils being the main drivers of the inflammatory process.[23] Consistent with these reports from animal models, in patients with metastatic melanoma there was a shorter survival time if metastases contained a high proportion of macrophages.[103]

Non-melanoma skin cancer. Tumours induced by UV radiation are highly antigenic. UV-induced immune suppression plays a critical role in the development of NMSC as evidenced by the dramatically increased incidence in immunosuppressed people, for example, following organ transplantation.[251] This is especially shown for SCCs in organ transplant recipients receiving immunosuppressive drugs that suppress T cell activity, suggesting that effector T cells are of particular importance in the control of SCC.[270] Furthermore, T_{regs} induced by UV irradiation infiltrate SCCs and surround BCCs. Pharmacologically blocking steps in the pathway of UV-induced immunosuppression may be effective in preventing the development of skin cancers and actinic keratoses.[270, 349, 360]

UV-induced vitamin D and its impact on health

Metabolism of vitamin D

Vitamin D can be synthesised in the skin or ingested in the diet or as a supplement. The pathway by which vitamin D is produced in the skin and metabolised to its active form, 1,25-dihydroxyvitamin D ($1,25(OH)_2D$) is shown in Fig. 4. Synthesis is initiated by absorption of UV-B radiation by 7-dehydrocholesterol. The enzymatic steps converting vitamin D to $1,25(OH)_2D$ occur predominantly in the liver and the kidney but also in other tissues, including the skin.

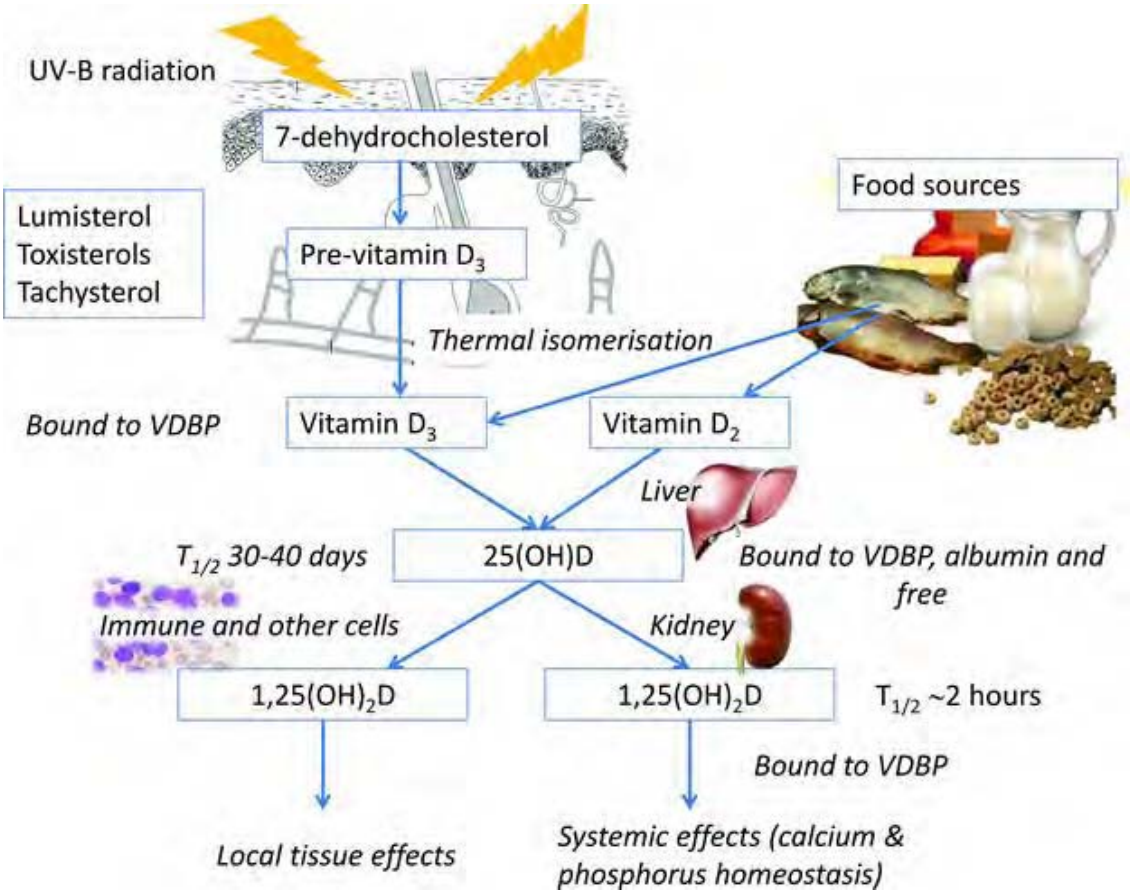

Fig. 4 Synthesis of vitamin D and the vitamin D metabolic pathway. VDBP: vitamin D binding protein; 25(OH)D: 25-hydroxyvitamin D; $1,25(OH)_2D$: 1,25-dihydroxyvitamin D; $T_{1/2}$: half-life

Both pre-vitamin D_3 and vitamin D_3 can be converted to inactive photoproducts by continued UV-A or UV-B irradiation (discussed in Galkin & Terenetskaya[120] and Norval et al.[269]). Once pre-vitamin D has formed and isomerization to vitamin D has occurred, there is preferential degradation of vitamin D compared with synthesis of pre-vitamin D at wavelengths of UV radiation between 300–330 nm.[386] This may explain why vitamin D toxicity from exposure to solar UV radiation does not occur and may be of importance to public health messages about safe exposure to the sun -- recurrent shorter periods of exposure to the sun are preferable to prolonged exposure to achieve vitamin D production while minimizing UV-induced damage of DNA.[389]

Vitamin D status – assessment and geographic variability

Vitamin D status is assessed by measuring the concentration of the intermediate metabolite, 25-hydroxyvitamin D (25(OH)D) (Fig. 4) in serum. Vitamin D deficiency is reportedly widespread globally, but it is important to note that there are considerable problems with the accuracy and reproducibility of vitamin D assays[327] as well as a lack of consensus on the concentration of 25(OH)D that denotes deficient, insufficient, sufficient, or optimal vitamin D status.[317] Common cut-off points are provided in Table 3

Table 3 Commonly used cut-off points for vitamin D status based on serum concentrations of 25(OH)D in nmol L^{-1}

Author	Year	Concentration of 25(OH)D in nmol L^{-1}			
		Deficiency	**Insufficiency**	**Sufficiency**	**Optimal**
Hollis[166]	2005			>80	
U.S. Institute of Medicine[176]	2010	<30	30-50	≥50	
Pearce and Cheetham[284]	2010	<25	25-50	50-75	>75
US Endocrine Society[165]	2011	<50	52.5-72.5	≥75	

There is a striking lack of data on the vitamin D status of infants, children, and adolescents and an almost complete lack of data from Africa and South America.[157, 280, 382]

Variation in vitamin D status according to latitude is apparent when results arise from a single assay with good agreement across batches of samples,[222] and is stronger where blood is taken in winter compared to summer.[223] Comparisons across studies may not show a latitudinal gradient due to the analytical challenges and lack of standardisation of the season of blood collection.[157, 280, 382] In addition, contributions to vitamin D status from dietary intake and sunny holidays may obscure latitudinal gradients that would otherwise occur. For example, a lower latitude holiday in the previous year with the purpose of sun-bathing was associated with higher 25(OH)D levels by 20-30 nmol L^{-1} in the following winter months in residents of Uppsala, Sweden.[39]

Skin pigmentation and vitamin D status

Within a given location, people with darker skin commonly have lower concentrations of 25(OH)D than those with fairer skin[296, 310] and this is usually attributed to the photoprotective properties of melanin. However, recent work highlights the importance of cultural practices, or personal preferences, leading to avoidance of the sun.[186] In a recent study, however, black Americans (n=2,085) had lower concentrations of 25(OH)D, but also lower concentrations of vitamin D binding protein, than white Americans.[296] The consequence of this was similar (calculated) levels of “free” (not bound to vitamin D binding protein) or loosely bound (to albumin), i.e. bioavailable, 25(OH)D. This observation may explain why black people with low total 25(OH)D have higher bone mineral density than white people with similar 25(OH)D concentrations. Furthermore, it may mean that vitamin D status should be defined by the concentration of bioavailable, rather than total, 25(OH)D.[36, 295]

Several recent experimental studies have examined the impact of pigmentation of the skin on synthesis of vitamin D. Most of these,[210, 340] although not all,[44] show that, for a specific dose of simulated solar UV irradiation there is a greater increase in the concentration of 25(OH)D in fairer-skinned than in darker-skinned participants. The lack of effect in the latter study has been attributed to the short wavelength UV-B output from the source lamp, resulting in penetration only into the superficial layers of the epidermis above the main concentration of melanin.[40]

Exposure to the sun and vitamin D status

In general, laboratory studies show an initial linear dose-response between exposure to UV radiation and change in concentration of 25(OH)D,[46] but a plateau with continuing exposures over a longer period of time.[236, 293, 312, 389] Results suggest that the shape of the dose-response curve depends on the baseline concentration of 25(OH)D, with a greater response to UV irradiation[44] and no plateau effect in those with a lower starting concentration (<50 nmol L^{-1}),[248] although conflicting results have also been obtained.[107]

Understanding the relationship between the dose of UV radiation, the surface area of skin exposed and the production of vitamin D is important for the development of public health messages. Results from population-based epidemiological studies and experimental studies using artificial irradiation, demonstrate that exposing a larger area of skin to UV radiation results in a greater increase in the concentration of 25(OH)D.[45, 188] Field studies have shown that increases in the concentrations of 25(OH)D are positively associated with DNA damage (assessed by concentration of CPDs in urine), suggesting that improved vitamin D status is always associated with some potentially mutagenic damage to DNA.[289] However, production of vitamin D may be optimised, and skin DNA damage minimised, by increasing the body surface area exposed, and decreasing the UVB-dose per unit area.

The World Health Organization's INTERSUN programme recommends sun protection when the UV Index is ≥3 and there have been concerns that there may be little or no vitamin D production when the UV Index is <3. However, recent computational work suggests that vitamin D could be synthesised at these lower levels of UV radiation, albeit more slowly.[237] Webb and colleagues have shown that, for the white-skinned population of Manchester, UK, a normal lifestyle with relatively short, regular exposures to summer sunlight in northern mid-latitudes could increase vitamin D enough at the end of summer to maintain sufficiency levels (>50 nmol L^{-1} or 20 ng ml^{-1}) throughout the winter.[388, 389]

Evidence of associations between vitamin D and human disease

The vital role of 1,25$(OH)_2$D in maintaining the concentration of calcium in the blood within a narrow range is well-established; vitamin D deficiency causes rickets in children and osteomalacia in adults. In recent years, many protective functions have been attributed to vitamin D. However, two recent systematic reviews of observational and intervention studies cast doubt on the importance of vitamin D in decreasing the risk of many of these diseases.[18, 361]

Immune function, infections, autoimmune diseases and cancer

Many of the cell types involved in immune function are able to convert 25(OH)D to the active form, 1,25$(OH)_2$D.[392] The actions of 1,25$(OH)_2$D are mediated through ligation with a nuclear vitamin D receptor (VDR) that regulates gene transcription, or via rapid-response membrane receptors. The VDR is expressed on many human cells, including those with immune functions. Polymorphisms in the VDR can affect the effectiveness of gene transcription, altering the action of the active hormone. Immunostimulatory and immunosuppressive pathways are induced by 1,25$(OH)_2$D (reviewed in Hewison[68, 156] and Christakos et al.[255]). Immunostimulatory effects include the production of AMPs such as cathelicidin by macrophages, neutrophils, and epithelial cells, and the maturation of macrophages. Immunosuppressive effects include the inhibition of proinflammatory cytokines and the differentiation and maturation of dendritic cells and their ability to present antigens. Furthermore, 1,25$(OH)_2$D can inhibit the differentiation and proliferation of B cells and their production of antibodies, and activate T_{reg} cells that have suppressor activity. These multiple effects make it difficult to determine what role, if any, vitamin D has in protection against disorders of immunity. Studies of infectious diseases (using tuberculosis and respiratory viral infections as examples), autoimmune diseases (using multiple sclerosis as an example), and the risk of cancer incidence and progression are discussed below.

Vitamin D and tuberculosis. Tuberculosis (TB), a disease caused by infection with the bacterium *Mycobacterium tuberculosis*, is a massive global health burden, with an estimated 9 million new cases and 1.7 million deaths each year. Infection can lead to symptomatic active disease or, more commonly, to a latent infection which can reactivate later in a small proportion of cases. Recent studies suggest an association between low vitamin D status (or lower ambient UV radiation as a presumed proxy) and the prevalence of TB (reviewed in Ralph et al.[302]), but it is not clear whether low vitamin D status increases the risk of symptomatic TB or vice versa. A beneficial effect of vitamin D is plausible through its immune properties, such as the macrophage-induced death of the *M. tuberculosis*.[302] However vitamin D supplementation as an adjuvant to standard antimicrobial therapy has shown no clinical benefit in most studies.[231, 303, 390] In a trial in Mongolian children, supplementation with vitamin D stimulated innate immunity against *M. tuberculosis*, which could be sufficient to prevent the infectious process.[122] Further research using optimal doses of vitamin D supplementation and with exploration of the effect of host determinants, such as VDR genotype, are required to establish whether improving vitamin D status could aid in the prevention or treatment of TB.

Vitamin D and respiratory infections. Viruses infecting the respiratory tract and causing disease, such as bronchiolitis and pneumonia, are a leading cause of hospitalisations and death in young children, and of serious illness and death in those over 65 years. Examples include influenza virus, respiratory syncytial virus, and rhinovirus. Viral respiratory infections are most common in winter and least common in summer. This seasonal pattern is diminished in the tropics where there is also relatively little seasonal variation in solar UV-B radiation, although there are two peaks of infection in some countries, perhaps reflecting the rainy seasons.[42] It is hypothesised that vitamin D-dependent immunoregulation mediates these seasonal patterns.[325]

Recent observational studies typically show that lower concentrations of 25(OH)D are associated with greater risk of having a respiratory tract infection (for example[35, 54, 128, 161]). However, in most cases, study participants had disease symptoms when they were first assessed, so that low vitamin D status could be either a cause or a consequence of the infection. The results from supplementation trials with vitamin D are inconsistent, as indicated by the following studies. Separate trials in Japanese[370] and Mongolian[57] children showed reduced incidence of respiratory infection in the supplemented groups, and there is some evidence of benefit in postmenopausal women,[6] young Finnish men[200] and older Australian adults (using antibiotic use as a surrogate for infection).[364] In contrast, trials of supplementation in adults from the United States[208, 304] and New Zealand[254] failed to show any beneficial effect of vitamin D.

Reducing the risk of infectious diseases would have significant impacts on personal morbidity and global economies; however, the role of vitamin D in promoting this is unclear at this time.

Vitamin D and multiple sclerosis. Observational studies consistently show that higher concentrations of 25(OH)D are associated with lower risk of MS (reviewed in Hewer et al.[155]), and that vitamin D deficiency is associated with decreased responsiveness to MS treatment, and may be a risk factor for higher MS disease activity and more rapid progression (for example, Ascherio et al.[15]).

Most studies, however, cannot distinguish between cause and effect; that is, does low vitamin D status cause the disease or does the disease cause the low vitamin D status? Indeed, there is evidence that concentrations of 25(OH)D are reduced by inflammation.[308] Further, a review of randomised controlled trials of supplementation with vitamin D in people with MS found no evidence of improvement in clinical endpoints.[18] Overall, the authors hypothesised that either uncontrolled confounding or reverse causality provided an explanation for the strong and consistent associations in observational studies and the lack of effect of supplementation.

It is also important to consider possible heterogeneity in MS, coupled with a lack of understanding of the timing of the onset of disease pathology and thus the most appropriate time to test vitamin D status or to give vitamin D supplementation. In addition, the risk factors for disease onset may differ from those of progression.[220]

Vitamin D and cancer risk. Vitamin D deficiency may increase the risk of developing cancer as 1,25$(OH)_2$D has regulatory effects on cellular growth, apoptosis and formation of new blood vessels. Observational studies consistently show associations between low circulating 25(OH)D and increased risk of colorectal cancer (reviewed in Autier et al.[18]) but, for other cancers, there have either been too few studies or the results are inconsistent.[18, 361] Trials do not show evidence of beneficial effects with vitamin D supplementation.[38] In addition to the reasons discussed above for similar discrepant findings in relation to MS, the null findings from trials with supplementation of vitamin D may be due to too low a supplement dose, poor compliance, too short a follow-up, inadequate statistical power of the study, or, parsimoniously, suggest that vitamin D has no effect.[18]

It is particularly difficult to assess the effects of vitamin D on risk of skin cancer, as UV radiation induces both. Production of 1,25$(OH)_2$D in the skin enhances the repair of UV-induced DNA damage.[76, 133] Cohort studies have shown protective[351, 374] and adverse[1] associations between concentrations of 25(OH)D and risk of NMSC and similar inconsistencies for risk of CMM.[1, 226] Post-hoc analyses of the Women's Health Initiative trial did not show a protective effect of supplementation with vitamin D on risk of NMSC or CMM, but in people with a history of NMSC, the incidence of CMM was reduced in those randomised to 400 IU of vitamin D per day.[352]

In summary, the evidence that higher vitamin D status is protective for cancer is weak and inconsistent, except possibly for colorectal cancer risk. If vitamin D deficiency is truly a risk factor, it is low concentrations of 25(OH)D (i.e. <30 nmol L^{-1}) that are associated with increased risk with little additional benefit for concentrations >50 nmol L^{-1}.[286]

Vitamin D and cancer-survival. Higher vitamin D status has been positively associated with survival from a number of different cancers,[18, 329] but there is a paucity of trial data, and confounding by severity of disease or co-morbidities is highly likely. At this time there is insufficient evidence to draw any conclusions.

Effects of vitamin D on other health conditions. Several studies suggest that maternal vitamin D deficiency is associated with adverse outcomes in the offspring across multiple domains: bone mineral content,[410] cognitive function,[393] depression and risk of eating disorders,[5] and autism.[393] Furthermore, vitamin D deficiency in early life has been linked to increased risk of schizophrenia in later life.[234] These results may indicate that vitamin D status during pregnancy is important for foetal development, but further research will be required to confirm whether these are causal associations or due to a related factor(s).

Prospective studies have reported moderate to strong inverse correlations between concentrations of 25(OH)D and cardiovascular diseases, concentrations of serum lipids, inflammation, disorders of glucose metabolism, weight gain, mood disorders, declining cognitive function, dementia, Alzheimer's disease, impaired physical functioning, and mortality. In contrast, intervention trials show no effect of vitamin D supplementation on these outcomes.[18]

U-shaped associations between vitamin D metabolites and disease

Recent research shows that both high and low concentrations of 25(OH)D are associated with increased disease risk – a so-called U-shaped association. Table 4 provides a summary of studies showing this effect.

Table 4 Health outcomes for which a U-shaped association with serum 25(OH)D levels has been described, and the 25(OH)D level of lowest risk

Disease / condition and reference	Concentration (nmol L^{-1}) of lowest risk, i.e. the turning point of the U-shaped dose response
All-cause mortality[94, 239, 328]	80-100
Cardiovascular events[91, 412]	50-100
Cancer mortality[117, 240]	100 (men only)
Prostate cancer[367]; [[50]]	50 [≤55 (highest risk, 91-106)]
Pancreatic cancer[345]	<100
Allergen-specific IgE during childhood[319]	50-74.9
Tuberculosis[265]	76-140
Schizophrenia (neonatal vitamin D status)[234]	47
Small-for-gestational-age births among white women[43]	60-70
Physical frailty in older women[99]	50-74.9

An additional U-shaped association has been shown between concentration of 1,25$(OH)_2$D and viral load in patients with HIV.[29]

There is a trend to advocate ever higher cut-offs to denote the concentration of 25(OH)D concentrations that is optimal to prevent disease.[380] It is therefore important to continue to investigate possible disease risks at higher concentrations of 25(OH)D, especially if the aim is to maintain such levels over the long-term.

Other effects of solar UV radiation on human health

Chronic exposure to UV radiation has been weakly linked to a range of other adverse health outcomes, including: decreased epidermal[22] and subcutaneous[187] lipid synthesis resulting in weakening of the barrier function of the skin; hearing impairment, through oxidative stress pathways;[241, 243] lactase non-persistence;[350] increased risk of prostate cancer;[255] and acquired bilateral nevus-of-Ota-like macule, a common pigmentation disorder in Asian females.[384]

In contrast, there is evidence of a protective effect of higher UV radiation on development of restless legs syndrome[191] and keloid formation in scars.[396] There are a growing number of studies examining the apparently beneficial effects of exposure to the sun. A recent study has shown that UV-A irradiation is effective in lowering blood pressure, possibly through UV-A-induced nitric oxide bioactivity.[214] A reduced risk of cancer and particularly breast cancer has been reported in association with greater exposure to the sun in early life,[404] as well as a decreased risk of myocardial infarction, and all-cause mortality, and hip fracture in those below age 90, where history of skin cancer was the measure of past exposure to the sun.[52] In Chile the most frequent cases of food-related anaphylaxis occur at higher latitudes where there is lower solar radiation.[168]

Personal protection from solar UV radiation

The threat of increasing levels of UV-B radiation due to stratospheric ozone depletion, and rising skin cancer incidence rates, led to the development of sun protection programs and strategies. Despite the partial recovery of the ozone layer (reviewed in Chapter 1), such strategies remain important because changes in climate are likely to alter both ambient UV radiation and behaviour that affects exposure to the sun.

A sustained effort is required to change attitudes and behaviours in relation to exposure to the sun, especially in young people.[24] Several recent surveys indicate that adults,[55, 119] adolescents,[309] and children,[89, 96] still commonly report having been sunburned in the previous year, and this applies to both fair- and dark-skinned populations.[27]

While in some locations, a majority of children use some form of photoprotection, particularly shade,[89, 96, 105] this is not true of adults.[55] Good knowledge of protection from the sun may not translate into attitudes and practices for reducing exposure.[89, 105, 253] Further, more education about the specific needs for photoprotection in different situations may be required. In a sample of young German children, parental knowledge of appropriate use of shade, clothing, a sunhat, and sunscreen was considered to be adequate for summer holidays at the beach, but not for everyday outdoor activities.[209] In a Danish study, travel to a sunny destination was common (almost 50% of those aged 15-59 years took such a holiday each year), with a high likelihood of sunburn and intentional tanning.[192] There are limited data on strategies for photoprotection in tropical countries but one survey in adolescents living in Bangkok, Thailand, found that sunscreens, sun-protective clothing, and shade were seldom used, particularly in males, compared with Western countries.[356] In a study in Philadelphia, USA, Hispanic adolescents and young adults who showed evidence of greater adoption of US culture were less likely to use sunscreen and more likely to deliberately expose themselves to the sun than those who retained their traditional culture.[151] Barriers to personal protection from the sun in young Australians include peer pressure, lifestyle, fashion and social norms.[294]

The ultraviolet index (UVI) is routinely published in the media in some countries, available online,[58] on a mobile phone,[17] on mobile phone apps,[92] or can be approximated using a compact disk as a sundial.[59] However, its use to guide behaviour in relation to exposure to the sun remains limited.[252] Furthermore, the specific guidance in relation to the UVI varies across different countries. For example, in Australia, photoprotection is recommended when the UV Index is ≥3.[58] In New Zealand, a "UV Sun protection Alert Period" is provided daily, rather than the UVI, and is defined as the period of the day where the forecast clear-sky UVI is >3.[301] The United States Environmental Protection Agency provides a UV Alert when the forecast UVI is at ≥6, with advice to minimise time in the sun and use protection.[100] As noted, exposure to the sun when the UVI is <3 is relatively ineffective for vitamin D production, whereas, for some fair-skinned individuals, even short exposures at a UVI of 6 may result in erythema. It is difficult to provide blanket recommendations, even according to the UVI and skin type, as there is wide variation in the minimal erythema dose (MED, the dose of UV radiation required to cause a slight reddening of the skin) even within a specific skin type, and different messages may be required for different regions.[408]

It is not generally realised that measures for protection against the sun may be required on cloudy days, in addition to clear days, due to diffuse solar UV radiation,[7, 378] and that some shade devices, such as umbrellas, provide incomplete protection from UV-B radiation.[198]

Sunscreens

Public health bodies have long advocated the use of sunscreens as a means of photoprotection. A long-term prospective study in Queensland, Australia, showed that daily use of sunscreen reduced the incidence of SCC[372] with some evidence of reduction in the incidence of CMM.[134] In addition, such use also reduced photoageing of the skin.[171] However, a recent meta-analysis of the effectiveness of interventions promoting use of sunscreen in adults and children in recreational settings showed no reduction of sunburn in adults and only a modest effect in children.[315]

Sunscreens are formulated and tested for their ability to prevent erythema (inflammation) *in vivo* and their index of efficacy is the sun protection factor (SPF).[178] The labelled SPF is equal to: [MED $_{\text{protected skin}}$]/[MED $_{\text{unprotected skin}}$], when tested under laboratory conditions with simulated solar radiation. The erythema action spectrum dictates that this is primarily an index of protection from UV-B radiation although sunscreens are also required to have a measure of protection against UV-A radiation.[113] Sunscreens with uniform absorption across the whole UV spectrum (broad-spectrum) provide photoprotection that is similar to shade or some types of clothing fabric[87] (for more detail, see Chapter 7). Some UV radiation filters may also have anti-inflammatory properties,[71] in which case the SPF may be more than a measure of optical filtering.[322]

One requirement of the SPF test is that sunscreen is applied at a coverage of 2 mg cm^{-2}, but several studies have shown that people apply much less (for example, Petersen et al.[287]). The thickness of the application is also dependent on the formulation, with coverage of only 0.22 mg cm^{-2} achieved by children applying sunscreen with a roll-on.[85] Use of a higher SPF sunscreen or two applications of sunscreen can achieve a greater level of protection.[290, 357] In addition to inadequate thickness of application, failure to apply sunscreen to all areas of exposed skin also limits the amount of photoprotection achieved. There are concerns that using sunscreen will decrease synthesis of vitamin D. Current evidence suggests that, if sunscreen is correctly applied, there may be no increase in concentrations of 25(OH)D following exposure to the sun.[109] However, with usual applications, there is minimal impairment of the synthesis of vitamin D.[213, 374]

Traditional topical sunscreens depend on the filtering or scattering of UV radiation, i.e. "passive" photoprotection. Table 5 summarizes some recent developments in compounds providing "active" photoprotection at a topical and systemic level.[179]

Table 5 Newer active sunscreens and evidence of their effectiveness

Class	Route and Effectiveness
α-melanocyte stimulating hormone analogues - stimulate melanogenesis (tanning), e.g., afamelanotide	Sub-cutaneous; Effective in some photosensitive patients[150, 204]
Natural anti-oxidants, e.g., Vitamin A (retinol), Vitamin C (ascorbic acid), Vitamin E (tocopherol), Pycnogenol (pine bark extract), Carotenoids	Oral; Not as effective as topical sunscreens[66, 179]
Nicotinamide (an amide form of vitamin B3)	Topical; enhances DNA repair, prevents UV-induced immunosuppression, reduces incidence of NMSC[65]
Resveratrate, found in red wine, grapes, plums and peanuts	Topical; Application immediately after exposure to the sun protected against erythema and sunburn cell formation[401]
Flavonoids, e.g., luteolin (a)	Protects skin by a combination of UV-absorbing, DNA-protective, antioxidant and anti-inflammatory effects.[400]
Lycopene, found in tomato paste	Oral; Ingestion over a 12 week period reduced acute & chronic effects of photodamage[314]
Green tea polyphenols	Oral; Some evidence of modest effect[152, 313]
Diet rich in omega-3 fatty acids	Oral; May reduce risk of skin cancer [217, 373]

Class	Route and Effectiveness
Liposomes containing natural endonucleases or photolyases	Topical; Enhance nucleotide excision repair of UV-induced DNA damage; shown to reduce the incidence of solar keratoses and the severity of polymorphic light eruption.[32, 81, 164]

Overall, people are probably getting much less protection from the harmful effects of UV radiation than they believe when they use sunscreens, especially if their intention is to prolong their time in the sun. This is a public health issue that has to be addressed either by encouraging people not to go outdoors when the UVI is high, or to use appropriate clothing (see also Chapter 7) for sun protection.[58] Alternatively, people need to apply sunscreen more thickly, or use sunscreen of a higher SPF to compensate for inadequate application.

Clothing and Shade

Clothing modifies the skin surface area exposed to solar UV radiation. It offers good protection against sunburn, although this is dependent on the properties of the fabric such as colour, structure (e.g., woven vs. knit and tightness of the weave for woven fabrics), and wetness (see Chapter 7). Clothing typically strongly attenuates transmission of erythemally-effective UV radiation (i.e. weighted with the erythema action spectrum) to the skin. However, this blocking of UV-B radiation commonly leads to low vitamin D status in people who wear full body clothing,[275] for example for religious or cultural reasons.[25, 149] It may be possible to design and manufacture clothing from fabrics that allows synthesis of vitamin D while preventing a visible erythema.[339] However, it is likely that this will not protect from suberythemal damage, such as to the DNA of the epidermal cells.

Shade-seeking is a well-recognized and effective way of reducing exposure to solar UV radiation, as evidenced by a lower level of sunburn[212] and lower vitamin D status in adults from the USA who reported frequent use of shade on a sunny day, compared to those who used shade rarely.[213] Provision of shade over playgrounds, particularly in sunny locations, is a relatively inexpensive method of mass protection from the sun. Nevertheless, a systematic review of 23 publications found no evidence that health promotion interventions had any effect in increasing shade-seeking in adults or children.[315] Shade may be less effective at reducing exposure to diffuse UV radiation and this may account for about 80% of people's cumulative annual erythemal exposure.[378] A recent study has used a manikin head (in a fixed position) to measure exposure to UV radiation under different conditions of shade, cloud cover and solar angle.[283] This approach can be used to quantify the protective benefits of shade that are currently not well documented.

Preventing skin cancer versus ensuring adequate vitamin D status

There is no simple message to guide optimal levels of exposure to the sun. There is considerable variation between individuals in the doses of UV radiation that cause damage to DNA and induce synthesis of vitamin D. However, some broad recommendations can be made. Repeated short exposures to the sun are more efficient at vitamin D production than a single prolonged exposure.[389] Levels of UV-B radiation are greatest at midday and vitamin D synthesis is thus most efficient at this time,[238] although it is also the time when sunburn occurs most quickly.[387] The amount of time in the sun that is needed for the synthesis of vitamin D varies according to location, time of day, and time of year. After controlling for the level of exposure to UV radiation, having more skin not covered by clothing is associated with higher concentrations of 25(OH)D in serum.[45, 188] As noted above, there are conflicting results on the effect of darker pigmentation of skin on the UV-induced production of vitamin D. In high latitude locations where UV-B levels are too low for vitamin D synthesis and a cooler climate may mean that little skin is exposed to the sun even during summer, greater intake of vitamin D may be required to avoid vitamin D deficiency.

Protection of the eye

One of the cheapest and most practical methods of protecting the eye from exposure to UV-B radiation is wearing a hat with a brim of at least 6-7 cm.[58, 318] Sunglasses provide variable protection, and standards are more rigorous for UV-B than for UV-A radiation. For UV-B radiation the upper transmission limits range from 1.0% to 12.5% depending on the international jurisdiction and the type of use. For UV-A radiation, the limit is either a maximum of 50% of visible transmittance or is unspecified. The size of the frame and design can influence eye protection and some standards for sunglasses incorporate a minimum size limit.[337] Wrap-around designs are most protective and are especially important when in highly reflective conditions, for example when skiing.[337] Many ordinary eye-glass lenses have UV filters in them.

The American National Standards Institute (ANSI) requires that contact lenses absorb at least 95% of UV-B radiation and 70% of UV-A radiation for a “UV blocking” claim. A recent survey on a selection of lenses showed compliance with claims for photoprotection.[279]

Studies using manikin heads[123, 385] have shown that, although the ambient UV radiation is greatest at solar noon, the highest dose of UV radiation was received by the eye at 4 hours before and after noon, when the solar elevation angle was lower. Thus, photoprotection of the eyes during outdoor activities is important not only at noon, but also at other times, and during winter.[169] In some occupations, e.g., working on a building site, the reflectivity of the building materials may influence the amount of UV radiation received by the eye[368] and should be considered when wearing eye-protection.

Protection of the eyes from the sun should reduce the risk of pterygium; UV absorbing contact lenses that cover most of the cornea can protect against UV-induced damage.[64, 337] Eye drops for the prevention of pterygium and photokeratitis/photoconjunctivitis through anti-oxidant and anti-inflammatory pathways have been effective in animal models, but are not commonly used in humans.[62, 202]

Effects of interactions between solar UV radiation and the environment

Environmental contaminants may interact synergistically with UV radiation to harm human health. For example, in the presence of UV-B radiation, chrysene,[4] a common environmental contaminant produced by incomplete burning of fossil fuels, and some pesticides,[31] have adverse effects on human health, including through damage to DNA.[101] Topical corticosteroids are unstable under UV-B irradiation, possibly causing skin damage as well as loss of therapeutic effect.[246] Engineered nanoparticles (NPs) are increasingly incorporated into sporting equipment, sunscreens, clothing and cosmetics (see also Chapter 7). Concerns have been raised about possible health risks of NPs.[139, 199] A recent review of the evidence on NP in sunscreens concluded that “on current evidence, neither TiO_2 nor ZnO NPs are likely to cause harm when used as ingredients in sunscreens”.[362] Nevertheless, exposure of skin to UV radiation may enhance the penetration of engineered NPs,[180] and the formulations using these particles are often used around the time of irradiation when skin damage may occur. Further, UV-induced immunosuppression could potentially impair an immune protective response induced by engineered NPs applied to the skin.[180]

On the positive side, UV radiation is a potent environmental disinfectant able to inactivate viruses in clear water (for further discussion see Chapter 4). This property is used in the SODIS (solar disinfection) technique, where exposure of surface water within a transparent bottle to sunlight effectively disinfects the water, decreasing the incidence of diarrhoeal diseases (reviewed in McGuigan et al.[235]).

Health implications of interactions between ozone depletion and climate change

Past studies have estimated the health gains in terms of skin cancers avoided through the implementation of the Montreal Protocol and its amendments.[336] A recent update of this work that also integrated coupled climate-chemistry models has estimated that the world-wide incidence of skin cancer would have been 14% greater (2 million people) by 2030 without implementation of the Montreal Protocol and its amendments,[376] with the largest effects in the South West USA and in Australia (see Chapter 1} for further details).

Model estimates[21] suggest that, by 2050, any increases in erythemal UV radiation above present levels will be small and confined to the tropical region (reviewed in Chapter 1). These should have only a small effect on the incidence of skin cancer[79] but may impair immune responses to some vaccinations. However, outside the tropical region, erythemal UV radiation is projected to be lower especially in winter (reviewed Chapter 1) which could be detrimental for the vitamin D status of populations in these regions, as well as for diseases that may be modulated by exposure to UV radiation, such as some of the autoimmune diseases discussed above. Estimates of exposure times for erythema and vitamin D synthesis in Europe, taking account of ozone recovery and interactions with different concentrations of greenhouse gases (GHG),[79] suggest that there will be very little change in the exposure time for both endpoints for Southern Europe. However, an increased exposure time of about 30% for vitamin D production would be required in a worst case scenario in Stockholm in spring with high levels of GHGs.[79]

A major determinant of the received dose of UV radiation is behaviour in relation to exposure to the sun.[288] Ambient temperature is likely to influence time spent outdoors. In temperate parts of Australia, the increase in temperature is likely to increase skin cancer incidence because people will spend more time outside with less clothing.[206, 227] However, with the temperature increases in already warm climates, people will be more likely to stay indoors or to seek shade.[223] Warmer ambient temperatures may have direct physiological effects to accelerate both skin cancer development[371] and vitamin D production.[366]

In addition to these direct effects of interactions between climate change and ozone depletion and/or UV radiation for human health, there are potential indirect effects that may become important, but, at this stage remain ill-defined.[363] Concurrent changes in climate and levels of ambient UV radiation will influence aquatic and terrestrial ecosystems (see also Chapters 3 and 4) that may have consequences for food safety, quality and supply (reviewed in[363]).

Migration of populations, often with dark skin pigmentation, from low-lying tropical regions because of rising sea levels, to higher latitude regions may increase the diseases associated with vitamin D deficiency.

Higher temperatures should foster microbial growth in surface waters, and this will be more pronounced in the presence of lower levels of disinfecting UV-B radiation, or where increases in colour due to dissolved organic matter limit penetration of UV-B radiation (for more detail, see Chapter 3, 4 and 5). However there has been little research to date that allows prediction or quantification of the risks to human health that might arise from these interactions.

Gaps in our knowledge

Considerable evidence from animal models suggests that UV-induced immunosuppression may increase the risk of some infections and decrease the protection offered by vaccination (reviewed in Norval & Halliday[270]). Studies in humans are required to determine whether any increased risk is clinically relevant, for example, requiring changes in vaccination protocols. Although some animal studies similarly suggest that vitamin D status affects the outcomes of vaccination or immune responses to infection, results from clinical trials mostly show no effect.[106, 297]

There is currently considerable controversy about which health conditions are influenced by vitamin D. Large-scale vitamin D supplementation trials that are in progress will provide some answers (see Table 1 in Byrne[56]). While there is consensus that vitamin D is important for bone health, there is lack of agreement about the concentration of 25(OH)D required. In addition, there is substantial individual variability in the change in concentration in 25(OH)D in response to UV irradiation and vitamin D supplementation, and in the clinical effects associated with different concentrations of 25(OH)D. The reasons for this are poorly understood, but are likely to depend on variation in the genes encoding the vitamin D binding protein and/or the vitamin D receptor.

Production of vitamin D occurs readily at sub-erythemal doses, but repeated sub-erythemal exposures can also cause accumulation of CPDs that repair only slowly (over 24-36 hours) and thus may increase the risk of skin cancer.[326] Until there is a better understanding of the numbers of CPDs that accrue during brief sun exposures, and their importance in determining the risk of subsequent skin cancer, it is difficult to recommend safe exposures which would result in sufficient production of vitamin D.

There is a lack of data on the vitamin D status of infants, children, and adolescents and for populations in Africa and South America. Further, the lack, until recently, of accurate and precise assays has limited our ability to examine variability in vitamin D status across countries (for example those with and without fortification of food) and over time. The advent of the standardised vitamin D assays[60] means that this is now possible. Development of a less invasive sampling method, for example using saliva, would allow more widespread assessment of the vitamin D status of infants and children.

Protection from the sun is currently recommended by the World Health Organization when the UVI is ≥3. The corollary of this message is that photoprotection is not required when the UVI is <3. At these low UVI values, there is little UV-B radiation (and thus little vitamin D synthesis), but, with prolonged exposure, there may be a relatively high dose of UV-A radiation. With recognition that UV-A radiation can induce immune suppression[77] and is involved in the initiation of CMM, but may also have beneficial effects on blood pressure, the doses received and potential health effects need to be better defined.

The action spectra for a number of health outcomes have not been determined. These include cataract from protracted exposure, myopia, carcinoma in deeply pigmented skin, melanoma and production of pre-vitamin D from a polychromatic source (the sun) and in both dark and fair skin types. However, the relevance of the currently available animal models is uncertain so obtaining these action spectra with definite relevance to humans is very difficult.

There is emerging evidence that exposure to the sun may have beneficial effects independently of vitamin D. The lack of a strong evidence-base challenges our ability to provide accurate guidance to the public regarding exposure to the sun.

As noted above, there is much uncertainty about the effect of the potential indirect interactions of climate change and ozone depletion on human health. Effects on disinfection of surface water and on supply and security of food could become important sources of risks to health, particularly in some regions of the world. Modelling now may be able to identify those areas at greatest risk, and allow forward planning to mitigate the risks.

References

1 Afzal S, Nordestgaard BG, Bojesen SE, 2013, Plasma 25-hydroxyvitamin D and risk of non-melanoma and melanoma skin cancer: a prospective cohort study, *J. Invest. Dermatol.*, **133**, 629-36.

2 Agbai ON, Buster K, Sanchez M, Hernandez C, Kundu RV, Chiu M, Roberts WE, Draelos ZD, Bhushan R, Taylor SC, Lim HW, 2014, Skin cancer and photoprotection in people of color: a review and recommendations for physicians and the public, *J. Am. Acad. Dermatol*, **70**, 748-62.

3 Albert MR, Ostheimer KG, 2003, The evolution of current medical and popular attitudes toward ultraviolet light exposure: part 2, *J. Am. Acad. Dermatol*, **48**, 909-18.

4 Ali D, Verma A, Mujtaba F, Dwivedi A, Hans RK, Ray RS, 2011, UVB-induced apoptosis and DNA damaging potential of chrysene via reactive oxygen species in human keratinocytes, *Toxicol. Lett.*, **204**, 199-207.

5 Allen KL, Byrne SM, Kusel MM, Hart PH, Whitehouse AJ, 2013, Maternal vitamin D levels during pregnancy and offspring eating disorder risk in adolescence, *Int. J. Eat. Disord.*, **46**, 669-76.

6 Aloia JF, Li-Ng M, 2007, Re: epidemic influenza and vitamin D, *Epideliol. Infect.*, **135**, 1095-6.

7 Andersen PA, Buller DB, Walkosz BJ, Scott MD, Maloy JA, Cutter GR, Dignan MD, 2010, Environmental cues to UV radiation and personal sun protection in outdoor winter recreation, *Arch. Dermatol.*, **146**, 1241-7.

8 Andersson K, Michael KM, Luostarinen T, Waterboer T, Gislefoss R, Hakulinen T, Forslund O, Pawlita M, Dillner J, 2012, Prospective study of human papillomavirus seropositivity and risk of nonmelanoma skin cancer, *Am. J. Epidemiol.*, **175**, 685-95.

9 Aquaron R, 1990, Oculocutaneous albinism in Cameroon. A 15-year follow-up study, *Ophthalmic. Paediatr. Genet.*, **11**, 255-63.

10 Arnold M, Holterhues C, Hollestein LM, Coebergh JW, Nijsten T, Pukkala E, Holleczek B, Tryggvadottir L, Comber H, Bento MJ, Diba Ch S, Micallef R, Primic-Zakelj M, Izarzugaza MI, Perucha J, Marcos-Gragera R, Galceran J, Ardanaz E, Schaffar R, Pring A, de Vries E, 2014, Trends in incidence and predictions of cutaneous melanoma across Europe up to 2015, *J. Eur. Acad. Dermatol. Venereol.*, **28**, 1170-8.

11 Arora R, Chang Y, Moore PS, 2012, MCV and Merkel cell carcinoma: a molecular success story, *Curr. Opin. Virol*, **2**, 489-98.

12 Artigas JM, Felipe A, Navea A, Fandino A, Artigas C, 2012, Spectral transmission of the human crystalline lens in adult and elderly persons: color and total transmission of visible light, *Invest. Ophthalmol. Vis. Sci.*, **53**, 4076-84.

13 Artornsombudh P, Sanpavat A, Tinnungwattana U, Tongkhomsai V, Sansopha L, Tulvatana W, 2013, Prevalence and clinicopathologic findings of conjunctival epithelial neoplasia in pterygia, *Ophthalmol.*, **120**, 1337-40.

14 Ascherio A, Munger KL, 2007, Environmental risk factors for multiple sclerosis. Part I: the role of infection, *Ann. Neurol.*, **61**, 288-99.

15 Ascherio A, Munger KL, White R, Kochert K, Simon KC, Polman CH, Freedman MS, Hartung HP, Miller DH, Montalban X, Edan G, Barkhof F, Pleimes D, Radu EW, Sandbrink R, Kappos L, Pohl C, 2014, Vitamin D as an early predictor of multiple sclerosis activity and progression, *J. Am. Med. Assoc. Neurol.*, **71**, 306-14.

16 Asokan R, Venkatasubbu RS, Velumuri L, Lingam V, George R, 2012, Prevalence and associated factors for pterygium and pinguecula in a South Indian population, *Ophthalmic Physiol. Opt.*, **32**, 39-44.

17 Australian Radiation and Nuclear Safety Agency, 2014, Australian UV levels for mobile phones, http://www.arpansa.gov.au/uvindex/realtime/cellrt.htm, accessed 31 July, 2014.

18 Autier P, Boniol M, Pizot C, Mullie P, 2014, Vitamin D status and ill health: a systematic review, *Lancet Diab. Endocrinol.*, **2**, 76-89.

19 Baade PD, Green AC, Smithers BM, Aitken JF, 2011, Trends in melanoma incidence among children: possible influence of sun-protection programs, *Expet. Rev. Anticancer Ther.*, **11**, 661-4.

20 Baarnhielm M, Hedstrom AK, Kockum I, Sundqvist E, Gustafsson SA, Hillert J, Olsson T, Alfredsson L, 2012, Sunlight is associated with decreased multiple sclerosis risk: no interaction with human leukocyte antigen-DRB1*15, *Eur. J. Neurol.*, **19**, 955-62.

21 Bais AF, Tourpali K, Kazantzidis A, Akiyoshi H, Bekki S, Braesicke P, Chipperfield MP, Dameris M, Eyring V, Garny H, Iachetti D, Jockel P, Kubin A, Langematz U, Mancini E, Michou M, Morgenstern O, Nakamura T, Newman PA, Pitari G, Plummer DA, Rozanov E, Shepherd TG, Shibata K, Tian W, Yamashita Y, 2011, Projections of UV radiation changes in the 21st century: impact of ozone recovery and cloud effects, *Atmos. Chem. Phys.*, **11**, 7533-7545.

22 Bak H, Hong SP, Jeong SK, Choi EH, Lee SE, Lee SH, Ahn SK, 2011, Altered epidermal lipid layers induced by long-term exposure to suberythemal-dose ultraviolet, *Int. J. Dermatol.*, **50**, 832-7.

23 Bald T, Quast T, Landsberg J, Rogava M, Glodde N, Lopez-Ramos D, Kohlmeyer J, Riesenberg S, van den Boorn-Konijnenberg D, Homig-Holzel C, Reuten R, Schadow B, Weighardt H, Wenzel D, Helfrich I, Schadendorf D, Bloch W, Bianchi ME, Lugassy C, Barnhill RL, Koch M, Fleischmann BK, Forster I, Kastenmuller W, Kolanus W, Holzel M, Gaffal E, Tuting T, 2014, Ultraviolet-radiation-induced inflammation promotes angiotropism and metastasis in melanoma, *Nature*, **507**, 109-13.

24 Balk SJ, 2011, Ultraviolet radiation: a hazard to children and adolescents, *Pediatrics*, **127**, e791-817.

25 Bassil D, Rahme M, Hoteit M, Fuleihan Gel H, 2013, Hypovitaminosis D in the Middle East and North Africa: Prevalence, risk factors and impact on outcomes, *Dermato-endocrinol.*, **5**, 274-98.

26 Basta NO, James PW, Craft AW, McNally RJ, 2011, Seasonal variation in the month of birth in teenagers and young adults with melanoma suggests the involvement of early-life UV exposure, *Pigment Cell Melanoma. Res.*, **24**, 250-3.

27 Battie C, Gohara M, Verschoore M, Roberts W, 2013, Skin cancer in skin of color: an update on current facts, trends, and misconceptions, *J. Drugs Dermatol.*, **12**, 194-8.

28 Bauer A, Diepgen TL, Schmitt J, 2011, Is occupational solar ultraviolet irradiation a relevant risk factor for basal cell carcinoma? A systematic review and meta-analysis of the epidemiological literature, *Br. J. Dermatol.*, **165**, 612-25.

29 Bearden A, Abad C, Gangnon R, Sosman JM, Binkley N, Safdar N, 2013, Cross-sectional study of vitamin D levels, immunologic and virologic outcomes in HIV-infected adults, *J. Clin. Endocrinol. Metab.*, **98**, 1726-33.

30 Becklund BR, Severson KS, Vang SV, Deluca HF, 2010, UV radiation suppresses experimental autoimmune encephalomyelitis independent of vitamin D production, *Proc. Nat. Acad. Sci. USA.*, **107**, 6418-6423.

31 Beketov MA, Speranza A, Liess M, 2011, Ultraviolet radiation increases sensitivity to pesticides: synergistic effects on population growth rate of Daphnia magna at low concentrations, *Bull. Environ. Contam. Toxicol.*, **87**, 231-7.

32 Berardesca E, Bertona M, Altabas K, Altabas V, Emanuele E, 2012, Reduced ultraviolet-induced DNA damage and apoptosis in human skin with topical application of a photolyase-containing DNA repair enzyme cream: clues to skin cancer prevention, *Mol. Med. Rep.*, **5**, 570-4.

33 Berger MF, Hodis E, Heffernan TP, Deribe YL, Lawrence MS, Protopopov A, Ivanova E, Watson IR, Nickerson E, Ghosh P, Zhang H, Zeid R, Ren X, Cibulskis K, Sivachenko AY, Wagle N, Sucker A, Sougnez C, Onofrio R, Ambrogio L, Auclair D, Fennell T, Carter SL, Drier Y, Stojanov P, Singer MA, Voet D, Jing R, Saksena G, Barretina J, Ramos AH, Pugh TJ, Stransky N, Parkin M, Winckler W, Mahan S, Ardlie K, Baldwin J, Wargo J, Schadendorf D, Meyerson M, Gabriel SB, Golub TR, Wagner SN, Lander ES, Getz G, Chin L, Garraway LA, 2012, Melanoma genome sequencing reveals frequent PREX2 mutations, *Nature*, **485**, 502-6.

34 Bernard HU, Burk RD, Chen Z, van Doorslaer K, zur Hausen H, de Villiers EM, 2010, Classification of papillomaviruses (PVs) based on 189 PV types and proposal of taxonomic amendments, *Virology*, **401**, 70-9.

35 Berry DJ, Hesketh K, Power C, Hypponen E, 2011, Vitamin D status has a linear association with seasonal infections and lung function in British adults, *Br. J. Nutr.*, **106**, 1433-40.

36 Bhan I, Powe CE, Berg AH, Ankers E, Wenger JB, Karumanchi SA, Thadhani RI, 2012, Bioavailable vitamin D is more tightly linked to mineral metabolism than total vitamin D in incident hemodialysis patients, *Kidney Internat.*, **82**, 84-9.

37 Bhatia S, Afanasiev O, Nghiem P, 2011, Immunobiology of Merkel cell carcinoma: implications for immunotherapy of a polyomavirus-associated cancer, *Curr. Oncol. Rep.*, **13**, 488-97.

38 Bjelakovic G, Gluud LL, Nikolova D, Whitfield K, Krstic G, Wetterslev J, Gluud C, 2014, Vitamin D supplementation for prevention of cancer in adults, *Cochrane Database Syst. Rev.*, **6**, CD007469.

39 Bjork A, Andersson A, Johansson G, Bjorkegren K, Bardel A, Kristiansson P, 2013, Evaluation of sun holiday, diet habits, origin and other factors as determinants of vitamin D status in Swedish primary

health care patients: a cross-sectional study with regression analysis of ethnic Swedish and immigrant women, *BMC Fam. Prac.*, **14**, 129.

40 Bjorn LO, 2010, Vitamin D synthesis may be independent of skin pigmentation only with UV of short wavelength, *J. Invest. Dermatol.*, **130**, 2848-50.

41 Black AT, Gordon MK, Heck DE, Gallo MA, Laskin DL, Laskin JD, 2011, UVB light regulates expression of antioxidants and inflammatory mediators in human corneal epithelial cells, *Biochem. Pharmacol.*, **81**, 873-80.

42 Bloom-Feshbach K, Alonso WJ, Charu V, Tamerius J, Simonsen L, Miller MA, Viboud C, 2013, Latitudinal variations in seasonal activity of influenza and respiratory syncytial virus (RSV): a global comparative review, *PLoS One*, **8**, e54445.

43 Bodnar LM, Catov JM, Zmuda JM, Cooper ME, Parrott MS, Roberts JM, Marazita ML, Simhan HN, 2010, Maternal serum 25-hydroxyvitamin D concentrations are associated with small-for-gestational age births in white women, *J. Nutr.*, **140**, 999-1006.

44 Bogh MK, Schmedes AV, Philipsen PA, Thieden E, Wulf HC, 2010, Vitamin D production after UVB exposure depends on baseline vitamin D and total cholesterol but not on skin pigmentation, *J. Invest. Dermatol.*, **130**, 546-53.

45 Bogh MK, Schmedes AV, Philipsen PA, Thieden E, Wulf HC, 2011, Interdependence between body surface area and ultraviolet B dose in vitamin D production: a randomized controlled trial, *Br. J. Dermatol.*, **164**, 163-9.

46 Bogh MK, Schmedes AV, Philipsen PA, Thieden E, Wulf HC, 2011, Vitamin D production depends on ultraviolet-B dose but not on dose rate: a randomized controlled trial, *Exp. Dermatol.*, **20**, 14-8.

47 Bourne R, Stevens GA, White R, Smith J, Flaxman S, Price H, Jonas JB, Keeffe J, Leasher J, Naidoo K, Pesudovs K, Resnikoff S, Taylor H, Vision Loss Expert Group, 2013, Causes of vision loss worldwide, 1990-2010: a systematic analysis, *Lancet Glob. Health*, **1**, e339-49.

48 Bouwes Bavinck JN, Feltkamp M, Struijk L, ter Schegget J, 2001, Human papillomavirus infection and skin cancer risk in organ transplant recipients, *J. Invest. Dermatol. Symp. Proc.*, **6**, 207-11.

49 Bradford PT, Anderson WF, Purdue MP, Goldstein AM, Tucker MA, 2010, Rising melanoma incidence rates of the trunk among younger women in the United States, *Cancer Epidemiol. Biomarkers. Prev.*, **19**, 2401-6.

50 Brandstedt J, Almquist M, Manjer J, Malm J, 2012, Vitamin D, PTH, and calcium and the risk of prostate cancer: a prospective nested case-control study, *Cancer Causes Control*, **23**, 1377-85.

51 Brash DE, Ziegler A, Jonason AS, Simon JA, Kunala S, Leffell DJ, 1996, Sunlight and sunburn in human skin cancer: p53, apoptosis, and tumor promotion, *J. Invest. Dermatol. Symp. Proc.*, **1**, 136-42.

52 Brondum-Jacobsen P, Nordestgaard BG, Nielsen SF, Benn M, 2013, Skin cancer as a marker of sun exposure associates with myocardial infarction, hip fracture and death from any cause, *Int. J. Epidemiol.*, **42**, 1486-96.

53 Brooks BP, Thompson AH, Bishop RJ, Clayton JA, Chan CC, Tsilou ET, Zein WM, Tamura D, Khan SG, Ueda T, Boyle J, Oh KS, Imoto K, Inui H, Moriwaki S, Emmert S, Iliff NT, Bradford P, Digiovanna JJ, Kraemer KH, 2013, Ocular Manifestations of Xeroderma Pigmentosum: Long-Term Follow-up Highlights the Role of DNA Repair in Protection from Sun Damage, *Ophthalmol.*, **120**, 1324-36.

54 Bryson KJ, Nash AA, Norval M, 2014, Does vitamin D protect against respiratory viral infections?, *Epideliol. Infect.*, **142**, 1789-801.

55 Buller DB, Cokkinides V, Hall HI, Hartman AM, Saraiya M, Miller E, Paddock L, Glanz K, 2011, Prevalence of sunburn, sun protection, and indoor tanning behaviors among Americans: review from national surveys and case studies of 3 states, *J. Am. Acad. Dermatol*, **65**, S114-23.

56 Byrne SN, 2014, How much sunlight is enough?, *Photochem. Photobiol. Sci.*, **13**, 840-52.

57 Camargo CA, Jr., Ganmaa D, Frazier AL, Kirchberg FF, Stuart JJ, Kleinman K, Sumberzul N, Rich-Edwards JW, 2012, Randomized trial of vitamin D supplementation and risk of acute respiratory infection in Mongolia, *Pediatrics*, **130**, e561-7.

58 Cancer Council Victoria, 2014, SunSmart, http://www.sunsmart.com.au, accessed 31 July, 2014.

59 Casale GR, Siani AM, Colosimo A, 2014, A UV Index Sundial on compact disk, *Household Person. Care Today*, **9**, 45-7.

60 Cashman KD, Kiely M, Kinsella M, Durazo-Arvizu RA, Tian L, Zhang Y, Lucey A, Flynn A, Gibney MJ, Vesper HW, Phinney KW, Coates PM, Picciano MF, Sempos CT, 2013, Evaluation of Vitamin D Standardization Program protocols for standardizing serum 25-hydroxyvitamin D data: a case study of the program's potential for national nutrition and health surveys, *Am. J. Clin. Nutr.*, **97**, 1235-42.

61 Cejka C, Luyckx J, Cejkova J, 2012, Central corneal thickness considered an index of corneal hydration of the UVB irradiated rabbit cornea as influenced by UVB absorber, *Physiol. Res.*, **61**, 299-306.

62 Cejkova J, Cejka C, Luyckx J, 2012, Trehalose treatment accelerates the healing of UVB-irradiated corneas. Comparative immunohistochemical studies on corneal cryostat sections and corneal impression cytology, *Histol. Histopathol.*, **27**, 1029-40.

63 Chaillol I, Boniol M, Middleton R, Dore JF, Autier P, Gavin A, 2011, Seasonality of cutaneous melanoma diagnosis in Northern Ireland with a review, *Melanoma. Res.*, **21**, 144-51.

64 Chandler H, 2011, Ultraviolet absorption by contact lenses and the significance on the ocular anterior segment, *Eye Contact Lens*, **37**, 259-66.

65 Chen AC, Damian DL, 2014, Nicotinamide and the skin, *Australasian. J. Dermatol.*, **55**, 169-175.

66 Chen L, Hu JY, Wang SQ, 2012, The role of antioxidants in photoprotection: A critical review, *J. Am. Acad. Dermatol*, **67**, 1013-24.

67 Chou WC, Takeo M, Rabbani P, Hu H, Lee W, Chung YR, Carucci J, Overbeek P, Ito M, 2013, Direct migration of follicular melanocyte stem cells to the epidermis after wounding or UVB irradiation is dependent on Mc1r signaling, *Nature Med.*, **19**, 924-9.

68 Christakos S, Hewison M, Gardner DG, Wagner CL, Sergeev IN, Rutten E, Pittas AG, Boland R, Ferrucci L, Bikle DD, 2013, Vitamin D: beyond bone, *Ann. N.Y. Acad Sci*, **1287**, 45-58.

69 Clairwood M, Ricketts J, Grant-Kels J, Gonsalves L, 2013, Melanoma in skin of color in Connecticut: an analysis of melanoma incidence and stage at diagnosis in non-Hispanic blacks, non-Hispanic whites, and Hispanics, *Int. J. Dermatol.*, **53**, 425-433.

70 Cockburn MG, Zadnick J, Deapen D, 2006, Developing epidemic of melanoma in the Hispanic population of California, *Cancer*, **106**, 1162-8.

71 Couteau C, Chauvet C, Paparis E, Coiffard L, 2012, UV filters, ingredients with a recognized anti-inflammatory effect, *PLoS One*, **7**, e46187.

72 Crispin MK, Fuentes-Duculan J, Gulati N, Johnson-Huang LM, Lentini T, Sullivan-Whalen M, Gilleaudeau P, Cueto I, Suarez-Farinas M, Lowes MA, Krueger JG, 2013, Gene profiling of narrowband UVB-induced skin injury defines cellular and molecular innate immune responses, *J. Invest. Dermatol.*, **133**, 692-701.

73 Crump C, Sundquist K, Sieh W, Winkleby MA, Sundquist J, 2014, Season of birth and other perinatal risk factors for melanoma, *Int. J. Epidemiol.*, **43**, 793-801.

74 Cullen AP, 2002, Photokeratitis and other phototoxic effects on the cornea and conjunctiva, *Int. J. Toxicol.*, **21**, 455-64.

75 Cust AE, Jenkins MA, Goumas C, Armstrong BK, Schmid H, Aitken JF, Giles GG, Kefford RF, Hopper JL, Mann GJ, 2011, Early-life sun exposure and risk of melanoma before age 40 years, *Cancer Causes Control*, **22**, 885-97.

76 Damian DL, Kim YJ, Dixon KM, Halliday GM, Javeri A, Mason RS, 2010, Topical calcitriol protects from UV-induced genetic damage but suppresses cutaneous immunity in humans, *Exp. Dermatol.*, **19**, e23-30.

77 Damian DL, Matthews YJ, Phan TA, Halliday GM, 2011, An action spectrum for ultraviolet radiation-induced immunosuppression in humans, *Br. J. Dermatol.*, **164**, 657-9.

78 David CV, 2013, Oculocutaneous albinism, *Cutis*, **91**, E1-4.

79 de Paula Correa M, Godin-Beekmann S, Haeffelin M, Bekki S, Saiag P, Badosa J, Jegou F, Pazmino A, Mahe E, 2013, Projected changes in clear-sky erythemal and vitamin D effective UV doses for Europe over the period 2006 to 2100, *Photochem. Photobiol. Sci.*, **12**, 1053-64.

80 de Paula Correa M, Pires LC, 2013, Doses of erythemal ultraviolet radiation observed in Brazil, *Int. J. Dermatol.*, **52**, 966-73.

81 DeBoyes T, Kouba D, Ozog D, Fincher E, Moy L, Iwata K, Moy R, 2010, Reduced number of actinic keratoses with topical application of DNA repair enzyme creams, *J. Drugs Dermatol.*, **9**, 1519-21.

82 Demetriou SK, Ona-Vu K, Sullivan EM, Dong TK, Hsu SW, Oh DH, 2012, Defective DNA repair and cell cycle arrest in cells expressing Merkel cell polyomavirus T antigen, *Int. J. Cancer*, **131**, 1818-27.

83 Dessinioti C, Antoniou C, Katsambas A, Stratigos AJ, 2010, Basal cell carcinoma: what's new under the sun, *Photochem. Photobiol.*, **86**, 481-91.

84 Di Girolamo N, 2012, Association of human papilloma virus with pterygia and ocular-surface squamous neoplasia, *Eye*, **26**, 202-11.

85 Diaz A, Neale RE, Kimlin MG, Jones L, Janda M, 2012, The children and sunscreen study: a crossover trial investigating children's sunscreen application thickness and the influence of age and dispenser type, *Arch. Dermatol.*, **148**, 606-12.

86 Diffey B, 2008, A behavioral model for estimating population exposure to solar ultraviolet radiation, *Photochem. Photobiol.*, **84**, 371-5.

87 Diffey BL, Brown MW, 2012, The ideal spectral profile of topical sunscreens, *Photochem. Photobiol.*, **88**, 744-7.

88 DiGiovanna JJ, Kraemer KH, 2012, Shining a light on xeroderma pigmentosum, *J. Invest. Dermatol.*, **132**, 785-96.

89 Dobbinson S, Wakefield M, Hill D, Girgis A, Aitken JF, Beckmann K, Reeder AI, Herd N, Spittal MJ, Fairthorne A, Bowles KA, 2012, Children's sun exposure and sun protection: Prevalence in Australia and related parental factors, *J. Am. Acad. Dermatol*, **66**, 938-47.

90 Doutch JJ, Quantock AJ, Joyce NC, Meek KM, 2012, Ultraviolet light transmission through the human corneal stroma is reduced in the periphery, *Biophys. J*, **102**, 1258-64.

91 Dror Y, Giveon SM, Hoshen M, Feldhamer I, Balicer RD, Feldman BS, 2013, Vitamin D levels for preventing acute coronary syndrome and mortality: evidence of a nonlinear association, *J. Clin. Endocrinol. Metab.*, **98**, 2160-7.

92 Dunstone K, Conway C, 2014, There is an app for that! Communicating UV via the SunSmart app, in *UV radiation and its effects: an update 2014*, National Institute for Water and Atmosphere, Auckland, NZ.

93 Durinck S, Ho C, Wang NJ, Liao W, Jakkula LR, Collisson EA, Pons J, Chan SW, Lam ET, Chu C, Park K, Hong SW, Hur JS, Huh N, Neuhaus IM, Yu SS, Grekin RC, Mauro TM, Cleaver JE, Kwok PY, LeBoit PE, Getz G, Cibulskis K, Aster JC, Huang H, Purdom E, Li J, Bolund L, Arron ST, Gray JW, Spellman PT, Cho RJ, 2011, Temporal dissection of tumorigenesis in primary cancers, *Cancer Discov.*, **1**, 137-43.

94 Durup D, Jorgensen HL, Christensen J, Schwarz P, Heegaard AM, Lind B, 2012, A reverse J-shaped association of all-cause mortality with serum 25-hydroxyvitamin D in general practice, the CopD Study, *J. Clin. Endocrinol. Metab.*, **97**, 2644-52.

95 Duschek N, Skvara H, Kittler H, Delir G, Fink A, Pinkowicz A, Waldhor T, 2013, Melanoma epidemiology of Austria reveals gender-related differences, *Eur. J. Dermatol.*, **23**, 872-8.

96 Dusza SW, Halpern AC, Satagopan JM, Oliveria SA, Weinstock MA, Scope A, Berwick M, Geller AC, 2012, Prospective study of sunburn and sun behavior patterns during adolescence, *Pediatrics*, **129**, 309-17.

97 Eggermont AM, Spatz A, Robert C, 2013, Cutaneous melanoma, *Lancet*, **383**, 816-27.

98 Emmanuel B, Ruder E, Lin SW, Abnet C, Hollenbeck A, Mbulaiteye S, 2012, Incidence of squamous-cell carcinoma of the conjunctiva and other eye cancers in the NIH-AARP Diet and Health Study, *Ecancermedicalscience*, **6**, 254.

99 Ensrud KE, Ewing SK, Fredman L, Hochberg MC, Cauley JA, Hillier TA, Cummings SR, Yaffe K, Cawthon PM, 2010, Circulating 25-hydroxyvitamin D levels and frailty status in older women, *J. Clin. Endocrinol. Metab.*, **95**, 5266-73.

100 EPA, 2014, UV Alert, United States Environmental Protection Agency, http://www2.epa.gov/sunwise/uv-alert, accessed 11 May, 2014.

101 Epe B, 2012, DNA damage spectra induced by photosensitization, *Photochem. Photobiol. Sci.*, **11**, 98-106.

102 Epstein EH, 2008, Basal cell carcinomas: attack of the hedgehog, *Nature REv. Cancer*, **8**, 743-54.

103 Erdag G, Schaefer JT, Smolkin ME, Deacon DH, Shea SM, Dengel LT, Patterson JW, Slingluff CL, Jr., 2012, Immunotype and immunohistologic characteristics of tumor-infiltrating immune cells are associated with clinical outcome in metastatic melanoma, *Cancer. Res.*, **72**, 1070-80.

104 Erdmann F, Lortet-Tieulent J, Schuz J, Zeeb H, Greinert R, Breitbart EW, Bray F, 2013, International trends in the incidence of malignant melanoma 1953-2008--are recent generations at higher or lower risk?, *Int. J. Cancer*, **132**, 385-400.

105 Ergul S, Ozeren E, 2011, Sun protection behavior and individual risk factors of Turkish Primary School Students associated with skin cancer: a questionnaire-based study, *Asian Pac. J. Cancer Prev.*, **12**, 765-70.

106 Esposito S, Baggi E, Bianchini S, Marchisio P, Principi N, 2013, Role of vitamin D in children with respiratory tract infection, *Int. J. Immunopathol. Pharmacol.*, **26**, 1-13.

107 Farrar MD, Webb AR, Kift R, Durkin MT, Allan D, Herbert A, Berry JL, Rhodes LE, 2013, Efficacy of a dose range of simulated sunlight exposures in raising vitamin D status in South Asian adults: implications for targeted guidance on sun exposure, *Am. J. Clin. Nutr.*, **97**, 1210-6.

108 Farzan SF, Waterboer T, Gui J, Nelson HH, Li Z, Michael KM, Perry AE, Spencer SK, Demidenko E, Green AC, Pawlita M, Karagas MR, 2013, Cutaneous alpha, beta and gamma human papillomaviruses in relation to squamous cell carcinoma of the skin: a population-based study, *Int. J. Cancer*, **133**, 1713-20.

109 Faurschou A, Beyer DM, Schmedes A, Bogh MK, Philipsen PA, Wulf HC, 2012, The relation between sunscreen layer thickness and vitamin D production after ultraviolet B exposure: a randomized clinical trial, *Br. J. Dermatol.*, **167**, 391-5.

110 Ferlay J, Bray F, Pisani P, Parkin D, 2001, GLOBOCAN 2000: Cancer Incidence, Mortality and Prevalence Worldwide, International Agency for Research on Cancer Report No. CancerBase No. 5, Lyon

111 Flohil SC, Proby CM, Forrest AD, van Tiel S, Saksela O, Pitkanen S, Ahti T, Micallef R, de Vries E, 2012, Basal cell carcinomas without histological confirmation and their treatment: an audit in four European regions, *Br. J. Dermatol.*, **167 Suppl 2**, 22-8.

112 Flohil SC, Seubring I, van Rossum MM, Coebergh JW, de Vries E, Nijsten T, 2013, Trends in Basal cell carcinoma incidence rates: a 37-year Dutch observational study, *J. Invest. Dermatol.*, **133**, 913-8.

113 Fourtanier A, Moyal D, Seite S, 2012, UVA filters in sun-protection products: regulatory and biological aspects, *Photochem. Photobiol. Sci.*, **11**, 81-9.

114 Franceschi S, Levi F, Randimbison L, La Vecchia C, 1996, Site distribution of different types of skin cancer: new aetiological clues, *Int. J. Cancer*, **67**, 24-8.

115 Franco-Lie I, Iversen T, Robsahm TE, Abdelnoor M, 2011, Incidence trends of melanoma of the skin compared with other localisations, in the Norwegian population, 1956-2005, *Ann. Oncol.*, **22**, 1443-50.

116 Frangos JE, Duncan LM, Piris A, Nazarian RM, Mihm MC, Jr., Hoang MP, Gleason B, Flotte TJ, Byers HR, Barnhill RL, Kimball AB, 2012, Increased diagnosis of thin superficial spreading melanomas: A 20-year study, *J. Am. Acad. Dermatol*, **67**, 387-94.

117 Freedman DM, Looker AC, Abnet CC, Linet MS, Graubard BI, 2010, Serum 25-hydroxyvitamin D and cancer mortality in the NHANES III study (1988-2006), *Cancer. Res.*, **70**, 8587-97.

118 Fuglede NB, Brinck-Claussen UO, Deltour I, Boesen EH, Dalton SO, Johansen C, 2011, Incidence of cutaneous malignant melanoma in Denmark, 1978-2007, *Br. J. Dermatol.*, **165**, 349-53.

119 Galan I, Rodriguez-Laso A, Diez-Ganan L, Camara E, 2011, Prevalence and correlates of skin cancer risk behaviors in Madrid (Spain), *Gac. Sanit.*, **25**, 44-9.

120 Galkin ON, Terenetskaya IP, 1999, 'Vitamin D' biodosimeter: basic characteristics and potential applications, *J. Photochem. Photobiol. B.*, **53**, 12-9.

121 Gambichler T, Terras S, Kampilafkos P, Kreuter A, Skrygan M, 2013, T regulatory cells and related immunoregulatory factors in polymorphic light eruption following ultraviolet A1 challenge, *Br. J. Dermatol.*, **169**, 1288-94.

122 Ganmaa D, Giovannucci E, Bloom BR, Fawzi W, Burr W, Batbaatar D, Sumberzul N, Holick MF, Willett WC, 2012, Vitamin D, tuberculin skin test conversion, and latent tuberculosis in Mongolian school-age children: a randomized, double-blind, placebo-controlled feasibility trial, *Am. J. Clin. Nutr.*, **96**, 391-6.

123 Gao N, Hu LW, Gao Q, Ge TT, Wang F, Chu C, Yang H, Liu Y, 2012, Diurnal variation of ocular exposure to solar ultraviolet radiation based on data from a manikin head, *Photochem. Photobiol.*, **88**, 736-43.

124 Gatenby P, Lucas R, Swaminathan A, 2013, Vitamin D deficiency and risk for rheumatic diseases: an update, *Curr. Opin. Rheumatol.*, **25**, 184-91.

125 Geller AC, Clapp RW, Sober AJ, Gonsalves L, Mueller L, Christiansen CL, Shaikh W, Miller DR, 2013, Melanoma epidemic: an analysis of six decades of data from the Connecticut Tumor Registry, *J. Clin. Oncol.*, **31**, 4172-8.

126 Gendron SP, Bastien N, Mallet JD, Rochette PJ, 2013, The 3895-bp mitochondrial DNA deletion in the human eye: a potential involvement in corneal ageing and macular degeneration, *Mutagenesis*, **28**, 197-204.

127 Gibbs NK, Norval M, 2013, Photoimmunosuppression: a brief overview, *Photodermatol. Photoimmunol. Photomed.*, **29**, 57-64.

128 Ginde AA, Mansbach JM, Camargo CA, Jr., 2009, Association between serum 25-hydroxyvitamin D level and upper respiratory tract infection in the Third National Health and Nutrition Examination Survey, *Arch. Intern. Med.*, **169**, 384-90.

129 Girschik J, Thorn K, Beer TW, Heenan PJ, Fritschi L, 2011, Merkel cell carcinoma in Western Australia: a population-based study of incidence and survival, *Br. J. Dermatol.*, **165**, 1051-7.

130 Glaser R, Navid F, Schuller W, Jantschitsch C, Harder J, Schroder JM, Schwarz A, Schwarz T, 2009, UV-B radiation induces the expression of antimicrobial peptides in human keratinocytes in vitro and in vivo, *Invest. Ophthalmol. Vis. Sci.*, **123**, 1117-23.

131 Gloster HM, Jr., Neal K, 2006, Skin cancer in skin of color, *J. Am. Acad. Dermatol*, **55**, 741-60; quiz 761-4.

132 Golu T, Mogoanta L, Streba CT, Pirici DN, Malaescu D, Mateescu GO, Mutiu G, 2011, Pterygium: histological and immunohistochemical aspects, *Rom. J. Morphol. Embryol.*, **52**, 153-8.

133 Gordon-Thomson C, Gupta R, Tongkao-on W, Ryan A, Halliday GM, Mason RS, 2012, 1alpha,25 dihydroxyvitamin D3 enhances cellular defences against UV-induced oxidative and other forms of DNA damage in skin, *Photochem. Photobiol. Sci.*, **11**, 1837-47.

134 Green AC, Williams GM, Logan V, Strutton GM, 2011, Reduced melanoma after regular sunscreen use: randomized trial follow-up, *J. Clin. Oncol.*, **29**, 257-63.
135 Gronskov K, Ek J, Brondum-Nielsen K, 2007, Oculocutaneous albinism, *Orphanet J. Rare. Dis.*, **2**, 43.
136 Gruber-Wackernagel A, Byrne SN, Wolf P, 2014, Polymorphous light eruption: clinic aspects and pathogenesis, *Dermatol. Clin.*, **32**, 315-34, viii.
137 Guggenheim JA, Northstone K, McMahon G, Ness AR, Deere K, Mattocks C, Pourcain BS, Williams C, 2012, Time outdoors and physical activity as predictors of incident myopia in childhood: a prospective cohort study, *Invest. Ophthalmol. Vis. Sci.*, **53**, 2856-65.
138 Guinot C, Cheffai S, Latreille J, Dhaoui MA, Youssef S, Jaber K, Nageotte O, Doss N, 2010, Aggravating factors for melasma: a prospective study in 197 Tunisian patients, *J. Eur. Acad. Dermatol. Venereol.*, **24**, 1060-9.
139 Gulson B, McCall M, Korsch M, Gomez L, Casey P, Oytam Y, Taylor A, McCulloch M, Trotter J, Kinsley L, Greenoak G, 2010, Small amounts of zinc from zinc oxide particles in sunscreens applied outdoors are absorbed through human skin, *Toxicol. Sci.*, **118**, 140-9.
140 Guo Y, Liu LJ, Xu L, Lv YY, Tang P, Feng Y, Meng M, Jonas JB, 2013, Outdoor activity and myopia among primary students in rural and urban regions of Beijing, *Ophthalmol.*, **120**, 277-83.
141 Guo Y, Liu LJ, Xu L, Tang P, Lv YY, Feng Y, Meng M, Jonas JB, 2013, Myopic Shift and Outdoor Activity among Primary School Children: One-Year Follow-Up Study in Beijing, *PLoS One*, **8**, e75260.
142 Halder RM, Bridgeman-Shah S, 1995, Skin cancer in African Americans, *Cancer*, **75**, 667-73.
143 Handel AC, Lima PB, Tonolli VM, Miot LD, Miot HA, 2014, Risk factors for facial melasma in women: a case-control study, *Br. J. Dermatol.*, **171**, 588-94.
144 Handoko HY, Rodero MP, Boyle GM, Ferguson B, Engwerda C, Hill G, Muller HK, Khosrotehrani K, Walker GJ, 2013, UVB-induced melanocyte proliferation in neonatal mice driven by CCR2-independent recruitment of Ly6c(low)MHCII(hi) macrophages, *J. Invest. Dermatol.*, **133**, 1803-12.
145 Harrison S, Nowak M, Devine S, Saunders V, Smith A, Buettner P, 2013, An intervention to discourage Australian mothers from unnecessarily exposing their babies to the sun for therapeutic reasons, *J. Trop. Pediat.*, **59**, 403-6.
146 Harrison SL, Buettner PG, MacLennan R, 1999, Why do mothers still sun their infants?, *J. Pediatr. Child Health*, **35**, 296-9.
147 Hart PH, Gorman S, Finlay-Jones JJ, 2011, Modulation of the immune system by UV radiation: more than just the effects of vitamin D?, *Nature Rev. Immunol.*, **11**, 584-96.
148 Hart PH, Gorman S, 2013, Exposure to UV Wavelengths in Sunlight Suppresses Immunity. To What Extent is UV-induced Vitamin D3 the Mediator Responsible?, *Clin. Biochem. Rev.*, **34**, 3-13.
149 Hatun S, Islam O, Cizmecioglu F, Kara B, Babaoglu K, Berk F, Gokalp AS, 2005, Subclinical vitamin D deficiency is increased in adolescent girls who wear concealing clothing, *J. Nutr.*, **135**, 218-22.
150 Haylett AK, Nie Z, Brownrigg M, Taylor R, Rhodes LE, 2011, Systemic photoprotection in solar urticaria with alpha-melanocyte-stimulating hormone analogue [Nle4-D-Phe7]-alpha-MSH, *Br. J. Dermatol.*, **164**, 407-14.
151 Heckman CJ, Cohen-Filipic J, 2012, Brief Report: Ultraviolet Radiation Exposure, Considering Acculturation Among Hispanics (Project URECAH), *J. Cancer Educ.*, **27**, 342-6.
152 Heinrich U, Moore CE, De Spirt S, Tronnier H, Stahl W, 2011, Green tea polyphenols provide photoprotection, increase microcirculation, and modulate skin properties of women, *J. Nutr.*, **141**, 1202-8.
153 Hernan MA, Olek MJ, Ascherio A, 1999, Geographic variation of MS incidence in two prospective studies of US women, *Neurology*, **53**, 1711-8.
154 Hernandez-Barrera R, Torres-Alvarez B, Castanedo-Cazares JP, Oros-Ovalle C, Moncada B, 2008, Solar elastosis and presence of mast cells as key features in the pathogenesis of melasma, *Clin. Exp. Dermatol.*, **33**, 305-8.
155 Hewer S, Lucas R, van der Mei I, Taylor BV, 2013, Vitamin D and multiple sclerosis, *J. Clin. Neurosci.*, **20**, 634-41.
156 Hewison M, 2012, Vitamin D and immune function: An overview, *Proc. Nutrit. Soc.*, **71**, 50-61.
157 Hilger J, Friedel A, Herr R, Rausch T, Roos F, Wahl DA, Pierroz DD, Weber P, Hoffmann K, 2014, A systematic review of vitamin D status in populations worldwide, *Br. J. Nutr.*, **111**, 23-45.
158 Hill VK, Gartner JJ, Samuels Y, Goldstein AM, 2013, The genetics of melanoma: recent advances, *Annu. Rev. Genomics Hum. Genet.*, **14**, 257-79.
159 Hiramoto K, Yamate Y, Kobayashi H, Ishii M, 2012, Long-term ultraviolet A irradiation of the eye induces photoaging of the skin in mice, *Arch. Dermatol. Res.*, **304**, 39-45.

160 Hiramoto K, Yamate Y, Kobayashi H, Ishii M, Sato EF, Inoue M, 2013, Ultraviolet B irradiation of the mouse eye induces pigmentation of the skin more strongly than does stress loading, by increasing the levels of prohormone convertase 2 and alpha-melanocyte-stimulating hormone, *Clin. Exp. Dermatol.*, **38**, 71-6.

161 Hirani V, 2013, Associations between vitamin D and self-reported respiratory disease in older people from a nationally representative population survey, *J. Am. Geriat. Soc.*, **61**, 969-73.

162 Hodgson NC, 2005, Merkel cell carcinoma: changing incidence trends, *J. Surg. Oncol.*, **89**, 1-4.

163 Hodis E, Watson IR, Kryukov GV, Arold ST, Imielinski M, Theurillat JP, Nickerson E, Auclair D, Li L, Place C, Dicara D, Ramos AH, Lawrence MS, Cibulskis K, Sivachenko A, Voet D, Saksena G, Stransky N, Onofrio RC, Winckler W, Ardlie K, Wagle N, Wargo J, Chong K, Morton DL, Stemke-Hale K, Chen G, Noble M, Meyerson M, Ladbury JE, Davies MA, Gershenwald JE, Wagner SN, Hoon DS, Schadendorf D, Lander ES, Gabriel SB, Getz G, Garraway LA, Chin L, 2012, A landscape of driver mutations in melanoma, *Cell*, **150**, 251-63.

164 Hofer A, Legat FJ, Gruber-Wackernagel A, Quehenberger F, Wolf P, 2011, Topical liposomal DNA-repair enzymes in polymorphic light eruption, *Photochem. Photobiol. Sci.*, **10**, 1118-28.

165 Holick MF, Binkley NC, Bischoff-Ferrari HA, Gordon CM, Hanley DA, Heaney RP, Murad MH, Weaver CM, 2011, Evaluation, Treatment, and Prevention of Vitamin D Deficiency: an Endocrine Society Clinical Practice Guideline, *J. Clin. Endocrinol. Metab.*, **96**, 1911-1930.

166 Hollis BW, 2005, Circulating 25-hydroxyvitamin D levels indicative of vitamin D sufficiency: implications for establishing a new effective dietary intake recommendation for vitamin D, *J. Nutr.*, **135**, 317-22.

167 Hong ES, Zeeb H, Repacholi MH, 2006, Albinism in Africa as a public health issue, *BMC Public Health*, **6**, 212.

168 Hoyos-Bachiloglu R, Morales PS, Cerda J, Talesnik E, Gonzalez G, Camargo CA, Jr., Borzutzky A, 2014, Higher latitude and lower solar radiation influence on anaphylaxis in Chilean children, *Pediatr. Allergy Immu.*, **25**, 338-43.

169 Hu L, Gao Q, Gao N, Liu G, Wang Y, Gong H, Liu Y, 2013, Solar UV exposure at eye is different from environmental UV: diurnal monitoring at different rotation angles using a manikin, *J. Occup. Environ. Hyg.*, **10**, 17-25.

170 Hughes AM, Lucas RM, Ponsonby AL, Chapman C, Coulthard A, Dear K, Dwyer T, Kilpatrick TJ, McMichael AJ, Pender MP, Taylor BV, Valery P, van der Mei IA, Williams D, 2011, The role of latitude, ultraviolet radiation exposure and vitamin D in childhood asthma and hayfever: an Australian multicenter study, *Pediatr. Allergy Immu.*, **22**, 327-33.

171 Hughes MC, Williams GM, Baker P, Green AC, 2013, Sunscreen and prevention of skin aging: a randomized trial, *Ann. Intern. Med.*, **158**, 781-90.

172 Hughes MP, Hardee ME, Cornelius LA, Hutchins LF, Becker JC, Gao L, 2014, Merkel Cell Carcinoma: Epidemiology, Target, and Therapy, *Curr. Dermatol. Rep.*, **3**, 46-53.

173 Iannacone MR, Wang W, Stockwell HG, O'Rourke K, Giuliano AR, Sondak VK, Messina JL, Roetzheim RG, Cherpelis BS, Fenske NA, Rollison DE, 2012, Patterns and timing of sunlight exposure and risk of basal cell and squamous cell carcinomas of the skin--a case-control study, *BMC Cancer*, **12**, 417.

174 IARC, 2014, Globocan 2012. Estimated cancer incidence, mortality and prevalence worldwide in 2012, International Agency for Research on Cancer, http://globocan.iarc.fr/Pages/summary_table_site_sel.aspx, accessed 28 June 2014,

175 Ibuki Y, Allanson M, Dixon KM, Reeve VE, 2007, Radiation sources providing increased UVA/UVB ratios attenuate the apoptotic effects of the UVB waveband UVA-dose-dependently in hairless mouse skin, *J. Invest. Dermatol.*, **127**, 2236-44.

176 Institute of Medicine, 2010, Dietary Reference Intakes for Calcium and Vitamin D, Institute of Medicine of the National Academies Report No. http://www.iom.edu/Reports/2010/Dietary-Reference-Intakes-for-Calcium-and-Vitamin-D.aspx

177 Ishikawa Y, Hashizume K, Kishimoto S, Tezuka Y, Nishigori H, Yamamoto N, Kondo Y, Maruyama N, Ishigami A, Kurosaka D, 2012, Effect of vitamin C depletion on UVR-B induced cataract in SMP30/GNL knockout mice, *Exp. Eye Res.*, **94**, 85-9.

178 Jansen R, Osterwalder U, Wang SQ, Burnett M, Lim HW, 2013, Photoprotection: Part II. Sunscreen: Development, efficacy, and controversies, *J. Am. Acad. Dermatol*, **69**, 867 e1-867 e14.

179 Jansen R, Wang SQ, Burnett M, Osterwalder U, Lim HW, 2013, Photoprotection: Part I. Photoprotection by naturally occurring, physical, and systemic agents, *J. Am. Acad. Dermatol*, **69**, 853 e1-853 e12.

180 Jatana S, Delouise LA, 2014, Understanding engineered nanomaterial skin interactions and the modulatory effects of ultraviolet radiation skin exposure, *Wiley Interdisciplinary Reviews: Nanomedicine and NanobiotechnologyS*, **6**, 61-79.

181 Jayaraman SS, Rayhan DJ, Hazany S, Kolodney MS, 2014, Mutational landscape of basal cell carcinomas by whole-exome sequencing, *J. Invest. Dermatol.*, **134**, 213-20.

182 Jobanputra R, Bachmann M, 2000, The effect of skin diseases on quality of life in patients from different social and ethnic groups in Cape Town, South Africa, *Int. J. Cancer*, **39**, 826-31.

183 Kanavy HE, Gerstenblith MR, 2011, Ultraviolet radiation and melanoma, *Semin. Cutan. Med. Surg.*, **30**, 222-8.

184 Katalinic A, Waldmann A, Weinstock MA, Geller AC, Eisemann N, Greinert R, Volkmer B, Breitbart E, 2012, Does skin cancer screening save lives?: an observational study comparing trends in melanoma mortality in regions with and without screening, *Cancer*, **118**, 5395-402.

185 Khalesi M, Whiteman DC, Doi SA, Clark J, Kimlin MG, Neale RE, 2013, Cutaneous markers of photo-damage and risk of Basal cell carcinoma of the skin: a meta-analysis, *Cancer Epidemiol. Biomarkers. Prev.*, **22**, 1483-9.

186 Kift R, Berry JL, Vail A, Durkin MT, Rhodes LE, Webb AR, 2013, Lifestyle factors including less cutaneous sun exposure contribute to starkly lower vitamin D status in UK South Asians compared to the white Caucasian population, *Br. J. Dermatol.*, **169**, 1272-8.

187 Kim EJ, Kim YK, Kim JE, Kim S, Kim MK, Park CH, Chung JH, 2011, UV modulation of subcutaneous fat metabolism, *J. Invest. Dermatol.*, **131**, 1720-6.

188 Kimlin MG, Lucas RM, Harrison SL, van der Mei I, Armstrong BK, Whiteman DC, Kricker A, Nowak M, Brodie AM, Sun J, 2014, The contributions of solar ultraviolet radiation exposure and other determinants to serum 25-hydroxyvitamin D concentrations in Australian adults: The AusD Study, *Am. J. Epidemiol.*, **179**, 864-74.

189 Kiprono SK, Chaula BM, Beltraminelli H, 2014, Histological review of skin cancers in African Albinos: a 10-year retrospective review, *BMC Cancer*, **14**, 157.

190 Klein BE, Lee KE, Danforth LG, Schaich TM, Cruickshanks KJ, Klein R, 2010, Selected sun-sensitizing medications and incident cataract, *Arch. Ophthalmol.*, **128**, 959-63.

191 Koo BB, 2012, Restless legs syndrome: Relationship between prevalence and latitude, *Sleep Breath.*, **16**, 1237-45.

192 Koster B, Thorgaard C, Philip A, Clemmensen IH, 2011, Vacations to sunny destinations, sunburn, and intention to tan: a cross-sectional study in Denmark, 2007-2009, *Scand. J. Public Health*, **39**, 64-9.

193 Krauthammer M, Kong Y, Ha BH, Evans P, Bacchiocchi A, McCusker JP, Cheng E, Davis MJ, Goh G, Choi M, Ariyan S, Narayan D, Dutton-Regester K, Capatana A, Holman EC, Bosenberg M, Sznol M, Kluger HM, Brash DE, Stern DF, Materin MA, Lo RS, Mane S, Ma S, Kidd KK, Hayward NK, Lifton RP, Schlessinger J, Boggon TJ, Halaban R, 2012, Exome sequencing identifies recurrent somatic RAC1 mutations in melanoma, *Nature Genet.*, **44**, 1006-14.

194 Kricker A, Armstrong BK, English DR, Heenan PJ, 1991, Pigmentary and cutaneous risk factors for non-melanocytic skin cancer--a case-control study, *Int. J. Cancer*, **48**, 650-62.

195 Kromberg JG, Jenkins T, 1982, Prevalence of albinism in the South African negro, *S. Afr. Med. J.*, **61**, 383-6.

196 Kronschlager M, Galichanin K, Ekstrom J, Lou MF, Soderberg PG, 2012, Protective effect of the thioltransferase gene on in vivo UVR-300 nm-induced cataract, *Invest. Ophthalmol. Vis. Sci.*, **53**, 248-52.

197 Krstic G, 2011, Asthma prevalence associated with geographical latitude and regional insolation in the United States of America and Australia, *PLoS One*, **6**, e18492.

198 Kudish AI, Harari M, Evseev EG, 2011, The solar ultraviolet B radiation protection provided by shading devices with regard to its diffuse component, *Photodermatol. Photoimmunol. Photomed.*, **27**, 236-44.

199 Kunisue T, Chen Z, Buck Louis GM, Sundaram R, Hediger ML, Sun L, Kannan K, 2012, Urinary concentrations of benzophenone-type UV filters in U.S. women and their association with endometriosis, *Environ. Sci. Technol.*, **46**, 4624-32.

200 Laaksi I, Ruohola JP, Mattila V, Auvinen A, Ylikomi T, Pihlajamaki H, 2010, Vitamin D supplementation for the prevention of acute respiratory tract infection: a randomized, double-blinded trial among young Finnish men, *J. Infect. Dis.*, **202**, 809-14.

201 Laishram R, Banerjee A, Punyabati P, Chandra L, Sharma A, 2010, Pattern of skin malignancies in Manipur, India: A 5-year histopathological review, *J. Pak. Assoc. Dermatol.*, **20**, 128-132.

202 Lan W, Petznick A, Heryati S, Rifada M, Tong L, 2012, Nuclear Factor-kappaB: central regulator in ocular surface inflammation and diseases, *Ocul. Surf.*, **10**, 137-48.

203 Landers J, Henderson T, Craig J, 2011, Prevalence of pterygium in indigenous Australians within central Australia: the Central Australian Ocular Health Study, *Clin. Experiment. Ophthalmol.*, **39**, 604-6.

204 Langan EA, Nie Z, Rhodes LE, 2010, Melanotropic peptides: more than just 'Barbie drugs' and 'sun-tan jabs'?, *Br. J. Dermatol.*, **163**, 451-5.

205 Le Marchand L, Saltzman BS, Hankin JH, Wilkens LR, Franke AA, Morris SJ, Kolonel LN, 2006, Sun exposure, diet, and melanoma in Hawaii Caucasians, *Am. J. Epidemiol.*, **164**, 232-45.

206 Lemus-Deschamps L, Makin JK, 2012, Fifty years of changes in UV Index and implications for skin cancer in Australia, *Int. J. Biometeorol.*, **56**, 727-35.

207 Levine H, Afek A, Shamiss A, Derazne E, Tzur D, Astman N, Keinan-Boker L, Mimouni D, Kark JD, 2013, Country of origin, age at migration and risk of cutaneous melanoma: a migrant cohort study of 1,100,000 Israeli men, *Int. J. Cancer*, **133**, 486-94.

208 Li-Ng M, Aloia JF, Pollack S, Cunha BA, Mikhail M, Yeh J, Berbari N, 2009, A randomized controlled trial of vitamin D3 supplementation for the prevention of symptomatic upper respiratory tract infections, *Epideliol. Infect.*, **137**, 1396-404.

209 Li J, Uter W, Pfahlberg A, Gefeller O, 2012, A comparison of patterns of sun protection during beach holidays and everyday outdoor activities in a population sample of young German children, *Br. J. Dermatol.*, **166**, 803-10.

210 Libon F, Cavalier E, Nikkels AF, 2013, Skin color is relevant to vitamin D synthesis, *Dermatol.*, **227**, 250-4.

211 Lin SW, Wheeler DC, Park Y, Cahoon EK, Hollenbeck AR, Freedman DM, Abnet CC, 2012, Prospective study of ultraviolet radiation exposure and risk of cancer in the United States, *Int. J. Cancer*, **131**, E1015-23.

212 Linos E, Keiser E, Fu T, Colditz G, Chen S, Tang JY, 2011, Hat, shade, long sleeves, or sunscreen? Rethinking US sun protection messages based on their relative effectiveness, *Cancer Causes Control*, **22**, 1067-71.

213 Linos E, Keiser E, Kanzler M, Sainani KL, Lee W, Vittinghoff E, Chren MM, Tang JY, 2012, Sun protective behaviors and vitamin D levels in the US population: NHANES 2003-2006, *Cancer Causes Control*, **23**, 133-40.

214 Liu D, Fernandez BO, Hamilton A, Lang NN, Gallagher JM, Newby DE, Feelisch M, Weller RB, 2014, UVA irradiation of human skin vasodilates arterial vasculature and lowers blood pressure independently of nitric oxide synthase, *J. Invest. Dermatol.*, **134**, 1839-46.

215 Lofgren S, Michael R, Soderberg PG, 2012, Impact of iris pigment and pupil size in ultraviolet radiation cataract in rat, *Acta Ophthalmol.*, **90**, 44-8.

216 Lomas A, Leonardi-Bee J, Bath-Hextall F, 2012, A systematic review of worldwide incidence of nonmelanoma skin cancer, *Br. J. Dermatol.*, **166**, 1069-80.

217 Lou YR, Peng QY, Li T, Medvecky CM, Lin Y, Shih WJ, Conney AH, Shapses S, Wagner GC, Lu YP, 2011, Effects of high-fat diets rich in either omega-3 or omega-6 fatty acids on UVB-induced skin carcinogenesis in SKH-1 mice, *Carcinogenesis*, **32**, 1078-84.

218 Lowe NJ, Meyers DP, Wieder JM, Luftman D, Borget T, Lehman MD, Johnson AW, Scott IR, 1995, Low doses of repetitive ultraviolet A induce morphologic changes in human skin, *J. Invest. Dermatol.*, **105**, 739-43.

219 Luande J, Henschke CI, Mohammed N, 1985, The Tanzanian human albino skin. Natural history, *Cancer*, **55**, 1823-8.

220 Lucas R, Taylor B, 2013, Challenges in exposure and outcome definition in neuroepidemiology: the case of vitamin D and multiple sclerosis, *Australas. Epidemiol.*, **20**, 4-8.

221 Lucas RM, Ponsonby AL, Dear K, Valery PC, Pender MP, Taylor BV, Kilpatrick TJ, Dwyer T, Coulthard A, Chapman C, van der Mei I, Williams D, McMichael AJ, 2011, Sun exposure and vitamin D are independent risk factors for CNS demyelination, *Neurology*, **76**, 540-8.

222 Lucas RM, Ponsonby AL, Dear K, Valery PC, Taylor B, van der Mei I, McMichael AJ, Pender MP, Chapman C, Coulthard A, Kilpatrick TJ, Stankovich J, Williams D, Dwyer T, 2013, Vitamin D status: multifactorial contribution of environment, genes and other factors in healthy Australian adults across a latitude gradient, *J. Steriod Biochem. Mol. Biol.*, **136**, 300-8.

223 Lucas RM, Valery P, van der Mei I, Dwyer T, Pender MP, Taylor B, Ponsonby AL, Ausimmune Investigator G, 2013, Sun exposure over a lifetime in Australian adults from latitudinally diverse regions, *Photochem. Photobiol.*, **89**, 737-44.

224 Ludema C, Cole SR, Poole C, Smith JS, Schoenbach VJ, Wilhelmus KR, 2013, Association between unprotected ultraviolet radiation exposure and recurrence of ocular herpes simplex virus, *Am. J. Epidemiol.*, **179**, 208-15.

225 Mabula JB, Chalya PL, McHembe MD, Jaka H, Giiti G, Rambau P, Masalu N, Kamugisha E, Robert S, Gilyoma JM, 2012, Skin cancers among Albinos at a University teaching hospital in Northwestern Tanzania: a retrospective review of 64 cases, *BMC Dermatol* **12**, 5.

226 Major JM, Kiruthu C, Weinstein SJ, Horst RL, Snyder K, Virtamo J, Albanes D, 2012, Pre-diagnostic circulating vitamin D and risk of melanoma in men, *PLoS One*, **7**, e35112.

227 Makin J, 2011, Implications of climate change for skin cancer prevention in Australia, *Health Promo. J. Aust.*, **22 Spec No**, S39-41.

228 Mallet JD, Gendron SP, Drigeard Desgarnier MC, Rochette PJ, 2014, Implication of ultraviolet light in the etiology of uveal melanoma: a review, *Photochem. Photobiol.*, **90**, 15-21.

229 Manga P, Kerr R, Ramsay M, Kromberg JG, 2013, Biology and genetics of oculocutaneous albinism and vitiligo - common pigmentation disorders in southern Africa, *S. Afr. Med. J.*, **103**, 984-8.

230 Margrain TH, Boulton M, Marshall J, Sliney DH, 2004, Do blue light filters confer protection against age-related macular degeneration?, *Prog. Retin. Eye Res.*, **23**, 523-31.

231 Martineau AR, Timms PM, Bothamley GH, Hanifa Y, Islam K, Claxton AP, Packe GE, Moore-Gillon JC, Darmalingam M, Davidson RN, Milburn HJ, Baker LV, Barker RD, Woodward NJ, Venton TR, Barnes KE, Mullett CJ, Coussens AK, Rutterford CM, Mein CA, Davies GR, Wilkinson RJ, Nikolayevskyy V, Drobniewski FA, Eldridge SM, Griffiths CJ, 2011, High-dose vitamin D(3) during intensive-phase antimicrobial treatment of pulmonary tuberculosis: a double-blind randomised controlled trial, *Lancet*, **377**, 242-50.

232 Matthews YJ, Halliday GM, Phan TA, Damian DL, 2010, Wavelength dependency for UVA-induced suppression of recall immunity in humans, *J. Dermatol. Sci.*, **59**, 192-7.

233 McGee HM, Malley RC, Muller HK, Woods GM, 2011, Neonatal exposure to UVR alters skin immune system development, and suppresses immunity in adulthood, *Immunol. Cell. Biol.*, **89**, 767-76.

234 McGrath JJ, Eyles DW, Pedersen CB, Anderson C, Ko P, Burne TH, Norgaard-Pedersen B, Hougaard DM, Mortensen PB, 2010, Neonatal vitamin D status and risk of schizophrenia: a population-based case-control study, *Arch. Gen. Psychiatry.*, **67**, 889-94.

235 McGuigan KG, Conroy RM, Mosler HJ, du Preez M, Ubomba-Jaswa E, Fernandez-Ibanez P, 2012, Solar water disinfection (SODIS): a review from bench-top to roof-top, *J. Haz. Matter.*, **235-236**, 29-46.

236 McKenzie R, Scragg R, Liley B, Johnston P, Wishart J, Stewart A, Prematunga R, 2012, Serum 25-hydroxyvitamin-D responses to multiple UV exposures from solaria: inferences for exposure to sunlight, *Photochem. Photobiol. Sci.*, **11**, 1174-85.

237 McKenzie R, Liley B, Johnston P, Scragg R, Stewart A, Reeder AI, Allen MW, 2013, Small doses from artificial UV sources elucidate the photo-production of vitamin D, *Photochem. Photobiol. Sci.*, **12**, 1726-37.

238 McKenzie RL, Liley JB, Bjorn LO, 2009, UV radiation: balancing risks and benefits, *Photochem. Photobiol.*, **85**, 88-98.

239 Melamed ML, Michos ED, Post W, Astor B, 2008, 25-hydroxyvitamin D levels and the risk of mortality in the general population, *Arch. Intern. Med.*, **168**, 1629-37.

240 Michaelsson K, Baron JA, Snellman G, Gedeborg R, Byberg L, Sundstrom J, Berglund L, Arnlov J, Hellman P, Blomhoff R, Wolk A, Garmo H, Holmberg L, Melhus H, 2010, Plasma vitamin D and mortality in older men: a community-based prospective cohort study, *Am. J. Clin. Nutr.*, **92**, 841-8.

241 Michikawa T, Nishiwaki Y, Asakura K, Hillebrand G, Miyamoto K, Ono M, Kinjo Y, Akiba S, Takebayashi T, 2013, Sunlight Exposure May Be a Risk Factor of Hearing Impairment: A Community-Based Study in Japanese Older Men and Women, *J. Gerontol. A Biol. Sci. Med. Sci.*, **68**, 96-103.

242 Millen AE, Voland R, Sondel SA, Parekh N, Horst RL, Wallace RB, Hageman GS, Chappell R, Blodi BA, Klein ML, Gehrs KM, Sarto GE, Mares JA, 2011, Vitamin D status and early age-related macular degeneration in postmenopausal women, *Arch. Ophthalmol.*, **129**, 481-9.

243 Miller RA, Dolan D, Han M, Kohler W, Schacht J, 2011, Resistance of skin fibroblasts to peroxide and UV damage predicts hearing loss in aging mice, *Aging Cell*, **10**, 362-3.

244 Miller RW, Rabkin CS, 1999, Merkel cell carcinoma and melanoma: etiological similarities and differences, *Cancer Epidemiol. Biomarkers. Prev.*, **8**, 153-8.

245 Milliken SV, Wassall H, Lewis BJ, Logie J, Barker RN, Macdonald H, Vickers MA, Ormerod AD, 2012, Effects of ultraviolet light on human serum 25-hydroxyvitamin D and systemic immune function, *J. Allergy. Clin. Immunol.*, **129**, 1554-61.

246 Miolo G, Caffieri S, Dalzoppo D, Gallocchio F, Fasani E, Beyersbergen van Henegouwen GM, 2011, Photoactivation of corticosteroids in UVB-exposed skin, *J. Photochem. Photobiol. B.*, **103**, 35-41.

247 Mitchell DL, Fernandez AA, 2011, Different types of DNA damage play different roles in the etiology of sunlight-induced melanoma, *Pigment Cell Melanoma. Res.*, **24**, 119-24.

248 Moan J, Lagunova Z, Cicarma E, Aksnes L, Dahlback A, Grant WB, Porojnicu AC, 2009, Sunbeds as vitamin D sources, *Photochem. Photobiol.*, **85**, 1474-9.

249 Mody VC, Jr., Kakar M, Soderberg PG, Lofgren S, 2012, High lenticular tolerance to ultraviolet radiation-B by pigmented guinea-pig; application of a safety limit strategy for UVR-induced cataract, *Acta Ophthalmol.*, **90**, 226-30.

250 Mogha A, Fautrel A, Mouchet N, Guo N, Corre S, Adamski H, Watier E, Misery L, Galibert MD, 2010, Merkel cell polyomavirus small T antigen mRNA level is increased following in vivo UV-radiation, *PLoS One*, **5**, e11423.

251 Moloney FJ, Comber H, O'Lorcain P, O'Kelly P, Conlon PJ, Murphy GM, 2006, A population-based study of skin cancer incidence and prevalence in renal transplant recipients, *Br. J. Dermatol.*, **154**, 498-504.

252 Morris J, Laing-Morton T, Marno P, Curnow A, 2011, An investigation into the awareness and understanding of the ultraviolet index forecasts in the South West of England, *Photochem. Photobiol. Sci.*, **10**, 103-8.

253 Mousavi F, Golestan B, Vaseie M, Vaseie L, Khajeh-Kazemi R, 2011, Knowledge, attitude, and practice of adults to the protective actions against sun in northwest Tehran, Iran, *Arch. Iran. Med.*, **14**, 126-31.

254 Murdoch DR, Slow S, Chambers ST, Jennings LC, Stewart AW, Priest PC, Florkowski CM, Livesey JH, Camargo CA, Scragg R, 2012, Effect of vitamin D3 supplementation on upper respiratory tract infections in healthy adults: the VIDARIS randomized controlled trial, *J. Am. Med. Assoc.*, **308**, 1333-9.

255 Nair-Shalliker V, Smith DP, Egger S, Hughes AM, Kaldor JM, Clements M, Kricker A, Armstrong BK, 2012, Sun exposure may increase risk of prostate cancer in the high UV environment of New South Wales, Australia: a case-control study, *Int. J. Cancer*, **131**, E726-32.

256 Nan H, Xu M, Kraft P, Qureshi AA, Chen C, Guo Q, Hu FB, Curhan G, Amos CI, Wang LE, Lee JE, Wei Q, Hunter DJ, Han J, 2011, Genome-wide association study identifies novel alleles associated with risk of cutaneous basal cell carcinoma and squamous cell carcinoma, *Hum. Mol. Genet.*, **20**, 3718-24.

257 National Cancer Registry of South Africa, 2014, Cancer in South Africa, http://www.nioh.ac.za/?page=national_cancer_registry&id=41, accessed 29 July, 2014.

258 Navid F, Boniotto M, Walker C, Ahrens K, Proksch E, Sparwasser T, Muller W, Schwarz T, Schwarz A, 2012, Induction of regulatory T cells by a murine beta-defensin, *J. Immunol.*, **188**, 735-43.

259 Naylor EC, Watson RE, Sherratt MJ, 2011, Molecular aspects of skin ageing, *Maturitas*, **69**, 249-56.

260 Neale RE, Davis M, Pandeya N, Whiteman DC, Green AC, 2007, Basal cell carcinoma on the trunk is associated with excessive sun exposure, *J. Am. Acad. Dermatol*, **56**, 380-6.

261 Neale RE, Weissenborn S, Abeni D, Bavinck JN, Euvrard S, Feltkamp MC, Green AC, Harwood C, de Koning M, Naldi L, Nindl I, Pawlita M, Proby C, Quint WG, Waterboer T, Wieland U, Pfister H, 2013, Human papillomavirus load in eyebrow hair follicles and risk of cutaneous squamous cell carcinoma, *Cancer Epidemiol. Biomarkers. Prev.*, **22**, 719-27.

262 Nebbioso M, Plateroti AM, Pucci B, Pescosolido N, 2014, Role of the dopaminergic system in the development of myopia in children and adolescents, *J. Child Neurol.*, **epub, ahead of print**.

263 Nerich V, Jantchou P, Boutron-Ruault MC, Monnet E, Weill A, Vanbockstael V, Auleley GR, Balaire C, Dubost P, Rican S, Allemand H, Carbonnel F, 2011, Low exposure to sunlight is a risk factor for Crohn's disease, *Aliment. Pharmacol. Ther.*, **33**, 940-5.

264 Ng RL, Scott NM, Strickland DH, Gorman S, Grimbaldeston MA, Norval M, Waithman J, Hart PH, 2013, Altered immunity and dendritic cell activity in the periphery of mice after long-term engraftment with bone marrow from ultraviolet-irradiated mice, *J. Immunol.*, **190**, 5471-84.

265 Nielsen NO, Skifte T, Andersson M, Wohlfahrt J, Soborg B, Koch A, Melbye M, Ladefoged K, 2010, Both high and low serum vitamin D concentrations are associated with tuberculosis: a case-control study in Greenland, *Br. J. Nutr.*, **104**, 1487-91.

266 Nikolaou V, Stratigos AJ, 2014, Emerging trends in the epidemiology of melanoma, *Br. J. Dermatol.*, **170**, 11-9.

267 Noonan FP, Zaidi MR, Wolnicka-Glubisz A, Anver MR, Bahn J, Wielgus A, Cadet J, Douki T, Mouret S, Tucker MA, Popratiloff A, Merlino G, De Fabo EC, 2012, Melanoma induction by ultraviolet A but not ultraviolet B radiation requires melanin pigment, *Nature Commun.*, **3**, 884.

268 Norval M, Garssen J, Van Loveren H, el-Ghorr AA, 1999, UV-induced changes in the immune response to microbial infections in human subjects and animal models, *J. Epidemiol*, **9**, S84-92.

269 Norval M, Bjorn LO, de Gruijl FR, 2010, Is the action spectrum for the UV-induced production of previtamin D3 in human skin correct?, *Photochem. Photobiol. Sci.*, **9**, 11-7.

270 Norval M, Halliday GM, 2011, The consequences of UV-induced immunosuppression for human health, *Photochem. Photobiol.*, **87**, 965-77.

271 Norval M, Woods GM, 2011, UV-induced immunosuppression and the efficacy of vaccination, *Photochem. Photobiol. Sci.*, **10**, 1267-74.
272 Norval M, Kellett P, Wright CY, 2014, The incidence and body site of skin cancers in the population groups of South Africa, *Photodermatol. Photoimmunol. Photomed.*, **30**, 262-5.
273 Nthumba PM, Cavadas PC, Landin L, 2011, Primary cutaneous malignancies in sub-Saharan Africa, *Ann. Plast. Surg.*, **66**, 313-20.
274 Oellers P, Karp CL, Sheth A, Kao AA, Abdelaziz A, Matthews JL, Dubovy SR, Galor A, 2013, Prevalence, treatment, and outcomes of coexistent ocular surface squamous neoplasia and pterygium, *Ophthalmol.*, **120**, 445-50.
275 Ojah RC, Welch JM, 2012, Vitamin D and musculoskeletal status in Nova Scotian women who wear concealing clothing, *Nutrients*, **4**, 399-412.
276 Oktaria V, Dharmage SC, Burgess JA, Simpson JA, Morrison S, Giles GG, Abramson MJ, Walters EH, Matheson MC, 2013, Association between latitude and allergic diseases: a longitudinal study from childhood to middle-age, *Ann. Allergy Asthma Immunol.*, **110**, 80-5.e1.
277 Okuno T, Nakanishi-Ueda T, Ueda T, Yasuhara H, Koide R, 2012, Ultraviolet action spectrum for cell killing of primary porcine lens epithelial cells, *J. Occup. Health*, **54**, 181-6.
278 Olsen CM, Carroll HJ, Whiteman DC, 2010, Familial melanoma: a meta-analysis and estimates of attributable fraction, *Cancer Epidemiol. Biomarkers. Prev.*, **19**, 65-73.
279 Osuagwu UL, Ogbuehi KC, Almubrad TM, 2014, Changes in ultraviolet transmittance of hydrogel and silicone-hydrogel contact lenses induced by wear, *Eye Contact Lens*, **40**, 28-36.
280 Palacios C, Gonzalez L, 2014, Is vitamin D deficiency a major global public health problem?, *J. Steriod Biochem. Mol. Biol.*, **144PA**, 138-145.
281 Paller AS, Hawk JL, Honig P, Giam YC, Hoath S, Mack MC, Stamatas GN, 2011, New insights about infant and toddler skin: implications for sun protection, *Pediatrics*, **128**, 92-102.
282 Papastefanou VP, Cohen VM, 2011, Uveal melanoma, *J. Skin Cancer*, **2011**, 573974.
283 Parisi AV, Eley R, Downs N, 2012, Determination of the usage of shade structures via a dosimetry technique, *Photochem. Photobiol.*, **88**, 1012-5.
284 Pearce SHS, Cheetham TD, 2010, Diagnosis and management of vitamin D deficiency, *Br. Med. J.*, **340**.
285 Perry PK, Silverberg NB, 2001, Cutaneous malignancy in albinism, *Cutis*, **67**, 427-30.
286 Peterlik M, 2012, Vitamin D insufficiency and chronic diseases: hype and reality, *Food Funct.*, **3**, 784-94.
287 Petersen B, Datta P, Philipsen PA, Wulf HC, 2013, Sunscreen use and failures--on site observations on a sun-holiday, *Photochem. Photobiol. Sci.*, **12**, 190-6.
288 Petersen B, Thieden E, Philipsen PA, Heydenreich J, Wulf HC, Young AR, 2013, Determinants of personal ultraviolet-radiation exposure doses on a sun holiday, *Br. J. Dermatol.*, **168**, 1073-9.
289 Petersen B, Wulf HC, Triguero-Mas M, Philipsen PA, Thieden E, Olsen P, Heydenreich J, Dadvand P, Basagana X, Liljendahl TS, Harrison GI, Segerback D, Schmalwieser AW, Young AR, Nieuwenhuijsen MJ, 2014, Sun and ski holidays improve vitamin D status, but are associated with high levels of DNA damage, *J. Invest. Dermatol.*, **134**, 2806-13.
290 Pissavini M, Diffey B, 2013, The likelihood of sunburn in sunscreen users is disproportionate to the SPF, *Photodermatol. Photoimmunol. Photomed.*, **29**, 111-5.
291 Ponsonby AL, Lucas RM, van der Mei IA, 2005, UVR, Vitamin D and three autoimmune diseases - Multiple Sclerosis, Type 1 Diabetes, Rheumatoid Arthritis, *Photochem. Photobiol.*, **81**, 1267-75.
292 Poon TS, Barnetson RS, Halliday GM, 2005, Sunlight-induced immunosuppression in humans is initially because of UVB, then UVA, followed by interactive effects, *J. Invest. Dermatol.*, **125**, 840-6.
293 Porojnicu AC, Bruland OS, Aksnes L, Grant WB, Moan J, 2008, Sun beds and cod liver oil as vitamin D sources, *J. Photochem. Photobiol. B.*, **91**, 125-31.
294 Potente S, Coppa K, Williams A, Engels R, 2011, Legally brown: using ethnographic methods to understand sun protection attitudes and behaviours among young Australians 'I didn't mean to get burnt--it just happened!', *Health. Educ. Res.*, **26**, 39-52.
295 Powe CE, Ricciardi C, Berg AH, Erdenesanaa D, Collerone G, Ankers E, Wenger J, Karumanchi SA, Thadhani R, Bhan I, 2011, Vitamin D-binding protein modifies the vitamin D-bone mineral density relationship, *J. Bone Mineral Res.*, **26**, 1609-16.
296 Powe CE, Evans MK, Wenger J, Zonderman AB, Berg AH, Nalls M, Tamez H, Zhang D, Bhan I, Karumanchi SA, Powe NR, Thadhani R, 2013, Vitamin D-binding protein and vitamin D status of black Americans and white Americans, *N. Engl. J. Med.*, **369**, 1991-2000.
297 Principi N, Marchisio P, Terranova L, Zampiero A, Baggi E, Daleno C, Tirelli S, Pelucchi C, Esposito S, 2013, Impact of vitamin D administration on immunogenicity of trivalent inactivated influenza vaccine in previously unvaccinated children, *Hum. Vaccin. Immunotherap.*, **9**, 969-74.

298 Proby CM, Harwood CA, Neale RE, Green AC, Euvrard S, Naldi L, Tessari G, Feltkamp MC, de Koning MN, Quint WG, Waterboer T, Pawlita M, Weissenborn S, Wieland U, Pfister H, Stockfleth E, Nindl I, Abeni D, Schegget JT, Bouwes Bavinck JN, 2011, A case-control study of betapapillomavirus infection and cutaneous squamous cell carcinoma in organ transplant recipients, *Am. J. Transplant.*, **11**, 1498-508.

299 Prokofyeva E, Zrenner E, 2012, Epidemiology of major eye diseases leading to blindness in Europe: a literature review, *Ophthalmic. Res.*, **47**, 171-88.

300 Raasch BA, Buettner PG, Garbe C, 2006, Basal cell carcinoma: histological classification and body-site distribution, *Br. J. Dermatol.*, **155**, 401-7.

301 Rajiv B, Gray R, 2014, Sun Protection Alert - a simple tool for a complex issue, in *UV radiation and its effects: an update 2014*, Auckland, NZ.

302 Ralph AP, Lucas RM, Norval M, 2013, Vitamin D and solar ultraviolet radiation in the risk and treatment of tuberculosis, *Lancet Infect. Dis.*, **13**, 77-88.

303 Ralph AP, Waramori G, Pontororing GJ, Kenangalem E, Wiguna A, Tjitra E, Sandjaja, Lolong DB, Yeo TW, Chatfield MD, Soemanto RK, Bastian I, Lumb R, Maguire GP, Eisman J, Price RN, Morris PS, Kelly PM, Anstey NM, 2013, L-arginine and vitamin D adjunctive therapies in pulmonary tuberculosis: a randomised, double-blind, placebo-controlled trial, *PLoS One*, **8**, e70032.

304 Rees JR, Hendricks K, Barry EL, Peacock JL, Mott LA, Sandler RS, Bresalier RS, Goodman M, Bostick RM, Baron JA, 2013, Vitamin D3 supplementation and upper respiratory tract infections in a randomized, controlled trial, *Clin. Infect. Dis.*, **57**, 1384-92.

305 Rees JR, Zens MS, Gui J, Celaya MO, Riddle BL, Karagas MR, 2014, Non melanoma skin cancer and subsequent cancer risk, *PLoS One*, **9**, e99674.

306 Reeve VE, Domanski D, Slater M, 2006, Radiation sources providing increased UVA/UVB ratios induce photoprotection dependent on the UVA dose in hairless mice, *Photochem. Photobiol.*, **82**, 406-11.

307 Reichrath J, 2014, Sunlight, Vitamin D and Skin Cancer, in *Advances in Experimental Medicine and Biology*, 2nd ed. (Eds.: Back N, Cohen I, Lajtha A, Lambris J, Poaletti R), Landes Bioscience / Springer Science + Business media.

308 Reid D, Toole BJ, Knox S, Talwar D, Harten J, O'Reilly DS, Blackwell S, Kinsella J, McMillan DC, Wallace AM, 2011, The relation between acute changes in the systemic inflammatory response and plasma 25-hydroxyvitamin D concentrations after elective knee arthroplasty, *Am. J. Clin. Nutr.*, **93**, 1006-11.

309 Reinau D, Meier C, Gerber N, Hofbauer GF, Surber C, 2012, Sun protective behaviour of primary and secondary school students in North-Western Switzerland, *Swiss Med. Wkly.*, **142**, w13520.

310 Renzaho AM, Halliday JA, Nowson C, 2011, Vitamin D, obesity, and obesity-related chronic disease among ethnic minorities: a systematic review, *Nutrition*, **27**, 868-79.

311 Rettberg P, Eschweiler U, Strauch K, Reitz G, Horneck G, Wanke H, Brack A, Barbier B, 2002, Survival of microorganisms in space protected by meteorite material: results of the experiment 'EXOBIOLOGIE' of the PERSEUS mission, *Adv. Space Res.*, **30**, 1539-45.

312 Rhodes LE, Webb AR, Fraser HI, Kift R, Durkin MT, Allan D, O'Brien SJ, Vail A, Berry JL, 2010, Recommended summer sunlight exposure levels can produce sufficient ($\geq$20 ng ml^{-1}) but not the proposed optimal ($\geq$32 ng ml^{-1}) 25(OH)D levels at UK latitudes, *J. Invest. Dermatol.*, **130**, 1411-8.

313 Rhodes LE, Darby G, Massey KA, Clarke KA, Dew TP, Farrar MD, Bennett S, Watson RE, Williamson G, Nicolaou A, 2013, Oral green tea catechin metabolites are incorporated into human skin and protect against UV radiation-induced cutaneous inflammation in association with reduced production of pro-inflammatory eicosanoid 12-hydroxyeicosatetraenoic acid, *Br. J. Nutr.*, **110**, 891-900.

314 Rizwan M, Rodriguez-Blanco I, Harbottle A, Birch-Machin MA, Watson RE, Rhodes LE, 2011, Tomato paste rich in lycopene protects against cutaneous photodamage in humans in vivo: a randomized controlled trial, *Br. J. Dermatol.*, **164**, 154-62.

315 Rodrigues A, Sniehotta FF, Araujo-Soares V, 2013, Are interventions to promote sun-protective behaviors in recreational and tourist settings effective? A systematic review with meta-analysis and moderator analysis, *Ann. Behav. Med.*, **45**, 224-38.

316 Rogers HW, Weinstock MA, Harris AR, Hinckley MR, Feldman SR, Fleischer AB, Coldiron BM, 2010, Incidence estimate of nonmelanoma skin cancer in the United States, 2006, *Arch. Dermatol.*, **146**, 283-7.

317 Rosen CJ, Abrams SA, Aloia JF, Brannon PM, Clinton SK, Durazo-Arvizu RA, Gallagher JC, Gallo RL, Jones G, Kovacs CS, Manson JE, Mayne ST, Ross AC, Shapses SA, Taylor CL, 2012, IOM committee members respond to Endocrine Society vitamin D guideline, *J. Clin. Endocrinol. Metab.*, **97**, 1146-52.

318 Rosenthal FS, Phoon C, Bakalian AE, Taylor HR, 1988, The ocular dose of ultraviolet radiation to outdoor workers, *Invest. Ophthalmol. Vis. Sci.*, **29**, 649-56.

319 Rothers J, Wright AL, Stern DA, Halonen M, Camargo CA, Jr., 2011, Cord blood 25-hydroxyvitamin D levels are associated with aeroallergen sensitization in children from Tucson, Arizona, *J. Allergy. Clin. Immunol.*, **128**, 1093-9.e1-5.

320 Rouhani P, Hu S, Kirsner RS, 2008, Melanoma in Hispanic and black Americans, *Cancer Control*, **15**, 248-53.

321 Rozanowska MB, 2012, Light-induced damage to the retina: current understanding of the mechanisms and unresolved questions: a symposium-in-print, *Photochem. Photobiol.*, **88**, 1303-8.

322 Sayre RM, Dowdy JC, Rosenberg EW, 2013, Sun-protection factor confounded by anti-inflammatory activity of sunscreen agents?, *J. Am. Acad. Dermatol*, **69**, 481.

323 Schmerling RA, Loria D, Cinat G, Ramos WE, Cardona AF, Sanchez JL, Martinez-Said H, Buzaid AC, 2011, Cutaneous melanoma in Latin America: the need for more data, *Rev. Panam. Salud. Pacific.*, **30**, 431-8.

324 Schwarz A, Navid F, Sparwasser T, Clausen BE, Schwarz T, 2012, 1,25-dihydroxyvitamin D exerts similar immunosuppressive effects as UVR but is dispensable for local UVR-induced immunosuppression, *J. Invest. Dermatol.*, **132**, 2762-9.

325 Science M, Maguire JL, Russell ML, Smieja M, Walter SD, Loeb M, 2013, Low serum 25-hydroxyvitamin D level and risk of upper respiratory tract infection in children and adolescents, *Clin. Infect. Dis.*, **57**, 392-7.

326 Seite S, Fourtanier A, Moyal D, Young AR, 2010, Photodamage to human skin by suberythemal exposure to solar ultraviolet radiation can be attenuated by sunscreens: a review, *Br. J. Dermatol.*, **163**, 903-14.

327 Sempos CT, Vesper H, Phinney K, Thienpont L, Coates P, Vitamin D Standardization Program, 2012, Vitamin D status as an international issue: National surveys and the problem of standardization, *Scand. J. Clin. Lab. Invest.*, **72**, 32-40.

328 Sempos CT, Durazo-Arvizu RA, Dawson-Hughes B, Yetley EA, Looker AC, Schleicher RL, Cao G, Burt V, Kramer H, Bailey RL, Dwyer JT, Zhang X, Gahche J, Thomas PR, Coates PM, Picciano MF, 2013, Is there a Reverse J-shaped Association between 25-Hydroxyvitamin D and All-Cause Mortality? Results from the US Nationally Representative NHANES, *J. Clin. Endocrinol. Metab.*, **98**, 3001-9.

329 Shanafelt TD, Drake MT, Maurer MJ, Allmer C, Rabe KG, Slager SL, Weiner GJ, Call TG, Link BK, Zent CS, Kay NE, Hanson CA, Witzig TE, Cerhan JR, 2011, Vitamin D insufficiency and prognosis in chronic lymphocytic leukemia, *Blood*, **117**, 1492-8.

330 Sharma VK, Sahni K, Wadhwani AR, 2013, Photodermatoses in pigmented skin, *Photochem. Photobiol. Sci.*, **12**, 65-77.

331 Sherwin JC, Hewitt AW, Coroneo MT, Kearns LS, Griffiths LR, Mackey DA, 2012, The association between time spent outdoors and myopia using a novel biomarker of outdoor light exposure, *Invest. Ophthalmol. Vis. Sci.*, **53**, 4363-70.

332 Sherwin JC, Hewitt AW, Kearns LS, Griffiths LR, Mackey DA, Coroneo MT, 2013, The association between pterygium and conjunctival ultraviolet autofluorescence: the Norfolk Island Eye Study, *Acta Ophthalmol.*, **91**, 363-70.

333 Sherwin JC, Hewitt AW, Kearns LS, Griffiths LR, Mackey DA, Coroneo MT, 2013, The association between pterygium and conjunctival ultraviolet autofluorescence: The Norfolk Island Eye Study, *Acta Ophthalmol.*, **91**, 363-70.

334 Sheth VM, Pandya AG, 2011, Melasma: a comprehensive update: part I, *J. Am. Acad. Dermatol*, **65**, 689-97; quiz 698.

335 Sivayathorn A, 1995, Melasma in Orientals, *Clin. Drug Invest.*, **10, Suppl 2**, 34-40.

336 Slaper H, Velders GJ, Daniel JS, de Gruijl FR, van der Leun JC, 1996, Estimates of ozone depletion and skin cancer incidence to examine the Vienna Convention achievements, *Nature*, **384**, 256-8.

337 Sliney DH, 2011, Intraocular and crystalline lens protection from ultraviolet damage, *Eye Contact Lens*, **37**, 250-8.

338 Sneyd MJ, Cox B, 2013, A comparison of trends in melanoma mortality in New Zealand and Australia: the two countries with the highest melanoma incidence and mortality in the world, *BMC Cancer*, **13**, 372.

339 Sobolewski PS, Krzyscin JW, Jaroslawski J, Wink J, Lesiak A, Narbutt J, 2014, Controlling adverse and beneficial effects of solar UV radiation by wearing suitable clothes - Spectral transmission of different kinds of fabrics, *J. Photochem. Photobiol. B.*, **140C**, 105-110.

340 Springbett P, Buglass S, Young AR, 2010, Photoprotection and vitamin D status, *J. Photochem. Photobiol. B.*, **101**, 160-8.

341 Stacey SN, Gudbjartsson DF, Sulem P, Bergthorsson JT, Kumar R, Thorleifsson G, Sigurdsson A, Jakobsdottir M, Sigurgeirsson B, Benediktsdottir KR, Thorisdottir K, Ragnarsson R, Scherer D, Rudnai P, Gurzau E, Koppova K, Hoiom V, Botella-Estrada R, Soriano V, Juberias P, Grasa M, Carapeto FJ, Tabuenca P, Gilaberte Y, Gudmundsson J, Thorlacius S, Helgason A, Thorlacius T, Jonasdottir A, Blondal T, Gudjonsson SA, Jonsson GF, Saemundsdottir J, Kristjansson K, Bjornsdottir G, Sveinsdottir SG, Mouy M, Geller F, Nagore E, Mayordomo JI, Hansson J, Rafnar T, Kong A, Olafsson JH, Thorsteinsdottir U, Stefansson K, 2008, Common variants on 1p36 and 1q42 are associated with cutaneous basal cell carcinoma but not with melanoma or pigmentation traits, *Nature Genet.*, **40**, 1313-8.

342 Stang A, Valiukeviciene S, Aleknaviciene B, Kurtinaitis J, 2006, Time trends of incidence, mortality, and relative survival of invasive skin melanoma in Lithuania, *Eur. J. Cancer. Prev.*, **42**, 660-7.

343 Staples J, Ponsonby AL, Lim L, 2010, Low maternal exposure to ultraviolet radiation in pregnancy, month of birth, and risk of multiple sclerosis in offspring: longitudinal analysis, *Br. Med. J.*, **340**, c1640.

344 Staples MP, Elwood M, Burton RC, Williams JL, Marks R, Giles GG, 2006, Non-melanoma skin cancer in Australia: the 2002 national survey and trends since 1985, *Med. J. Aust.*, **184**, 6-10.

345 Stolzenberg-Solomon RZ, Jacobs EJ, Arslan AA, Qi D, Patel AV, Helzlsouer KJ, Weinstein SJ, McCullough ML, Purdue MP, Shu XO, Snyder K, Virtamo J, Wilkins LR, Yu K, Zeleniuch-Jacquotte A, Zheng W, Albanes D, Cai Q, Harvey C, Hayes R, Clipp S, Horst RL, Irish L, Koenig K, Le Marchand L, Kolonel LN, 2010, Circulating 25-hydroxyvitamin D and risk of pancreatic cancer: Cohort Consortium Vitamin D Pooling Project of Rarer Cancers, *Am. J. Epidemiol.*, **172**, 81-93.

346 Storey P, Munoz B, Friedman D, West S, 2013, Racial differences in lens opacity incidence and progression: the Salisbury Eye Evaluation (SEE) study, *Invest. Ophthalmol. Vis. Sci.*, **54**, 3010-8.

347 Sui GY, Liu GC, Liu GY, Gao YY, Deng Y, Wang WY, Tong SH, Wang L, 2013, Is sunlight exposure a risk factor for age-related macular degeneration? A systematic review and meta-analysis, *Br. J. Opthalmol.*, **97**, 389-94.

348 Summers CG, 2009, Albinism: classification, clinical characteristics, and recent findings, *Optom. Vis. Sci.*, **86**, 659-62.

349 Surjana D, Halliday GM, Martin AJ, Moloney FJ, Damian DL, 2012, Oral nicotinamide reduces actinic keratoses in phase II double-blinded randomized controlled trials, *J. Invest. Dermatol.*, **132**, 1497-500.

350 Szilagyi A, Leighton H, Burstein B, Shrier I, 2011, Significant positive correlation between sunshine and lactase nonpersistence in Europe may implicate both in similarly altering risks for some diseases, *Nutr. Cancer.*, **63**, 991-9.

351 Tang JY, Parimi N, Wu A, Boscardin WJ, Shikany JM, Chren MM, Cummings SR, Epstein EH, Jr., Bauer DC, Osteoporotic Fractures in Men Study G, 2010, Inverse association between serum 25(OH) vitamin D levels and non-melanoma skin cancer in elderly men, *Cancer Causes Control*, **21**, 387-91.

352 Tang JY, Fu T, Leblanc E, Manson JE, Feldman D, Linos E, Vitolins MZ, Zeitouni NC, Larson J, Stefanick ML, 2011, Calcium plus vitamin D supplementation and the risk of nonmelanoma and melanoma skin cancer: post hoc analyses of the women's health initiative randomized controlled trial, *J. Clin. Oncol.*, **29**, 3078-84.

353 Taylor DM, Bennett D, Carter M, Garewal D, Finch CF, 2004, Acute injury and chronic disability resulting from surfboard riding, *J. Sci. Med. Sport.*, **7**, 429-37.

354 Taylor HR, West SK, Rosenthal FS, Munoz B, Newland HS, Abbey H, Emmett EA, 1988, Effect of ultraviolet radiation on cataract formation, *N. Engl. J. Med.*, **319**, 1429-33.

355 Taylor HR, West S, Munoz B, Rosenthal FS, Bressler SB, Bressler NM, 1992, The long-term effects of visible light on the eye, *Arch. Ophthalmol.*, **110**, 99-104.

356 Tempark T, Chatproedprai S, Wanankul S, 2012, Attitudes, knowledge, and behaviours of secondary school adolescents regarding protection from sun exposure: a survey in Bangkok, Thailand, *Photodermatol. Photoimmunol. Photomed.*, **28**, 200-206.

357 Teramura T, Mizuno M, Asano H, Naito N, Arakane K, Miyachi Y, 2012, Relationship between sun-protection factor and application thickness in high-performance sunscreen: double application of sunscreen is recommended, *Clin. Exp. Dermatol.*, **37**, 904-8.

358 Tewari A, Lahmann C, Sarkany R, Bergemann J, Young AR, 2012, Human erythema and matrix metalloproteinase-1 mRNA induction, in vivo, share an action spectrum which suggests common chromophores, *Photochem. Photobiol. Sci.*, **11**, 216-23.

359 Tewari A, Grage MM, Harrison GI, Sarkany R, Young AR, 2013, UVA1 is skin deep: molecular and clinical implications, *Photochem. Photobiol. Sci.*, **12**, 95-103.

360 Thanos SM, Halliday GM, Damian DL, 2012, Nicotinamide reduces photodynamic therapy-induced immunosuppression in humans, *Br. J. Dermatol.*, **167**, 631-6.

361 Theodoratou E, Tzoulaki I, Zgaga L, Ioannidis JP, 2014, Vitamin D and multiple health outcomes: umbrella review of systematic reviews and meta-analyses of observational studies and randomised trials, *Br. Med. J.*, **348**, g2035.
362 Therapeutic Goods Administration, 2013, Literature review on the safety of titanium dioxide and zinc oxide nanoparticles in sunscreens. Scientific review report, Department of Health and Ageing, Canberra, pp. 0-19.
363 Thomas P, Swaminathan A, Lucas RM, 2012, Climate change and health with an emphasis on interactions with ultraviolet radiation: a review, *Glob. Change Biol.*, **18**, 2392-2405.
364 Tran B, Armstrong BK, Ebeling PR, English DR, Kimlin MG, van der Pols JC, Venn A, Gebski V, Whiteman DC, Webb PM, Neale RE, 2014, Effect of vitamin D supplementation on antibiotic use: a randomized controlled trial, *Am. J. Clin. Nutr.*, **99**, 156-61.
365 Tryggvadottir L, Gislum M, Hakulinen T, Klint A, Engholm G, Storm HH, Bray F, 2010, Trends in the survival of patients diagnosed with malignant melanoma of the skin in the Nordic countries 1964-2003 followed up to the end of 2006, *Acta Oncologia*, **49**, 665-72.
366 Tsiaras WG, Weinstock MA, 2011, Factors influencing vitamin D status, *Acta Derm. Venereol.*, **91**, 115-24.
367 Tuohimaa P, Tenkanen L, Ahonen M, Lumme S, Jellum E, Hallmans G, Stattin P, Harvei S, Hakulinen T, Luostarinen T, Dillner J, Lehtinen M, Hakama M, 2004, Both high and low levels of blood vitamin D are associated with a higher prostate cancer risk: a longitudinal, nested case-control study in the Nordic countries, *Int. J. Cancer*, **108**, 104-8.
368 Turner J, Parisi AV, 2013, Influence of reflected UV irradiance on occupational exposure from combinations of reflective wall surfaces, *Photochem. Photobiol. Sci.*, **12**, 1589-95.
369 Ullrich SE, Byrne SN, 2012, The immunologic revolution: photoimmunology, *J. Invest. Dermatol.*, **132**, 896-905.
370 Urashima M, Segawa T, Okazaki M, Kurihara M, Wada Y, Ida H, 2010, Randomized trial of vitamin D supplementation to prevent seasonal influenza A in schoolchildren, *Am. J. Clin. Nutr.*, **91**, 1255-60.
371 van der Leun JC, Piacentini RD, de Gruijl FR, 2008, Climate change and human skin cancer, *Photochem. Photobiol. Sci.*, **7**, 730-3.
372 van der Pols JC, Williams GM, Pandeya N, Logan V, Green AC, 2006, Prolonged prevention of squamous cell carcinoma of the skin by regular sunscreen use, *Cancer Epidemiol. Biomarkers. Prev.*, **15**, 2546-8.
373 van der Pols JC, Xu C, Boyle GM, Hughes MC, Carr SJ, Parsons PG, Green AC, 2011, Serum omega-3 and omega-6 fatty acids and cutaneous p53 expression in an Australian population, *Cancer Epidemiol. Biomarkers. Prev.*, **20**, 530-6.
374 van der Pols JC, Russell A, Bauer U, Neale RE, Kimlin MG, Green AC, 2013, Vitamin D status and skin cancer risk independent of time outdoors: 11-year prospective study in an Australian community, *J. Invest. Dermatol.*, **133**, 637-41.
375 van der Rhee H, Coebergh JW, de Vries E, 2013, Is prevention of cancer by sun exposure more than just the effect of vitamin D? A systematic review of epidemiological studies, *Eur. J. Cancer. Prev.*, **49**, 1422-36.
376 van Dijk A, Slaper H, den Outer PN, Morgenstern O, Braesicke P, Pyle JA, Garny H, Stenke A, Dameris M, Kazantzidis A, Tourpali K, Bais AF, 2013, Skin cancer risks avoided by the Montreal Protocol--worldwide modeling integrating coupled climate-chemistry models with a risk model for UV, *Photochem. Photobiol.*, **89**, 234-46.
377 van Leeuwen MT, Webster AC, McCredie MR, Stewart JH, McDonald SP, Amin J, Kaldor JM, Chapman JR, Vajdic CM, Grulich AE, 2010, Effect of reduced immunosuppression after kidney transplant failure on risk of cancer: population based retrospective cohort study, *Br. Med. J.*, **340**, c570.
378 Vernez D, Milon A, Vuilleumier L, Bulliard JL, 2012, Anatomical exposure patterns of skin to sunlight: relative contributions of direct, diffuse and reflected ultraviolet radiation, *Br. J. Dermatol.*, **167**, 383-90.
379 Viros A, Sanchez-Laorden B, Pedersen M, Furney SJ, Rae J, Hogan K, Ejiama S, Girotti MR, Cook M, Dhomen N, Marais R, 2014, Ultraviolet radiation accelerates BRAF-driven melanomagenesis by targeting TP53, *Nature*, **511**, 478-82.
380 Vitamin D Council, 2013, Vitamin D Council, Johnson Avenue, San Luis Obispo, California, United States, 93401., www.vitamindcouncil.org, accessed 18 October, 2011,
381 Wadhwani AR, Sharma VK, Ramam M, Khaitan BK, 2013, A clinical study of the spectrum of photodermatoses in dark-skinned populations, *Clin. Exp. Dermatol.*, **38**, 823-9.

382 Wahl DA, Cooper C, Ebeling PR, Eggersdorfer M, Hilger J, Hoffmann K, Josse R, Kanis JA, Mithal A, Pierroz DD, Stenmark J, Stocklin E, Dawson-Hughes B, 2012, A global representation of vitamin D status in healthy populations, *Arch. Osteoporos.*, **7**, 155-72.

383 Wallingford SC, Alston RD, Birch JM, Green AC, 2011, Increases in invasive melanoma in England, 1979-2006, by anatomical site, *Br. J. Dermatol.*, **165**, 859-64.

384 Wang BQ, Shen ZY, Fei Y, Li H, Liu JH, Xu H, Zhang Z, Yu XH, Chen XD, 2011, A population-based study of acquired bilateral nevus-of-Ota-like macules in Shanghai, China, *J. Invest. Dermatol.*, **131**, 358-62.

385 Wang F, Gao Q, Hu L, Gao N, Ge T, Yu J, Liu Y, 2012, Risk of eye damage from the wavelength-dependent biologically effective UVB spectrum irradiances, *PLoS One*, **7**, e52259.

386 Webb AR, DeCosta BR, Holick MF, 1989, Sunlight regulates the cutaneous production of vitamin D3 by causing its photodegradation, *J. Clin. Endocrinol. Metab.*, **68**, 882-7.

387 Webb AR, Engelsen O, 2008, Ultraviolet exposure scenarios: risks of erythema from recommendations on cutaneous vitamin D synthesis, *Adv. Exp. Med. Biol.*, **624**, 72-85.

388 Webb AR, Kift R, Durkin MT, O'Brien SJ, Vail A, Berry JL, Rhodes LE, 2010, The role of sunlight exposure in determining the vitamin D status of the U.K. white adult population, *Br. J. Dermatol.*, **163**, 1050-5.

389 Webb AR, Kift R, Berry JL, Rhodes LE, 2011, The vitamin D debate: translating controlled experiments into reality for human sun exposure times, *Photochem. Photobiol.*, **87**, 741-5.

390 Wejse C, Gomes VF, Rabna P, Gustafson P, Aaby P, Lisse IM, Andersen PL, Glerup H, Sodemann M, 2009, Vitamin D as supplementary treatment for tuberculosis: a double-blind, randomized, placebo-controlled trial, *Am. J. Resp. Criti. Care Med.*, **179**, 843-50.

391 West SK, Rosenthal FS, Bressler NM, Bressler SB, Munoz B, Fine SL, Taylor HR, 1989, Exposure to sunlight and other risk factors for age-related macular degeneration, *Arch. Ophthalmol.*, **107**, 875-9.

392 White JH, 2012, Regulation of intracrine production of 1,25-dihydroxyvitamin D and its role in innate immune defense against infection, *Arch. Biochem. Biophys.*, **523**, 58-63.

393 Whitehouse AJ, Holt BJ, Serralha M, Holt PG, Kusel MM, Hart PH, 2012, Maternal serum vitamin D levels during pregnancy and offspring neurocognitive development, *Pediatrics*, **129**, 485-93.

394 WHO, 1994, *Environmental Health Criteria 160 - Ultraviolet Radiation*, World Health Organization.

395 Willer CJ, Dyment DA, Sadovnick AD, Rothwell PM, Murray TJ, Ebers GC, 2005, Timing of birth and risk of multiple sclerosis: population based study, *Br. Med. J.*, **330**, 120.

396 Wirohadidjojo YW, Radiono S, Budiyanto A, Soebono H, 2011, Cellular viability, collagen deposition, and transforming growth factor beta1 production among ultraviolet B-irradiated keloid fibroblasts, *Aesthetic. Plast. Surg.*, **35**, 1050-5.

397 Wolf P, Gruber-Wackernagel A, Rinner B, Griesbacher A, Eberhard K, Groselj-Strele A, Mayer G, Stauber RE, Byrne SN, 2013, Phototherapeutic hardening modulates systemic cytokine levels in patients with polymorphic light eruption, *Photochem. Photobiol. Sci.*, **12**, 166-73.

398 Wolf P, Gruber-Wackernagel A, Bambach I, Schmidbauer U, Mayer G, Absenger M, Frohlich E, Byrne SN, 2014, Photohardening of polymorphic light eruption patients decreases baseline epidermal Langerhans cell density while increasing mast cell numbers in the papillary dermis, *Exp. Dermatol.*, **23**, 428-30.

399 Wolfe RA, Roys EC, Merion RM, 2010, Trends in organ donation and transplantation in the United States, 1999-2008, *Am. J. Transplant.*, **10**, 961-72.

400 Wolfle U, Esser PR, Simon-Haarhaus B, Martin SF, Lademann J, Schempp CM, 2011, UVB-induced DNA damage, generation of reactive oxygen species, and inflammation are effectively attenuated by the flavonoid luteolin in vitro and in vivo, *Free Radical. Biol. Med.*, **50**, 1081-93.

401 Wu Y, Jia LL, Zheng YN, Xu XG, Luo YJ, Wang B, Chen JZ, Gao XH, Chen HD, Matsui M, Li YH, 2013, Resveratrate protects human skin from damage due to repetitive ultraviolet irradiation, *J. Eur. Acad. Dermatol. Venereol.*, **27**, 345-50.

402 Xiang F, Lucas R, Hales S, Neale RE, 2014, Incidence of nonmelanoma skin cancer in relation to ambient UV radiation in white populations, 1978-2012: empirical relationships, *J. Am. Med. Assoc. Dermatol.*, **150** 1063-71.

403 Yam JC, Kwok AK, 2014, Ultraviolet light and ocular diseases, *Int. Ophthalmol.*, **34**, 383-400.

404 Yang L, Veierod MB, Lof M, Sandin S, Adami HO, Weiderpass E, 2011, Prospective study of UV exposure and cancer incidence among Swedish women, *Cancer Epidemiol. Biomarkers. Prev.*, **20**, 1358-67.

405 Yazar S, Hewitt AW, Black LJ, McKnight CM, Mountain JA, Sherwin JC, Oddy WH, Coroneo MT, Lucas RM, Mackey DA, 2014, Myopia is associated with lower vitamin D status in young adults, *Invest. Ophthalmol. Vis. Sci.*, **55**, 4552-9.

406 Zaidi MR, Davis S, Noonan FP, Graff-Cherry C, Hawley TS, Walker RL, Feigenbaum L, Fuchs E, Lyakh L, Young HA, Hornyak TJ, Arnheiter H, Trinchieri G, Meltzer PS, De Fabo EC, Merlino G, 2011, Interferon-gamma links ultraviolet radiation to melanomagenesis in mice, *Nature*, **469**, 548-53.

407 Zaidi MR, De Fabo EC, Noonan FP, Merlino G, 2012, Shedding light on melanocyte pathobiology in vivo, *Cancer. Res.*, **72**, 1591-5.

408 Zaratti F, Piacentini RD, Guillen HA, Cabrera SH, Liley JB, McKenzie RL, 2014, Proposal for a modification of the UVI risk scale, *Photochem. Photobiol. Sci.*, **13**, 980-5.

409 Zhang J, Yan H, Lofgren S, Tian X, Lou MF, 2012, Ultraviolet radiation-induced cataract in mice: the effect of age and the potential biochemical mechanism, *Invest. Ophthalmol. Vis. Sci.*, **53**, 7276-85.

410 Zhu K, Whitehouse AJ, Hart P, Kusel M, Mountain J, Lye S, Pennell C, Walsh JP, 2013, Maternal vitamin D status during pregnancy and bone mass in offspring at 20 years of age: A prospective cohort study, *J. Bone Mineral Res.*, **29**, 1088-95.

411 Ziegler A, Jonason AS, Leffell DJ, Simon JA, Sharma HW, Kimmelman J, Remington L, Jacks T, Brash DE, 1994, Sunburn and p53 in the onset of skin cancer, *Nature*, **372**, 773-6.

412 Zittermann A, Kuhn J, Dreier J, Knabbe C, Gummert JF, Borgermann J, 2013, Vitamin D status and the risk of major adverse cardiac and cerebrovascular events in cardiac surgery, *Eur. Heart J.*, **34**, 1358-64.

413 Zivadinov R, Treu CN, Weinstock-Guttman B, Turner C, Bergsland N, O'Connor K, Dwyer MG, Carl E, Ramasamy DP, Qu J, Ramanathan M, 2013, Interdependence and contributions of sun exposure and vitamin D to MRI measures in multiple sclerosis, *J. Neurol. Neurosurg. Psychiatry.*

Chapter 3: Solar ultraviolet radiation and ozone depletion-driven climate change: Effects on terrestrial ecosystems

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Summary

In this assessment we summarise advances in our knowledge of how UV-B radiation (280-315 nm) together with other climate-change factors influence terrestrial organisms and ecosystems. We identify key uncertainties and knowledge gaps that limit our ability to fully evaluate the interactive effects of ozone depletion and climate change on these systems. We also evaluate the biological consequences of the way in which stratospheric ozone depletion has contributed to climate change in the Southern Hemisphere. Since the last assessment, several new findings or insights have emerged or been strengthened. These include 1) the increasing recognition that UV-B radiation has specific regulatory roles in plant growth and development that in turn can have beneficial consequences for plant productivity via effects on plant hardiness, enhanced plant resistance to herbivores and pathogens, and improved quality of agricultural products with subsequent implications for food security; 2) UV-B radiation together with UV-A (315-400 nm) and visible radiation (400-700 nm) are significant drivers of decomposition of plant litter in globally important arid and semi-arid ecosystems, such as grasslands and deserts. This occurs through the process of photodegradation, which has implications for nutrient cycling and carbon storage, although considerable uncertainty exists in quantifying its regional and global biogeochemical significance; 3) UV radiation can contribute to climate change via its stimulation of volatile organic compounds from plants, plant litter and soils, although the magnitude, rates and spatial patterns of these emissions remain highly uncertain at present. UV-induced release of carbon from plant litter and soils may also contribute to global warming; and 4) depletion of ozone in the Southern Hemisphere modifies climate directly via effects on seasonal weather patterns (precipitation and wind) and these in turn have been linked to changes in growth of plants across the Southern Hemisphere. Such research has broadened our understanding of the linkages that exist between the effects of ozone depletion, UV-B radiation and climate change on terrestrial ecosystems.

Introduction

We have focused mainly on recent work in order to highlight the progress made to date, and to attempt an analysis of the complexity of both independent and interacting factors on terrestrial ecosystems in terms of UV radiation and other environmental constraints, including emerging evidence of the role of stratospheric ozone trends in affecting climate.

Ozone depletion, changed exposure to ultraviolet-B (UV-B, 280-315 nm) radiation, and climate change exert both individual and interactive effects on biological systems, with intricate feedbacks.[12, 158] Some of the key factors interacting with UV radiation that affect organism response are water availability, temperature, and nutrient availability. UV radiation has also been implicated as a contributor to global warming through its stimulation of volatile organic compounds from plants, plant litter and soils. Emission of carbon dioxide (CO_2) from plant litter and soils may also contribute to global warming.[41, 76]

Ozone depletion modifies Southern Hemisphere summer weather through its effect on the Southern Annular Mode (SAM) with consequences for plant growth in South America, New Zealand, and Antarctica already reported.[114, 140, 145] These impacts of ozone depletion on other climate factors (e.g., wind patterns, precipitation, and warming) may result in an increase in the interactive effects of UV radiation with drought and temperature. Other seasonal weather phenomena need to be taken into account to gain an accurate perspective of the different determinants of UV exposure of terrestrial organisms. These include La Niña and El Niño events, which change cloud cover, winds, sea surface temperatures, and atmospheric pressure at sea level. In addition, changes in land-use and vegetation cover, which also feed-back to climate systems, have implications for the exposure and thus response of organisms to UV radiation.

During the course of research on the effects of UV radiation, much emphasis has been placed on the potential detrimental impacts on plants and ecosystems. However, the balance of recent evidence is shifting to show that while some detrimental effects do occur, UV radiation is also a key regulator of plant morphology and physiological, biochemical and genetic processes, and is important in animal and plant signalling. Following on from this line of investigation, it has also become apparent that UV radiation and climate variables can be usefully exploited for value-adding to, e.g., agricultural crops.[155] The emerging concept, that agricultural[156, 158] plants can become more hardy through exposure to UV radiation, represents a marked shift in perspective.[155, 156] In addition, certain plants produce more medicinal compounds with exposure to UV radiation.[164] The overall objective is to boost the quality and/or quantity of yield, usually selectively, e.g., by making plants less prone to attack by pests and diseases. Concepts such as that of “eustress” are also relevant. Eustress is analogous to ‘priming’ where a stress is imposed on plants to acclimatise them and develop tolerance, which facilitates better growth when exposed to a more severe stress.[88, 156]

Exposure to ecologically-relevant levels of UV radiation generally are not deleterious as long as plants are able to acclimate, although this depends on the environmental conditions including climate variables, latitudinal location[38] and plant type (e.g., whether plants are herbaceous or woody). Consequently, the direct negative effects of exposure to UV-B radiation on plant growth, photosynthesis, and productivity are generally minor, or not detectable (summarised in meta-analyses by Searles et al.[124] and Newsham and Robinson[99]). However, indirect effects of exposure to UV radiation are often more pronounced than direct effects and need to be addressed to obtain a holistic perspective of the role of UV radiation as a regulator and modifier of ecosystem and organism response.

In this current assessment, we focus on the way in which UV radiation, stratospheric ozone trends, climate and other phenomena affect the biosphere, in order to better understand the current interactive effects from different stresses and to identify possible new interactions and their implications. This will allow for an evaluation of the capability of terrestrial ecosystems to adapt to a changing environment in which UV radiation plays an integral part in the response. Additionally, an assessment of these interactive processes on organisms and ecosystems recognises that the effects of UV radiation often represent a balance of both positive and negative influences.[158] Although the role of UV-B radiation is a major consideration in this paper, other relevant and often interacting factors, such as stratospheric ozone trends and climate change cannot be meaningfully separated.

Multiple plant stresses and their implications in the response to UV radiation

Evaluation of the effect of different levels of exposure to UV-B radiation, whether beneficial or not, is complicated by the dependency on many other variables, including the sensitivity of diverse ecosystems and species. This differential sensitivity, which results in distinctive response patterns, reflects the complexity of the biosphere as our understanding increases.

UV radiation, temperature and drought

The volume of research concentrating on the impacts of UV radiation and drought is indicative of the increasing awareness of a changing climate coupled with other interlinking factors. However, there are still several knowledge gaps, e.g., at the mechanistic level around drought and UV-B signalling interactions and the consequences at the molecular level leading to plant response. Areas such as the Middle East, North Africa, certain regions of Australia and the Mediterranean are particularly vulnerable to climate change.[135] Research on plants originating from drought-prone regions (e.g., the Mediterranean area), provides insight into current and potential long-term constraints for growth of agricultural plants and ecosystems by increased temperature, scarcity of water and enhanced exposure to UV radiation.[28] Predicted decreased cloudiness in the Mediterranean area is likely to enhance exposure to UV-B and UV-A radiation (315-400 nm).[160] Other co-occurring factors modifying UV radiation at the Earth's surface include air pollution and aerosol load (see Chapter 6).

High solar radiation, high temperatures, and drought conditions can lead to an array of responses including oxidative stress and physiological and metabolic acclimation.[55] The frequently observed, although not universal cross-tolerance to drought stress and UV radiation is in contrast to the increased sensitivity to UV radiation that can occur in adequately watered plants(Caldwell et al.[30] and references therein and others[22, 143, 150]). For example, in many woody Mediterranean plants, several physiological and biochemical traits (e.g., plant growth, net rate of assimilation of CO_2, and photochemistry) show little response to changes in UV radiation against a background of high temperatures and drought periods.[22]

UV radiation and other stress factors can increase allocation of newly assimilated carbon to polyphenols, and in particular, the flavonoid compounds, indicative of an energy shift in order to acclimate to stress conditions (Ballaré et al.[12] and references therein and Guidi et al.[55]). The lack of a substantial response to UV radiation in many of the parameters measured in Mediterranean plants may also be explained by biochemical acclimation induced by the visible part of the solar spectrum, thus leading to acclimation to UV and ultimately adaptation.[55] This involves effective scavenging of reactive oxygen species and other protective mechanisms such as morphological, physiological, and biochemical changes[28] that contribute to drought and high temperature tolerance, as well as positive plant-insect interactions.[90] Decreased plant productivity and changes in crop quality may, however, occur with long-term and multiple stress exposure.

Significance of sequential stress

In the context of interactive stresses, recent work has continued to address the importance of the sequence in which plants are exposed to the different stresses (reviewed in Bandurska et al.[14], although further supporting research is needed in this area. Field studies also are lacking, which may be a reflection of the difficulties encountered in trying to evaluate sequential stresses under more natural conditions. A growth chamber study by Bandurska and Cieslak[14] showed that exposure of plants to UV-B radiation and drought, whether in combination or individually applied, affected metabolic processes differently at different locations within the plant. With separate applications of enhanced UV-B radiation and simulated drought conditions, plant growth is often retarded and oxidative stress increases. In general, exposure to both UV-B radiation and drought can elicit a number of physiological and biochemical responses that are common to both abiotic stresses. These involve increases in oxidative stress through production of reactive oxygen species, including hydrogen peroxide and nitric oxide, growth inhibition and, in some cases, the induction of phenolic compounds (Bandurska et al.[15] and references therein). UV-induced oxidative damage, such as lipid peroxidation, can be reduced by pre-exposing plants to mild drought conditions.

Sequential or simultaneous exposure to stress factors can also be genotype-specific. For example, as illustrated in a growth-chamber study, drought-susceptible genotypes were more adversely affected by simultaneous application of enhanced UV-B radiation and drought conditions than the drought-tolerant genotype.[60] However, the response may differ under natural environments. Where either drought or enhanced UV-B radiation is first supplied singly, the negative effects may be lessened when followed by the other stress.[60] Similarly, pre-exposure of plants to enhanced levels of UV-B radiation before exposure to high levels of visible light and high temperature results in an increase in photosynthesis and relative growth.[155] Pre-exposures to relatively high temperatures can also induce UV tolerance.[73]

These studies are of relevance particularly for horticultural practices, where vitality of plants can be increased through exposure to the relevant sequential stress prior to transfer from greenhouse/nursery to open field conditions.

Fertiliser application and nitrogen deposition

The degree of complexity of plant and ecosystem response to multiple environmental and climatic factors is becoming increasingly evident as research moves from single-stress experiments to more natural environmental conditions. This is exemplified by a number of recent field studies where application of fertiliser to plants exposed to enhanced UV radiation induced varied responses. Fertiliser can modify the effects of elevated temperature and UV-B radiation. For example, changes in some secondary metabolites, including certain phenolic compounds and alkaloids occur, as was shown in Norway spruce (*Picea abies* L.).[152] Furthermore, increased sensitivity towards enhanced UV-B radiation may result where fertiliser is applied in excess of recommended levels.[130] This was manifested in a shift in biomass towards the shoots of field-grown radish plants, causing a loss in yield as compared to growth under recommended levels of nitrogen (N), phosphorus (P), and potassium (K).[130] In contrast, additional but not excessive N may alleviate the negative effects of UV-B radiation stress.[57, 75]

Volatile organic compounds

Several environmental stresses, both biotic and abiotic, stimulate the emission of volatile organic compounds (VOCs) from plant tissues, partly as a protective mechanism.[63, 109] While a large diversity of VOCs are produced from terrestrial ecosystems, only a few of these compounds contribute substantially to the total emissions.[54] So far, only a few studies have focused on co-occurring stresses[63, 107] to elucidate the potential interactive effects on VOC emissions. These stressors include UV radiation, drought, soil moisture, temperature, tropospheric ozone, and herbivore attack, presenting a challenge in terms of quantifying their individual and combined contributions to emissions of VOCs at a local, regional and global level. This complexity is further overlaid by the variable nature of emissions according to type of plant. VOCs such as isoprene, are potential contributors to increasing greenhouse gases[110] and thus may modify atmospheric composition, including extending the lifetimes of methane.[7] For example, one of the major sources of tropospheric carbon monoxide (CO) is oxidation of isoprene, and scavenging of OH radicals by CO reduces the oxidation rate of methane, increasing its lifetime.

Isoprene, the most environmentally important VOC emitted from terrestrial plants, contributes ca 50% of the total global biogenic VOC.[54] While UV-B radiation and temperature can have interactive effects on VOC emissions, temperature is the more significant driver of increasing emissions. Those factors that stimulate VOC emission, including UV radiation,[80] result in an energy-cost to plants with a potential loss in productivity as a result of allocation of energy and carbon into, for example, synthesis of isoprene.[63, 128] The extent to which UV radiation plays a stimulatory role in VOC emissions is currently unknown.

VOCs from a range of terrestrial and certain marine systems have been widely measured including in extreme environments such as the Arctic regions and deserts. The effects of enhanced UV-B radiation on emissions of VOCs from sub-Arctic peatlands are highly variable, even when averaged over a growing season, ranging from no detectable change to 60% greater compared to ambient UV-B treatments[49, 141] and see Chapter 5. Thus, emissions of VOC from plants and peatlands reflect the prevailing environmental conditions, including temperature, availability of water and UV radiation[80, 83, 112] and can lead to further interactions and feedbacks within the biosphere.

Methane, the second most important greenhouse gas after carbon dioxide, is produced by both microbial and non-microbial mechanisms as well as through geological processes. Methane is emitted from peatlands and wetlands (Fig. 1) as well as from other vegetation types[112], soils, surface waters, animals, and fungi (Wang et al.[154] and references therein). Microbially-produced methane has been well documented (Wang et al.[154] and references therein), while methane production from oxygen-rich environments (non-microbial production) has only recently been investigated and its implications discussed. Recent estimates of emission of methane from plants indicate that they may be very low, although these estimates have varied substantially (e.g., contributing from <0.2% to 40% of all methane released to the atmosphere).[23, 70, 94, 163] The source of methane emitted from vegetation is still under investigation, with reports suggesting emission from an internal, plant structural cell wall component, pectin,[95] or from surface waxes of leaves, production of which may be stimulated by UV radiation.[26] Additional factors leading to the stimulation of methane emissions include production of reactive oxygen species induced by environmental stress and injury to plants.[5, 27, 96]

As is the case for many of the non-methane VOCs, the magnitude of methane emissions is variable and dependent on location and ambient conditions including UV radiation. A long-term study over 6 years showed that enhanced UV-B radiation in a boreal peatland increased methane emission.[112] A complementary study on emission of methane from trees growing in natural wetlands showed that emissions from trees exceeded those of the peatland on which they were growing. These studies found that wetland trees mediated emission of methane from the peatland.[101] In contrast, a study of a wetland (fen) in Northern Finland over three growing seasons did not show UV-B induced changes in net emission of methane, although enhanced UV-B radiation contributed to a slight increase in the organic acid precursors for methanogenesis.[98] In field experiments specifically studying the response of rice plants and paddy fields to enhanced UV-B radiation, UV-B supplementation using lamps significantly increased emission of methane from the paddy, especially between the tillering and heading stages of the rice. At the same time, decreased tiller number and biomass occurred as a response to the enhanced UV-B radiation levels.[84]

The important roles played by VOCs in ecosystem functioning – from inter- and intra-plant communications to plant chemical defence that decreases damage by herbivores – need to be analysed within a dynamic environment of interacting stresses from rapid and frequent climate events and changes in exposure to UV radiation. These factors should be considered when addressing the roles of different VOCs in mediating the diverse range of interactions occurring in ecosystems. In general, further investigations under natural environmental conditions are required to clarify the overall significance of UV radiation as a contributing factor to VOC emissions from plants and peatlands.

Fig. 1 Wetland ecosystems, such as in south-eastern Louisiana, USA, are important sources of methane and have been the subject of a number of studies examining effects of UV radiation on methane emissions (Photograph: P. Barnes).

The ozone 'hole' as a driver for Southern Hemisphere climate and ecosystem change

The role of ozone depletion in Southern Hemisphere climate processes_ENREF_61 (see Chapter 1) has been largely overlooked in the biological literature and this section highlights some of the ways ozone depletion, independent of UV radiation, has affected ecosystems through climatic change. While these climate perturbations are likely to have had a significant impact over the past few decades they have only recently started to be considered at the ecological level.

The ozone 'hole' moderates Southern Hemisphere climate

Ozone depletion and our response to it have had major implications for the Earth's climate. In the Southern Hemisphere, the ozone 'hole' has been a dominant driver[114, 140, 145] of atmospheric circulation changes in the Southern Hemisphere since the 1970's and has shielded Antarctica from much of the effect of global warming.[39, 139, 145, 146, 161]

The Southern Hemisphere Annular Mode (SAM), or Antarctic Oscillation, refers to the difference in atmospheric pressure between the mid- and high-latitudes of the Southern Hemisphere and thus the position of the polar jet. When the SAM index is positive the polar jet is located towards the South Pole, when it is negative it moves northwards. Since the late 1970s, the atmospheric polar jet has shifted south by 1–2° of latitude and increased in strength by 15–20%.[72, 147] The observed trend in the SAM has been largest during the austral summer and this is believed to be driven primarily by the development of the Antarctic ozone 'hole' (Thompson et al.[140] and references therein). From records of ice cores it appears that intensification of the westerlies started over a century ago, driven by increases in greenhouse gases, but in recent decades the intensification associated with ozone depletion has been more pronounced.[45] The SAM index is now at its highest level for at least 1000 years.[1]

Climate-related effects of ozone depletion on Southern Hemisphere ecosystems

The changes to circumpolar westerly winds attributed to ozone depletion are likely to have far-reaching consequences for biological ecosystems, particularly due to the influence of wind on availability of water. The availability of liquid water to organisms broadly depends on the balance between annual precipitation and losses by evaporation, sublimation, and freezing. Increased wind causes evaporation, and in polar and alpine environments, sublimation and scouring of snow,[40] In Antarctica, increased wind speeds have been linked to decreased growth rates of plants[37] and changes in biodiversity in lakes[62] in East Antarctica (Fig. 2). These changes are correlated with declining availability of water in East Antarctic coastal sites associated with increasing wind speeds and, in the case of moss growth rates, ozone depletion (Fig. 2). This research thus links ozone depletion to negative biodiversity outcomes through factors other than increasing UV-B radiation (reviewed in Robinson and Erickson.[114]).

Fig. 2 The Southern Hemisphere showing impacts of the positive phase of the Southern Annular Mode (SAM) on atmospheric circulation, wind patterns and precipitation, as well as oceanic currents and temperatures. Associated effects of these climate changes on terrestrial ecosystems are shown where available. Over the past century, increasing greenhouse gases and then ozone depletion over Antarctica have both pushed the SAM towards a more positive phase and the SAM index is now at its highest level for at least 1,000 years.[1] During the summer months the positive phase of the SAM is strongly associated with ozone depletion. NZ, New Zealand. Figure produced by Andrew Netherwood has been modified from Robinson et al.[114]

Winds also transport dust (including nutrients, seeds, spores, and other reproductive structures) from lower latitudes into the Southern Ocean and central West Antarctica (Fig. 2). Changes to either the location or strength of winds can affect the sources of dust and the quantities transported, with widespread implications including changes in productivity of the ocean. For example, increased wind-blown iron deposited into the ocean leads to phytoplankton blooms, indicative of increased productivity.[33, 93]

These biological impacts are not restricted to the Antarctic. Significant changes to tree growth across the Southern Hemisphere in the last 50 years, relative to the previous 250 years, correlate with ozone 'hole'-influenced changes to SAM[151] (Fig. 2). This is illustrated by the ca 50% of the decline in growth rates of three species of trees (*Austrocedrus chilensis, Araucaria aracana* and *Nothofagus betuloides)* in southernmost South America since the 1950s, associated with SAM-induced decreased precipitation in the Andes. Similarly, changes to circulation patterns have increased precipitation over sub-alpine areas of New Zealand resulting in greater than average rates of growth in another tree species (*Halocarpus biformis*). In this case, a third of the growth increase was attributed to changes in the SAM.[151]

Recent modelling studies suggest that stratospheric ozone losses since the 1970s have also increased the frequency and intensity of extreme precipitation in austral summer.[24, 111] This has resulted in drying in the southern tip of South America and SW Australia, wetter summers in SE Australia, E New Zealand and SE South America and increased precipitation and freshening (increase in freshwater input) in the Southern Ocean[69] (Fig. 2). Given the importance of water availability for all life on Earth, the vital role it plays in human and ecosystem health and for food security, these findings suggest that ozone depletion has far greater ecosystem impacts than previously anticipated. In particular, extremes of precipitation (droughts and floods) can be economically and socially devastating (cf. IPCC[64]).

Changes to the Southern Hemisphere circulation processes can have wider modifying effects than simply on wind speeds and associated water availability. It has been suggested that the shift to warmer summers in Southern Africa strongly correlates with the large ozone 'hole' era (1993-2010).[87] Manatsa et al.[87] re-analysed satellite data, focusing on October-December, to separate the effect of greenhouse gases on the SAM index from those effects attributed to the ozone 'hole' (Fig. 2). While this analysis does not specifically link to biological impacts, it illustrates the potential effects of the ozone 'hole' in terms of human health, natural ecosystems, and agriculture. It also illustrates the need to investigate the role of the ozone 'hole' in ecological processes and systems other than those directly related to changes in UV radiation. Since ozone depletion is driving multiple stressors across the Southern hemisphere (e.g., increased UV-B radiation combined with either increased drought or increased precipitation), the interactive effects described above need to be considered.

Recovery of the ozone 'hole' over the next century will have widespread and complex effects on the Southern Hemisphere climate processes with counter forcing from greenhouse gas emissions predicted to play a pivotal role.[108] Contrary to expectations, some consequences of ozone depletion have been positive, such as maintaining Antarctica's cold temperatures, and their reversal may have negative effects for life on Earth. A more holistic picture of the true ecological consequences of ozone depletion on terrestrial, aquatic and marine ecosystems in the Southern Hemisphere is required in order to better project future changes and ways of mitigating risk.[114]

UV-B radiation and litter decomposition

Decomposition of organic material is a crucial component of global biogeochemical cycles that affects soil fertility, the fate and residence times of carbon and nutrients in organic matter pools, and ultimately plant community composition and production (see Chapter 5).

Although the activity and make-up of the decomposing microbial community (bacteria and fungi) are key determinants of decomposition, solar radiation, including the UV-B component plays a significant role. Recent studies, including several meta-analyses,[71, 133] have increased our understanding of the ecological significance of UV-B radiation on decomposition, including the fundamental mechanisms by which UV-B (and UV-A) radiation modifies the decomposition process, and the potential linkages between changes in UV radiation and other climate change factors. These analyses indicate that UV-B radiation, at ambient or enhanced levels, has complex effects on decomposition of litter and can either retard or accelerate rates of decomposition depending on UV-B exposure, climatic factors (e.g., temperature and precipitation), and litter chemistry and structure. The conditions and ecosystems where UV-B radiation is expected to play a significant role in litter decomposition are described below.

UV exposure of litter and wavelength sensitivity of decomposition processes

Ultimately, the effectiveness of incident solar UV radiation on decomposition of litter is determined largely by exposure to UV and the sensitivity of the underlying decomposition processes to the wavelength (Fig. 3). At present, little is known of the precise nature of the dose-response relationships for the various mechanisms of UV-driven decomposition and what action spectra best describe the sensitivity of these processes. This makes it difficult to quantitatively assess the importance of the effects of ozone depletion and associated changes in UV radiation on decomposition of litter, storage of carbon by ecosystems and the emissions of CO_2 and other trace gases from decomposing plant litter. Recent studies have highlighted the importance of factors such as cloud cover,[12, 19] vegetation structure,[19] litter depth,[61] litter orientation,[78] and soil coverage[20] in altering the exposure of litter to UV radiation (Figs 3,4). Also, while several recent studies have shown that photodegradation can be driven by UV-A and visible radiation (photosynthetically active radiation; PAR, 400-700 nm) in addition to the UV-B component,[9, 122] little progress has been made in developing action spectra for specific biotic (microbial) and abiotic (photodegradation) decomposition processes (Barnes et al.[19] and references therein; but see Gao and Garcia-Pichel[51]).

Effects of UV radiation on decomposer microorganisms

Solar UV-B radiation affects litter decomposition in terrestrial ecosystems via several mechanisms including direct effects on microbes and abiotic photochemistry (photodegradation), as well as through indirect effects mediated through alterations in leaf chemistry (Fig. 3; Barnes et al.[19]) These mechanisms can interact with one another and multiple pathways of decomposition can occur within a given process (see below). These processes are difficult to differentiate under field conditions. Hence, the quantitative importance of individual effects is largely unknown. In general, UV-B radiation tends to have negative effects on the growth, survival, and reproduction of microbes, which then retards rates of decomposition (Fig. 3; see also[12, 19, 134]). However, microbial species vary in their sensitivity to UV-B radiation, as evidenced by studies demonstrating insensitivity of certain bacterial and fungal species to UV-B radiation in extreme environments.[4, 127] Consequently, the overall effect of solar UV radiation (UV-B + UV-A) on the community composition of microbial decomposers is complex[68, 106] and requires a multi-criteria approach.

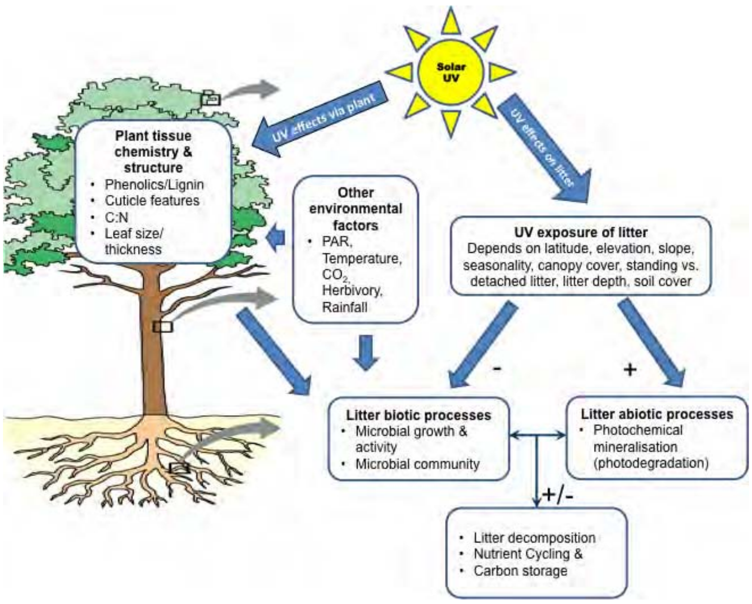

Fig. 3. Conceptual model of the direct and indirect effects of solar UV radiation (290-400 nm) on decomposition of terrestrial leaf litter, including potential interactions with other environmental factors. The total exposure to UV radiation of litter will depend on a combination of climatic, landscape/vegetation and species-specific factors. UV radiation generally reduces rates of biotic decomposition, whereas abiotic processes tend to enhance decomposition. Both processes exhibit distinct wavelength sensitivities (as seen from action spectra) depending on the underlying chromophores and mechanisms involved. Indirect effects of UV radiation are primarily mediated by those on leaf chemistry and structure, leading, e.g., to decreasing attractiveness of the litter for decomposing microbes. The role played by UV radiation on decomposition can depend also on other environmental factors interacting with biotic and abiotic processes and leaf chemistry and structure. The net effect of solar UV radiation on rates of decomposition, nutrient cycling and carbon storage will depend on the combined effects of biotic and abiotic processes and may be positive, negative or neutral. PAR, photosynthetically active radiation (400-700 nm).

UV radiation and photodegradation of litter

The abiotic process of photodegradation occurs via photochemical mineralisation of photo-reactive compounds, such as lignin, and/or the transformation of compounds as a result of UV-induced formation of reactive oxygen species and other intermediates.[9, 71] In addition, apparent photodegradation is enhanced in the presence of oxygen but can also occur under anoxic conditions,[76] indicative of involvement of multiple chemical pathways.[71] Generally, rates of photodegradation tend to increase with increasing moisture content of litter[122, 131] and air temperatures.[76]

The effects of UV radiation on biotic (microbial) and abiotic (photodegradation) processes are not entirely independent and there is evidence that photodegradation can modify or partially degrade compounds in ways that enhance or retard subsequent microbial decomposition of litter (i.e. "photopriming"[50, 85]) Thus, even when direct photodegradation has a minor effect on loss of mass of litter , subsequent biological turnover can be positively correlated with the length of prior exposure to radiation.[50] Photopriming may be of particular importance in the 'conditioning' of litter prior to its detachment from living vegetation (i.e. 'standing litter'; Fig. 4) and incorporation into the soil.[9] However, photopriming can enhance carbon mineralisation from organic matter at the soil surface.[89] In addition, susceptibility to photopriming will vary among plant species. Future photopriming experiments with multiple species in field situations are needed to assess whether this is a frequent or important facet of the photodegradation processes.

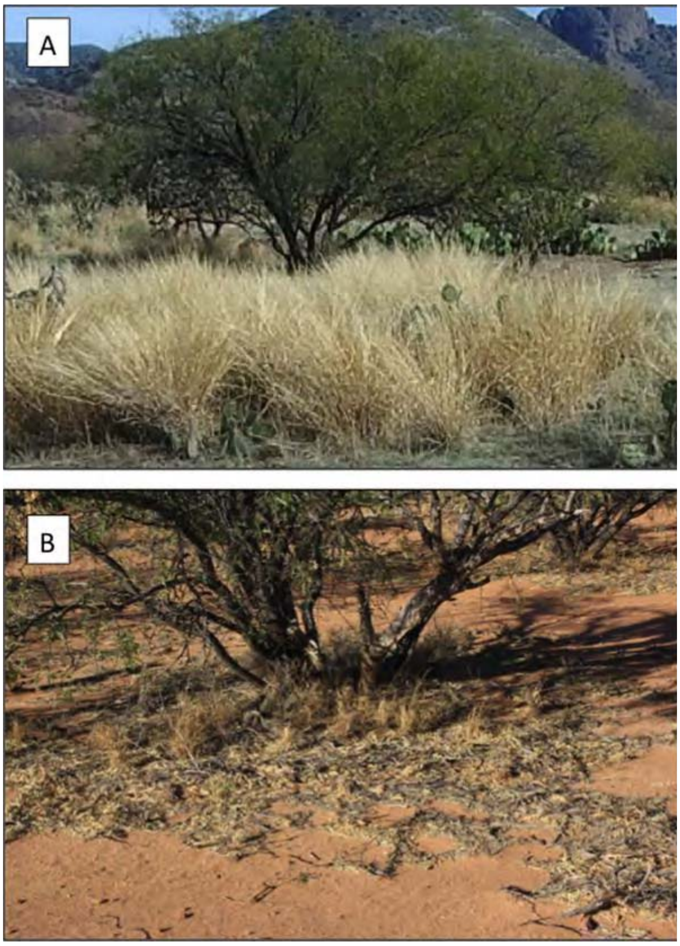

Fig. 4. Temporal and spatial aspects of litter production and distribution in a semi-desert savanna in the Sonoran Desert, southern Arizona, USA. **A.** End-of-growing season standing litter of the C4 grass, *Heteropogon contortus* with the winter-deciduous shrub, *Prosopis velutina* before leaf drop. At this time of year there is significant potential for photodegradation of the standing litter of the grass. **B.** Spatial variation in bare ground, surface litter accumulation and light conditions under and near a *P. velutina* canopy after leaf drop and prior to the onset of the growing season. Once litter reaches the ground it can be redistributed across the landscape and mixed with soil such that microbial-driven decomposition increases while photodegradation decreases (Photograph: S. Archer).

Effects of UV radiation on decomposition mediated by plants

Solar UV-B radiation can alter the chemistry and structure of living plant tissue, which then makes subsequent litter less suitable for the growth of decomposing microbes (Fig. 3;[19, 134]). These UV-induced changes in plant tissue chemistry generally involve stimulation of production of phenolic compounds that function in protection of plants against UV radiation,[3, 124] although concentrations of other chemical constituents (e.g., C, N, P, K, lignin, C:N) can change as well.[134] UV-B-induced changes in leaf chemistry need further evaluation for their potential role in photodegradation.

Interactive effects of UV radiation, climate and vegetation on decomposition

Photodegradation results in the efflux of a number of gases, including CO_2,[25, 76] CH_4,[23, 95] carbon monoxide (CO),[76, 122] and nitrous oxide (N_2O).[50] Analyses suggest that photodegradation of surface litter can have measurable effects on landscape-level rates of flux of CO_2, and ultimately carbon storage.[25, 120] The potential therefore exists for significant involvement of UV-driven photodegradation in influencing atmospheric CO_2 levels and carbon sequestration, at least in certain ecosystems. The magnitude of these effects, however, is at present uncertain.

Under field conditions, the effects of UV-B radiation on microbial decomposition and photodegradation usually occur simultaneously, such that the net impact of UV-B radiation will reflect the balance of the biotic and abiotic mechanisms[19, 131] (Fig. 3). Consequently, UV-B radiation can have a positive, negative or neutral effect on decomposition, depending on environmental conditions and quality of litter. Under dry conditions, exposure to UV-B radiation tends to increase decomposition via photodegradation. In contrast, where litter is exposed to UV-B radiation under moist conditions, rates of decomposition of litter generally decrease. This could reflect inhibition of microbial activity by the UV-B radiation. Results from a recent meta-analysis of 93 field and laboratory studies conducted across six biomes (natural environmental communities), revealed the complex role of UV-B radiation in decomposition of litter.[133] These investigators reported that the direct effects of elevated and ambient UV-B radiation tended to increase rates of decomposition (7 to 23%). However, the indirect effects (i.e. plant-mediated effects) were variable in magnitude and direction (-7 to 12%) depending on exposure to UV radiation. None of these positive and negative changes were statistically significant, however. Overall, the effects of UV-B radiation on litter decomposition are influenced by exposure to UV-B radiation, climatic factors (temperature and precipitation), and litter chemistry. While these findings are generally consistent with our understanding of the role of UV-B radiation on decomposition rates, they do indicate that detecting a statistically significant effect of UV-B radiation on decomposition of litter may be often difficult within the limits of field experiments.

In arid and semi-arid climates (referred to as dryland ecosystems), UV-B radiation has significant and measurable impacts on decomposition (Fig. 4). These ecosystems typically receive large solar UV radiation fluxes at ground level, high temperatures, and low and highly variable precipitation - conditions that tend to shift the balance of effects of UV-B radiation on decomposition in favour of abiotic photodegradation processes. Photodegradation is now being considered as an important process affecting carbon cycling and storage in these systems. However, most studies in drylands have not explicitly considered factors that routinely alter the exposure of litter to UV radiation (e.g., litter depth, soil-litter mixing and litter movement across the landscape). While such studies may reasonably determine decomposition of attached standing plant litter, their extrapolation to decomposition of detached plant litter on soil surfaces fails to account for these factors that can strongly mediate or even negate the abiotic effects. Thus, use of more realistic field conditions in experiments would serve to increase understanding and allow a more rigorous quantification of the role of solar UV-B and UV-A radiation on decomposition of litter and biogeochemistry. In general, these findings highlight the linkages between changes in UV-B radiation, climate, and land-cover and suggest that these may alter the magnitude and even the direction of the effect of UV-B radiation on decomposition in terrestrial ecosystems.

It is evident that the degree of photodegradation varies with plant species and chemical composition of the litter.[76, 149] A meta-analysis of data from 50 field studies largely from dryland ecosystems[71] showed that loss of mass due to photodegradation alone is, on average, 23%, but considerable variation occurs in rates among and within study sites. The variation in photodegradation was related to structural and chemical attributes of litter (area:mass and C:N ratios but not lignin content), precipitation, and exposure to solar radiation. This suggests that photodegradation may be an important but historically overlooked mechanism of decomposition in these systems and may account for the discrepancies between measured rates of decomposition and those predicted from ecosystem models based largely on climatic factors (temperature and precipitation) and initial litter quality.[2, 8, 71, 105] However, the role of the UV-B radiation component may be less effective than that of short wavelength visible radiation, as suggested by the meta-analysis of King et al.[71] although more evidence is needed to confirm this.

Elevated UV-B radiation and deposition of N also affect decomposition of plant litter, an important aspect of nutrient cycling (see Chapter 5). A field experiment in China showed that the combination of UV radiation and N deposition markedly increased the rate of litter decomposition under bamboo stands.[132] Also, loss of carbon, phosphorus, and lignin degradation were promoted. Nitrogen deposition changes the availability of N in soil as well as the enzymatic activity of soil microbes such that increasing N can stimulate decomposition of litter. In contrast, enhanced UV-B radiation may decrease release of N from plant litter, probably through a direct effect on the microbial decomposers. Opposite outcomes of the effects of UV-B radiation and deposition of N have also been documented where the type of litter and ambient environmental conditions differ.[132]

UV radiation, soil organisms and belowground processes

Previous assessments have reported that although UV radiation does not penetrate soil to any great extent, a variety of soil-dwelling organisms and processes below ground can be modified indirectly via the effects of UV radiation on plants and on plant litter. This occurs through UV-B-induced alterations in chemistry of the leaf, which in turn can affect the physiology and composition of species of decomposer microorganisms (bacteria and fungi) in soil. There is considerable variation in these responses, depending on species, ecosystem type and developmental stages of the associated plants.[12, 16, 31]

While certain compounds in roots, such as flavonoids, can change in response to aboveground exposure of plants to UV-B radiation,[77] a number of interactions in the soil immediately around root systems (rhizosphere) are mediated by flavonoids present in exudates of roots.[34] These include signalling between root and *Rhizobium* (N-fixing bacteria), mycorrhizal infection, and plant-plant allelochemistry (release of biochemicals by plants that may be harmful or beneficial, i.e. allelopathy).[59] Solar UV radiation has been implicated in playing a role in altering competitive interactions between invasive and native plant species by increasing the negative allelopathic effects of exotic species on native species.[35] In field studies,[129] exclusion of solar UV radiation significantly increased root growth, root nodulation, nitrogenase activity, and the leghaemoglobin and hemechrome contents in root nodules, suggesting a negative effect on fixation of nitrogen in certain species under ambient levels of solar radiation. The potential exists for significant modifications in soil invertebrate communities in Antarctic and Arctic ecosystems currently experiencing appreciable ozone depletion and climate change. Reduction in herbivory by insects under solar UV-B radiation would be expected to be driven largely by differences arising from plant biochemistry and composition of vegetation rather than by direct effects of elevated UV-B radiation on these organisms.[100] Although additional studies are clearly needed, these findings suggest a role for UV-B radiation in several belowground processes, which would have important consequences for mineral-nutrition of plants, storage of carbon in soil, biogeochemical cycles, and composition of plant species.

Implications of UV-induced changes in plant defence systems

Exposure of plants to solar UV-B radiation leads to an increase in several secondary metabolites that play a key role in the interactions of plants with other organisms, including herbivorous insects and microbial pathogens (Paul et al.[106]; reviewed in Ballaré et al.[11]). Reduction in herbivory in insects exposed to solar UV-B radiation is well documented in field-grown plants[12] with the majority (>80%) of such studies reporting increases in plant damage or insect growth when solar UV-B radiation is experimentally reduced.[13, 74] Direct avoidance of UV radiation by many insects partly accounts for the reduction in herbivory.[91, 92] There are also some indications that, under ambient levels of UV-B radiation, infection of plants by pathogens is reduced.[43, 56] Pretreatment of plants with UV-B radiation before inoculation with a pathogen can also increase resistance to infection.[43]

Some of the increased production of secondary metabolites by UV-B radiation that boost plant defenses against pests include leaf phenolics,[43, 116, 162] conjugated polyamines,[42] diterpenes[44] and, in some cases, defense-related proteins such as proteinase inhibitors.[42, 65, 136] On the other hand, phenolic compounds induced by UV-A radiation, may modulate the responses to UV-B radiation, via complex interactions between the UV-B photoreceptor, UVR8[66, 113] and UV-A/blue light signalling pathways.[97] The functional relationships between UV-B radiation and resistance of plants to pests [involving salicylic acid (SA) and jasmonic acid (JA) pathways] are not yet well characterised (for review, see Ballaré et al.[11]), although there is increasing evidence that some of the effects of UV-B radiation on resistance of plants to herbivory are mediated by increased JA signalling.[42, 44] In addition, UV-B radiation can affect plant defense against herbivores and pathogens via mechanisms that are not mediated by JA. For example, UV-B radiation, acting through UVR8, increases resistance of certain plants to the necrotrophic fungus *Botrytis cinerea*, and this effect is conserved in JA-insensitive genotypes.[43]

Protection and acclimation

Apart from plant defense mechanisms that protect against pests and disease, other UV-acclimative processes involving accumulation of UV-absorbing compounds that result in changes in plant optical properties (primarily epidermal transmittance Ballaré, et al.[12] and references therein). This acclimative response varies according to a wide range of prevailing conditions including geographical and temporal, as well as with plant morphology (e.g., Ruhland et al.[119]) and increases understanding of the capacity of plants to respond to changing levels of UV radiation. Examples of dynamic acclimation include that of mature shade leaves of *Populus tremuloides* and *Vicia faba* where epidermal transmittance of UV radiation decreases when plants are transferred to sunny environments. Sun leaves, on the other hand, do not immediately respond by decreasing UV-absorbing pigments upon transfer to shade conditions.[18] This ability to increase but not decrease transmittance of UV radiation rapidly may be associated with the location of the UV-absorbing compounds. Compounds bound to cell walls are less likely to be re-mobilised than those inside the cell.[36, 115]

Plants may also rapidly adjust their mechanism of UV-protection in response to daily changes in UV irradiances. Protection against UV radiation increases from dawn to midday and then decreases towards sunset.[17] How plants achieve these rapid changes and what the significance is for function beyond protection from UV radiation is not yet known. Increased allocation of carbon to UV-absorbing compounds may divert carbon from growth and photosynthetic functions,[138] such that reducing UV protection during times of the day when levels of UV radiation are small could enhance daily gain of carbon. In comparison to plants that maintain high UV protection throughout the day, plants that exhibit diurnal changes in epidermal UV transmittance experience increased UV radiation exposure to the underlying mesophyll both early and late in the day but not at midday. It is possible that increased penetration of UV radiation at these times may protect leaves from photoinhibition that can occur at midday.[155] Since UV-A radiation can also drive photosynthesis,[144] the increased penetration of UV-A radiation may enhance photosynthesis at times of the day when leaves are light-limited. Added to this, several of the compounds induced by UV radiation (e.g., quercetin, kaempferol) inhibit the plant growth regulator, auxin, and its transport within the plant.[48] Thus, maintaining high concentrations of flavonoids could interfere with plant growth during night-time periods. Although the processes of acclimation of plants to UV radiation are complex, it is now clear that the UV-absorbing acclimation involving UV-absorbers is much more flexible and dynamic than previously thought and has implications for evaluation of plant hardiness under different environmental conditions.

Revisiting the potential for reconstructing past variations in stratospheric ozone and UV-B radiation

The relationships between ozone and climate change are complex_ENREF_11 (see Chapter 1) and further investigation of the past nature of these relationships will lead to a better understanding of the physical interactions among solar activity, ozone and climate as well as more clarity on how ecosystems respond to changing UV-B radiation.[86] The near ubiquitous response of plants to produce chemically stable UV-absorbing compounds, and thus achieve protection from UV-B radiation, means that plant tissues preserved in herbaria and in sedimentary and ice-core archives can be used to reconstruct past variations (prior to the instrumental period) in stratospheric ozone and UV-B radiation.[81, 82, 118] In particular, UV-absorbing compounds bound to cell walls of plant tissues are extremely stable[37] and may even persist in fossils.[82, 118] In addition to tracking past UV-B radiation, plant material is increasingly being assessed for its usefulness as a biological proxy for historical availability of water ,[117] temperature, and concentration of CO_2 in the atmosphere (reviewed in Jordan[67]). Spores and pollen are common in the fossil record, and thus this type of proxy enables reconstruction of past UV-B radiation for providing spatial and temporal fidelity.[81]

UV-absorbing compounds (e.g., p-coumaric acid) in cell walls vary with latitude (and estimated exposure to UV-B radiation) in both spores of club mosses and in pine pollen. Greater variation is observed in samples collected from polar regions, where UV-B radiation has varied in recent decades due to ozone depletion, than in those collected from the tropics, where UV radiation levels have remained relatively stable.[82, 159] Similarly, UV-absorbing compounds in these same tissues show good temporal correlations with independent instrumental records and model results, allowing reconstruction of ozone concentration and flux of UV-B radiation over decades[82] to millennia.[159] However, further validation of proxies using UV-absorbing compounds requires development of UV radiation dose–response curves, as well as confirmation of the long-term chemical stability of the UV-absorbing compounds within paleobiological samples.[118]

Methodological advances, especially in microspectroscopy,[81, 82, 159] allow analysis of very small samples (e.g., 50 grains of pine pollen). Such micro-scale analysis would also permit UV-absorbing compounds to be tracked down the length of shoots of slow growing individual plants such as polar mosses.[37, 117] Proxies that provide concurrent information on past climate and UV-B radiation, over centuries to millennia, would be especially valuable for greater understanding of past polar environments.

Implications of exposure to UV radiation and climate interactions for food production and food quality

Given the way in which solar UV radiation, stratospheric ozone, and climate variables have multiple and often interdependent effects on terrestrial and agricultural systems, it is logical that these effects will modify development, production and crop quality of agricultural crops.[58, 123, 153, 156] However, there are currently few studies focusing on the interplay of climatic variables on crop quality.[123, 156] In contrast, many studies have reported both negative and positive effects of UV radiation and other climate variables on crop production. The type of response in the crop is largely dependent upon species and cultivar, geographical location, genetic differences, and the co-occurring environmental conditions (cf.[12, 79, 156]). Where UV-B radiation has had a negative effect on crop production, this has been manifested mainly as small decreases in biomass, and reduced leaf area (Ballaré et al.[12] and references therein). As noted in previous sections, there are also indirect effects of UV-B radiation on plant growth, such as decreased herbivory due to increased secondary metabolites such as phenols, which is a positive plant effect. [90, 106, 162]

Many investigations have documented changes in biochemical and regulatory pathways in plants under ambient and enhanced UV-B radiation, although few studies have explicitly related these to follow-on effects on quality of food crops.[123, 156] The UV-stimulated biochemical changes also contribute to differences in taste and aroma in e.g., herbs, such as mints.[46] Several field studies have shown that ambient UV-B radiation increases concentrations of chemical e.g., flavonols, esters and fatty acids, which can enhance the aroma and flavour of wine.[32, 53, 137] Terpene emission from grapes also increases with enhanced UV-B radiation and may be another modifier of quality.[52]

In general, a number of stress factors, including UV radiation, tend to increase the concentrations of proteins and antioxidants and reduce those of starch and lipids.[21, 153] While these biochemical changes often reflect acclimative response of plants to enhanced levels of UV radiation and other environmental stresses, they may have either positive or negative consequences for quality of crops in terms of nutrition and commercial use for specific products.

The degree to which plants can modulate acclimative response to often rapid changes in UV radiation is also of interest for agricultural and horticulture practices. A lag in this response has implications for UV susceptibility of crops that are propagated in low UV radiation environments (e.g., greenhouses) and then subsequently transplanted to the field. This is illustrated by growth chamber studies with lettuce (*Lactuca sativa*), where new developing leaves require at least 6-8 days to fully acclimate to UV-B radiation and high levels of visible light (PAR, photosynthetically active radiation, 400-700 nm).[155, 157]

In terms of the beneficial effects of UV radiation on food crops, increased exposure to UV radiation through, for example, land-use changes and climate change, as well as manipulations of controlled growth conditions can be exploited to enhance food quality and nutritional value through the induced changes in secondary metabolism of plants.

Visual sensitivity to and damage from UV radiation in terrestrial animals

The range of wavelengths an animal perceives depends on the spectrum available in the environment, the degree to which this is transmitted through the ocular media and the visual pigments found in the retina. Visible light represents the spectrum perceived by humans but other animals often see a different range of "colours" due to visual pigments absorbing elsewhere in the spectrum. UV-vision is used extensively by a wide range of invertebrates and vertebrates for critical life processes including mate selection and location of food resources in birds, fish, insects, spiders, and other taxa. Some invertebrates are specifically able to detect and respond to UV-B radiation under natural conditions.[91] The recent discovery that UV-vision (>300 nm) in mammals may be more widespread than previously recognised, suggests the need for more research into the ecological significance of this finding (Douglas and Jeffery[47], and references therein).

As with humans, animals can develop UV-related diseases, although research on these topics tends to be concentrated on economically important animals such as cattle. The occurrence of ocular squamous cell carcinoma (OSCC) or "cancer eye" has been reported in cattle worldwide, with 10-20% of animals in some Australian herds diagnosed with this disease. OSCC is the most common malignant tumour affecting cattle in North America and is responsible for significant economic losses (estimate of $20 million per annum in the United States alone; reviewed in Tsujita and Plummer[142]). In 2002, OSCC was the third-leading cause of carcass condemnation at slaughterhouses inspected by the US Department of Agriculture. European breeds of cattle, particularly those with light coloured skin such as Herefords and white-faced Holstein breeds, commonly develop OSCC, particularly when they are raised in regions with high natural levels of UV-B radiation (e.g., Australia, and the south-western USA); see also Ballaré et al.[12] While a proportion of the disease might be related to increasing UV radiation in areas affected by ozone depletion, the bulk appears to be caused by agricultural practices (e.g., lack of shade) and the movement of animals traditionally bred in low UV-B radiation environments to latitudes with higher UV-B radiation.

Progress in technical and experimental issues

Methodological issues in UV radiation supplementation studies, where filtered fluorescent UV lamps do not have a spectral output that perfectly matches the solar spectrum, were discussed previously.[12] Briefly, Biological Spectral Weighting Functions (BSWF), dimensionless factors that represent the relative effectiveness of the different wavelengths of UV radiation in influencing a particular biological response, are used to calculate "biologically effective" UV radiation (see Chapter 1). This has been the only way to compare artificial UV radiation levels in experiments with solar UV radiation.

A new filter termed the urate anion liquid filter has been developed that permits fluorescent UV lamps to much more closely approximate sunlight.[121] This new filter removes more of the shortwave UV-B radiation ($\lambda \leq 305$nm) than traditional cellulose diacetate filters and transmits more longwave UV-B ($\lambda \geq 310$ nm). While this filter was developed for laboratory use in algal studies, there is potential for it to be adapted to other systems.

Accurate measurement of UV radiation is an essential aspect of experimental work on effects of UV radiation (see Chaper 1). Ideally these measurements are done with a spectroradiometer, where radiation is quantified at discrete wavelengths. Usually, double-grating spectroradiometers are used for these measurements, where two gratings are linked in tandem to refine the signal sent to the detector. This double-grating system reduces "stray light" in the instrument. For example, a small amount of stray visible radiation could swamp radiation of a UV-B wavelength being measured. An instrumentation innovation that is rapidly supplementing the mechanical double-grating spectroradiometer is the diode-array spectroradiometer. This instrument has no moving parts and can produce a spectral irradiance measurement almost instantaneously. In contrast, typical mechanical double-grating units require several minutes to complete a scan, during which irradiation conditions can change.

Since diode-array spectroradiometers are much less costly than double-grating units, they may often replace broadband UV detectors in experimental studies. These spectral irradiance data will be much more valuable than the broadband measurements. The unit's small size and portability is also an asset. However, they have limitations that users need to take into account. Stray light is a considerable issue as these are basically single-grating spectroradiometers. Some features of the instrument can help minimise this problem, but measurements in full sunlight may still not be accurate. These issues are discussed at length by Aphalo et al.[6] and references therein.

Sensitivity of instruments to temperature is also an issue, especially when conducting measurements in the field. A 15% change in the sensitivity of a double-grating spectroradiometer over the range of 11.5 to 33.5 °C can occur.[10] Temperature also affects diode-array units as wavelength accuracy, dark current offset, and spectral responsivity are all influenced by temperature.[125] It is possible in some cases to develop correction algorithms for particular units (e.g., Baczynska et al.[10]), although one must consider whether differential heating of the unit in direct intense sunlight can be adequately simulated in a test chamber. Ideally spectroradiometers used in measuring sunlight should be temperature stabilised.

Some ecological studies require measurements of time-integrated biologically effective UV radiation in environments where there is considerable spatial variability in UV irradiance (e.g., within plant canopies, soil surfaces under plant canopies and others). These applications require deployment of a number of inexpensive devices to measure the UV radiation. UV-absorbing polymers that were originally developed as human UV dosimeters (see Chapters 1 and 2) have been used to characterise the UV radiation environment of individual leaves in canopies,[103] as well as to quantify fine-scale differences in exposure of plants to UV radiation in heterogeneous habitats.[102] While these devices are no substitute for spectroradiometers, they can provide useful and inexpensive estimates of exposures to UV radiation for certain applications.[126] Current polymers have wavelength sensitivities similar to common plant biological weighting functions[29, 148] and have been developed with the inclusion of neutral density filters allowing estimates of exposure to UV radiation over periods of days to weeks.[104] Provided these dosimeters are calibrated against spectroradiometers at the field locations where they are to be deployed, they may have particular utility for decomposition studies and those in areas under the ozone 'hole' where long-term continuous measurement of the incident UV radiation on standing and ground level plant litter is needed.

Increased attention needs to be given to developing techniques and approaches that allow for the determination of realistic exposures to UV radiation of individual plants, natural ecosystems, and agricultural environments. The spectral sensitivities and exposures to UV radiation are needed in models that evaluate the combined effects of changes in UV radiation, climate, and vegetation on terrestrial ecosystems. The numerous technical issues involved in conducting experiments with UV radiation can, however, be intimidating to researchers starting work in this field. A comprehensive guide to all aspects of experimental design, implementation, analysis and instrumentation by Aphalo et al.[6] will help standardize protocols and ensure reliable results that can be meaningfully assessed.

Gaps in knowledge

Since the last assessment,[12] evidence of the coupling of ozone depletion effects and those of climate change[158] has been strengthened, and has revealed the complexity of the interactions that are occurring. The success of the Montreal Protocol has been two-fold, viz., the phasing out of ozone depleting substances (ODS) and the contribution to decreasing some of the load of greenhouse gases, since many of the phased out ODS are themselves greenhouse gases. It should also be recognised that exposure to changing levels of UV radiation is not only ozone-dependent, but also reflects changes in land-use and climate-related phenomena, such as projected changes in rainfall, increased cloud cover in some regions, and snow and ice melting. These events are likely to affect ecosystem functioning and food production, all of which calls for a holistic approach to research that encompasses the role of UV radiation within a rapidly changing environment. From the research to date, evidence is accumulating that these interlinking factors of UV radiation, changes in ozone, climate, and environment are modifying responses of plants and ecosystems. Further evaluation of where the potential tipping points or beneficial effects are occurring will increase our understanding and ability to project potential future effects from the interactions between exposure to UV radiation and other simultaneously occurring environmental stresses. Currently, our knowledge of the consequences for the biosphere is far from comprehensive. What has become clear is that an integrative research approach under realistic conditions is essential for future projections of the response of ecosystems. For many of the processes discussed in this present paper, more empirical evidence is needed to determine the ecological significance of the role played by UV-B radiation in the presence of other environmental stresses.

Apart from the focus on UV radiation over more than 25 years of the Montreal Protocol, ozone depletion has been implicated in changes to the climate of the Southern Hemisphere, highlighting the need to assess the impact of such changes on the ecosystems of this region.[114] One of the key uncertainties here is the extent to which climate is affected by ozone depletion versus greenhouse gas forcing and particularly the seasonality of these effects. Resolving this will improve understanding of how ozone recovery will feed back on these climate processes and is vital to our ability to model future ecosystems across half of the globe.

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References

1 Abram NJ, Mulvaney R, Vimeux F, Phipps SJ, Turner J and England MH, 2014, Evolution of the Southern Annular Mode during the past millennium, *Nature Clim. Change*, **4**, 564-569.

2 Adair EC, Parton WJ, Del Grosso SJ, Silver WL, Harmon ME, Hall SA, Burke IC and Hart SC, 2008, Simple three-pool model accurately describes patterns of long-term litter decomposition in diverse climates, *Glob. Change Biol.*, **14**, 2636-2660.

3 Agati G, Brunetti C, Di Ferdinando M, Ferrini F, Pollastri S and Tattini M, 2013, Functional roles of flavonoids in photoprotection: New evidence, lessons from the past, *Plant Physiol. Biochem.*, **72**, 35-45.

4 Alharbi SA, 2012, How do bacteria survive UV irradiation in the stratosphere?, *J. Food Agric. Environ.*, **10**, 843-845.

5 Althoff F, Jugold A and Keppler F, 2010, Methane formation by oxidation of ascorbic acid using iron minerals and hydrogen peroxide, *Chemosphere*, **80**, 286-292.

6 Aphalo PJ, Albert A, Björn LO, McLeod A, Robson TM and Rosenqvist E, 2012, Beyond the visible: A handbook of best practice in plant UV photobiology, in *COST Action FA0906 UV4growth*, University of Helsinki, Department of Biosciences, Division of Plant Biology, Helsinki, Finland, p. 176.

7 Archibald AT, Levine JG, Abraham NL, Cooke MC, Edwards PM, Heard DE, Jenkin ME, Karunaharan A, Pike RC, Monks PS, Shallcross DE, Telford PJ, Whalley LK and Pyle JA, 2011, Impacts of HOx regeneration and recycling in the oxidation of isoprene: Consequences for the composition of past, present and future atmospheres, *Geophys. Res. Lett.*, **38**, GL046520.

8 Austin AT, 2011, Has water limited our imagination for aridland biogeochemistry?, *Trend. Ecol. Evol.*, **26**, 229-235.

9 Austin AT and Ballaré CL, 2010, Dual role of lignin in plant litter decomposition in terrestrial ecosystems, *Proc. Nat. Acad. Sci. USA.*, **107**, 4618-4622.

10 Baczynska K, O'Hagan JB, Pearson AJ and Eriksen P, 2011, Temperature Correction of UV Spectral Solar Measurements for ICEPURE Project, *Photochem. Photobiol.*, **87**, 1464-1467.

11 Ballaré CL, 2014, Light regulation of plant defense, *Annu. Rev. Plant Biol.*, **65**, 335-363.
12 Ballaré CL, Caldwell MM, Flint SD, Robinson SA and Bornman JF, 2011, Effects of solar ultraviolet radiation on terrestrial ecosystems. Patterns, mechanisms, and interactions with climate change, *Photochem. Photobiol. Sci.*, **10**, 226-241.
13 Ballaré CL, Mazza CA, Austin AT and Pierik R, 2012, Canopy Light and Plant Health, *Plant Physiol.*, **160**, 145-155.
14 Bandurska H and Cieslak M, 2013, The interactive effect of water deficit and UV-B radiation on salicylic acid accumulation in barley roots and leaves, *Environ. Exp. Bot.*, **94**, 9-18.
15 Bandurska H, Niedziela J and Chadzinikolau T, 2013, Separate and combined responses to water deficit and UV-B radiation, *Plant Sci.*, **213**, 98-105.
16 Bao X, Li Q, Hua J, Zhao T and Liang W, 2014, Interactive effects of elevated ozone and UV-B radiation on soil nematode diversity, *Ecotoxicol.*, **23**, 11-20.
17 Barnes PW, Flint SD, Slusser JR, Gao W and Ryel RJ, 2008, Diurnal changes in epidermal UV transmittance of plants in naturally high UV environments, *Physiol. Plant.*, **133**, 363-372.
18 Barnes PW, Kersting AR, Flint SD, Beyschlag W and Ryel RJ, 2013, Adjustments in epidermal UV-transmittance of leaves in sun-shade transitions, *Physiol. Plant.*, **149**, 200-213.
19 Barnes PW, Throop HL, Archer SR, Breshears DD, McCulley RL and Tobler MA, 2015, Sunlight and soil-litter mixing: Drivers of litter decomposition in drylands, *Prog. Botany*, **76**, 273-302.
20 Barnes PW, Throop HL, Hewins DB, Abbene ML and Archer SR, 2012, Soil coverage reduces photodegradation and promotes the development of soil-microbial films on dryland leaf litter, *Ecosystems*, **15**, 311-321.
21 Berli FJ, Alonso R, Bressan-Smith R and Bottini R, 2013, UV-B impairs growth and gas exchange in grapevines grown in high altitude, *Physiol. Plant.*, **149**, 127-140.
22 Bernal M, Llorens L, Badosa J and Verdaguer D, 2013, Interactive effects of UV radiation and water availability on seedlings of six woody Mediterranean species, *Physiol. Plant.*, **147**, 234-247.
23 Bloom AA, Lee-Taylor J, Madronich S, Messenger DJ, Palmer PI, Reay DS and McLeod AR, 2010, Global methane emission estimates from ultraviolet irradiation of terrestrial plant foliage, *New. Phytol.*, **187**, 417-425.
24 B. ning C, Dispert A, Visbeck M, SR R and Schwarzkopf F, 2008, The response of the Antarctic Circumpolar Current to recent climate change *Nature Geosci.*, **1**, 864-869.
25 Brandt LA, Bohnet C and King JY, 2009, Photochemically induced carbon dioxide production as a mechanism for carbon loss from plant litter in arid ecosystems, *J. Geophys. Res. Biogeosci.*, **114**, G02004.
26 Bruhn D, Mikkelsen TN, Rolsted MMM, Egsgaard H and Ambus P, 2014, Leaf surface wax is a source of plant methane formation under UV radiation and in the presence of oxygen, *Plant Biol.*, **16**, 512-516.
27 Bruhn D, Møller IM, Mikkelsen TN and Ambus P, 2012, Terrestrial plant methane production and emission, *Physiol. Plant.*, **144**, 201-209.
28 Bussotti F, Ferrini F, Pollastrini M and Fini A, 2014, The challenge of Mediterranean sclerophyllous vegetation under climate change: From acclimation to adaptation, *Environ. Exp. Bot.*, **103**, 80-98.
29 Caldwell MM, 1971, Solar UV irradiation and the growth and development of higher plants, *Photophysiology*, **6**, 131-177.
30 Caldwell MM, Björn LO, Bornman JF, Flint SD, Kulandaivelu G, Teramura AH and Tevini M, 1998, Effects of increased solar ultraviolet radiation on terrestrial ecosystems, *J. Photochem. Photobiol. B.*, **46**, 40-52.
31 Caldwell MM, Bornman JF, Ballaré CL, Flint SD and Kulandaivelu G, 2007, Terrestrial ecosystems, increased solar ultraviolet radiation, and interactions with other climate change factors, *Photochem. Photobiol. Sci.*, **6**, 252-266.
32 Carbonell-Bejerano P, Diago MP, Martinez-Abaigar J, Martinez-Zapater JM, Tardaguila J and Nunez-Olivera E, 2014, Solar ultraviolet radiation is necessary to enhance grapevine fruit ripening transcriptional and phenolic responses, *BMC Plant Biol.*, **14**, 183.
33 Cataldo M, Evangelista H, Simoes JC, Godoi RHM, Simmonds I, Hollanda MH, Wainer I, Aquino F and Van Grieken R, 2013, Mineral dust variability in central West Antarctica associated with ozone depletion, *Atmos. Chem. Phys.*, **13**, 2165-2175.
34 Cesco S, Neumann G, Tomasi N, Pinton R and Weisskopf L, 2010, Release of plant-borne flavonoids into the rhizosphere and their role in plant nutrition, *Plant and Soil*, **329**, 1-25.
35 Chen S, Xiao S and Callaway RM, 2012, Light intensity alters the allelopathic effects of an exotic invader, *Plant Ecol. Divers.*, **5**, 521-526.
36 Clarke LJ and Robinson SA, 2008, Cell wall-bound ultraviolet-screening compounds explain the high ultraviolet tolerance of the Antarctic moss, *Ceratodon purpureus*, *New. Phytol.*, **179**, 776-783.

37 Clarke LJ, Robinson SA, Hua Q, Ayre DJ and Fink D, 2012, Radiocarbon bomb spike reveals biological effects of Antarctic climate change, *Glob. Change Biol.*, **18**, 301-310.
38 Comont D, Martinez Abaigar J, Albert A, Aphalo P, Causton DR, Figueroa FL, Gaberscik A, Llorens L, Hauser M-T, Jansen MAK, Kardefelt M, de la Coba Luque P, Neubert S, Núñez-Olivera E, Olsen J, Robson M, Schreiner M, Sommaruga R, Strid Å, Torre S, Turunen M, Veljovic-Jovanovic S, Verdaguer D, Vidovic M, Wagner J, Winkler JB, Zipoli G and Gwynn-Jones D, 2012, UV responses of *Lolium perenne* raised along a latitudinal gradient across Europe: a filtration study, *Physiol. Plant.*, **145**, 604-618.
39 Convey P, Bindschadler R, di Prisco G, Fahrbach E, Gutt J, Hodgson DA, Mayewski PA, Summerhayes CP and Turner J, 2009, Antarctic climate change and the environment, *Antarctic. Sci.*, **21**, 541-563.
40 Convey P, Chown SL, Clarke A, Barnes DKA, Bokhorst S, Cummings V, Ducklow HW, Frati F, Green TGA, Gordon S, Griffiths HJ, Howard-Williams C, Huiskes AHL, Laybourn-Parry J, Lyons WB, McMinn A, Morley SA, Peck LS, Quesada A, Robinson SA, Schiaparelli S and Wall DH, 2014, The spatial structure of Antarctic biodiversity, *Ecol. Monogr.*, **84**, 203-244.
41 Cory RM, Crump BC, Dobkowski JA and Kling GW, 2013, Surface exposure to sunlight stimulates CO_2 release from permafrost soil carbon in the Arctic, *Proc. Nat. Acad. Sci. USA.*, **110**, 3429-3434.
42 Demkura PV, Abdala G, Baldwin IT and Ballaré CL, 2010, Jasmonate-dependent and -independent pathways mediate specific effects of solar ultraviolet-B radiation on leaf phenolics and antiherbivore defense, *Plant Physiol.*, **152**, 1084-1095.
43 Demkura PV and Ballaré CL, 2012, UVR8 Mediates UV-B-Induced Arabidopsis Defense Responses against *Botrytis cinerea* by Controlling Sinapate Accumulation, *Molecular Plant*, **5**, 642-652.
44 Đinh ST, Gális I and Baldwin IT, 2013, UVB radiation and 17-hydroxygeranyllinalool diterpene glycosides provide durable resistance against mirid (*Tupiocoris notatus*) attack in field-grown *Nicotiana attenuata* plants, *Plant. Cell. Environ.*, **36**, 590-606.
45 Dixon DA, Mayewski PA, D.Goodwin I, Marshall GJ, R.Freeman, Maasch KA and Sneed. SB, 2012, An ice-core proxy for northerly air mass incursions into West Antarctica, *Int. J Climatol.*, **32**, 1455-1465:.
46 Dolzhenko Y, Bertea CM, Occhipinti A, Bossi S and Maffei ME, 2010, UV-B modulates the interplay between terpenoids and flavonoids in peppermint (*Mentha piperita* L.), *J. Photochem. Photobiol. B.*, **100**, 67-75.
47 Douglas RH and Jeffery G, 2014, The spectral transmission of ocular media suggests ultraviolet sensitivity is widespread among mammals, *Proc. R. Soc. B. Biol. Sci.*, **281**, 20132995.
48 Falcone-Ferreyra ML, Rius SP and Casati P, 2012, Flavonoids: biosynthesis, biological functions, and biotchnological applications, *Front. Plant. Sci.*, **3**, Article 222.
49 Faubert P, Tiiva P, Rinnan A, Räsänen J, Holopainen JK, Holopainen T, Kyrö E and Rinnan R, 2010, Non-methane biogenic volatile organic compound emissions from a subarctic peatland under enhanced UV-B radiation, *Ecosystems*, **13**, 860-873.
50 Foereid B, Bellarby J, Meier-Augenstein W and Kemp H, 2010, Does light exposure make plant litter more degradable?, *Plant and Soil*, **333**, 275-285.
51 Gao Q and Garcia-Pichel F, 2011, Microbial ultraviolet sunscreens, *Nature Rev. Microbiol.*, **9**, 791-802.
52 Gil M, Bottini R, Berli F, Pontin M, Fernanda Silva M and Piccoli P, 2013, Volatile organic compounds characterized from grapevine (*Vitis vinifera* L. cv. Malbec) berries increase at pre-harvest and in response to UV-B radiation, *Phytochem.*, **96**, 148-157.
53 Gregan SM, Wargent JJ, Liu L, Shinkle J, Hofmann R, Winefield C, Trought M and Jordan B, 2012, Effects of solar ultraviolet radiation and canopy manipulation on the biochemical composition of Sauvignon Blanc grapes, *Aust. J. Grape Wine Res.*, **18**, 227-238.
54 Guenther A, 2013, Upscaling biogenic volatile compound emissions from leaves to landscapes, in *Biology, controls and models of tree volatile organic compound emissions* eds.: Niinemets Ü and Monson RK, Springer, Berlin, pp. 391-414.
55 Guidi L, Degl'Innocenti E, Remorini D, Biricolti S, Fini A, Ferrini F, Nicese FP and Tattini M, 2011, The impact of UV-radiation on the physiology and biochemistry of *Ligustrum vulgare* exposed to different visible-light irradiance, *Environ. Exp. Bot.*, **70**, 88-95.
56 Gunasekera TS, Paul ND and Ayres PG, 1997, The effects of ultraviolet-B (UV-B: 290-320 nm) radiation on blister blight disease of tea (*Camellia sinensis*), *Plant Pathol. (Oxf)*, **46**, 179-185.
57 Guo X-R, Chang B-W, Zu Y-G and Tang Z-H, 2014, The impacts of increased nitrate supply on *Catharanthus roseus* growth and alkaloid accumulations under ultraviolet-B stress, *J. Plant Interact.*, **9**, 640-646.

58 Gwynn-Jones D, Jones AG, Waterhouse A, Winters A, Comont D, Scullion J, Gardias R, Graae BJ, Lee JA and Callaghan TV, 2012, Enhanced UV-B and elevated CO_2 impacts sub-Arctic shrub berry abundance, quality and seed germination, *Ambio*, **41(S3)**, 256-268.
59 Hassan S and Mathesius U, 2012, The role of flavonoids in root-rhizosphere signalling: opportunities and challenges for improving plant-microbe interactions, *J. Exp. Bot.*, **63**, 3429-3444.
60 He L, Jia X, Gao Z and Li R, 2011, Genotype-dependent responses of wheat (*Triticum aestivum* L.) seedlings to drought, UV-B radiation and their combined stresses, *Afr. J. Biotechnol.*, **10**, 4046-4056.
61 Henry HAL, Brizgys K and Field CB, 2008, Litter decomposition in a California annual grassland: Interactions between photodegradation and litter layer thickness, *Ecosystems*, **11**, 545-554.
62 Hodgson DA, Roberts D, McMinn A, Verleyen E, Terry B, Corbett C and Vyverman W, 2006, Recent rapid salinity rise in three East Antarctic lakes, *J. Paleolimnol.*, **36**, 385-406.
63 Holopainen JK and Gershenzon J, 2010, Multiple stress factors and the emission of plant VOCs, *Trends Plant Sci.*, **15**, 176-184.
64 IPCC, 2014, Climate Change 2014: Impacts, Adaptation, and Vulnerability. Contribution of Working Group II to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. WGII AR5 Summary for Policymakers., Report No., IPCC, Geneva, Switzerland, p. 44 pp
65 Izaguirre MM, Scopel AL, Baldwin IT and Ballaré CL, 2003, Convergent responses to stress. Solar ultraviolet-B radiation and *Manduca sexta* herbivory elicit overlapping transcriptional responses in field-grown plants of *Nicotiana longiflora*, *Plant Physiol.*, **132**, 1755-1767.
66 Jenkins GI, 2014, The UV-B Photoreceptor UVR8: From Structure to Physiology, *Plant Cell*, **26**, 21-37.
67 Jordan GJ, 2011, A critical framework for the assessment of biological palaeoproxies: predicting past climate and levels of atmospheric CO2 from fossil leaves, *New. Phytol.*, **192**, 29-44.
68 Kadivar H and Stapleton AE, 2003, Ultraviolet radiation alters maize phyllosphere bacterial diversity, *Micro. Ecol.*, **45**, 353-361.
69 Kang SM, Polvani LM, Fyfe JC, Son SW, Sigmond M and Correa GJP, 2013, Modeling evidence that ozone depletion has impacted extreme precipitation in the austral summer, *Geophys. Res. Lett.*, **40**, 4054-4059.
70 Keppler F, Hamilton JTG, Brass M and Rockmann T, 2006, Methane emissions from terrestrial plants under aerobic conditions, *Nature*, **439**, 187-191.
71 King JY, Brandt LA and Adair EC, 2012, Shedding light on plant litter decomposition: advances, implications and new directions in understanding the role of photodegradation, *Biogeochemistry*, **111**, 57-81.
72 Korhonen H, Carslaw KS, Forster PM, Mikkonen S, Gordon ND and Kokkola H, 2010, Aerosol climate feedback due to decadal increases in Southern Hemisphere wind speeds, *Geophys. Res. Lett.*, **37**, GL041320.
73 Kravets EA, Zelena LB, Zabara EP and Blume YB, 2012, Adaptation strategy of barley plants to UV-B radiation., *Emirates J. Food Agric.*, **24**, 632-645.
74 Kuhlmann F and Müller C, 2011, Impacts of ultraviolet radiation on interactions between plants and herbivorous Insects: A chemo-ecological perspective, *Prog. Botany*, **72**, 305-347.
75 Lau TSL, Eno E, Goldstein G, Smith C and Christopher DA, 2006, Ambient levels of UV-B in Hawaii combined with nutrient deficiency decrease photosynthesis in near-isogenic maize lines varying in leaf flavonoids: Flavonoids decrease photoinhibition in plants exposed to UV-B, *Photosynthetica*, **44**, 394-403.
76 Lee H, Rahn T and Throop HL, 2012, An accounting of C-based trace gas release during abiotic plant litter degradation, *Glob. Change Biol.*, **18**, 1185-1195.
77 Li B, Krumbein A, Neugart S, Li L and Schreiner M, 2012, Mixed cropping with maize combined with moderate UV-B radiations lead to enhanced flavonoid production and root growth in faba bean, *J. Plant Interact.*, **7**, 333-340.
78 Lin Y and King JY, 2014, Effects of UV exposure and litter position on decomposition in a California grassland, *Ecosystems*, **17**, 158-168.
79 Liu B, Liu X-B, Li Y-S and Herbert SJ, 2013, Effects of enhanced UV-B radiation on seed growth characteristics and yield components in soybean, *Field. Crops. Res.*, **154**, 158-163.
80 Llusia J, Llorens L, Bernal M, Verdaguer D and Penuelas J, 2012, Effects of UV radiation and water limitation on the volatile terpene emission rates, photosynthesis rates, and stomatal conductance in four Mediterranean species, *Acta Physiol. Plant.*, **34**, 757-769.
81 Lomax BH, Fraser WT, Harrington G, Blackmore S, Sephton MA and Harris NBW, 2012, A novel palaeoaltimetry proxy based on spore and pollen wall chemistry, *Earth Planet Sci. Lett*, **353-354**, 22-28.

82 Lomax BH, Fraser WT, Sephton MA, Callaghan TV, Self S, Harfoot M, Pyle JA, Wellman CH and Beerling DJ, 2008, Plant spore walls as a record of long-term changes in ultraviolet-B radiation, *Nature Geosci.*, **1**, 592-596.

83 Loreto F and Schnitzler JP, 2010, Abiotic stresses and induced BVOCs, *Trends Plant Sci.*, **15**, 154-166.

84 Lou Y, Zhou W and Ren L, 2012, Elevated UV-B radiation increased CH4 emission in transgenic rice from a paddy soil, *Agric. Ecosyst. Environ.*, **151**, 16-20.

85 Ma S, Baldocchi D, Hatala J, Detto JM and Yuste J, 2012, Are rain-induced ecosystem respiration pulses enhanced by legacies of antecedent photodegradation in semi-arid environments?, *Agric. Forest Meteorol.*, **154-155**, 203-213.

86 Magri D, 2011, Past UV-B flux from fossil pollen: prospects for climate, environment and evolution, *New. Phytol.*, **192**, 310-312.

87 Manatsa D, Morioka Y, Behera SK, Yamagata T and Matarira CH, 2013, Link between Antarctic ozone depletion and summer warming over southern Africa, *Nature Geosci.*, **6**, 934-939.

88 Mauch-Mani B and Mauch F, 2005, The role of abscisic acid in plant-pathogen interactions, *Curr. Opin. Plant Biol.*, **8**, 409-414.

89 Mayer LM, Thornton KR, Schick LL, Jastrow JD and Harden JW, 2012, Photodissolution of soil organic matter, *Geoderma*, **170**, 314-321.

90 Mazza CA, Gimenez PI, Kantolic AG and Ballaré CL, 2013, Beneficial effects of solar UV-B radiation on soybean yield mediated by reduced insect herbivory under field conditions, *Physiol. Plant.*, **147**, 307-315.

91 Mazza CA, Izaguirre MM, Curiale J and Ballaré CL, 2010, A look into the invisible. Ultraviolet-B sensitivity in an insect (*Caliothrips phaseoli*) revealed through a behavioural action spectrum., *Proc. R. Soc. B. Biol. Sci.*, **277**, 367-373.

92 Mazza CA, Izaguirre MM, Zavala J, Scopel AL and Ballaré CL, 2002, Insect perception of ambient ultraviolet-B radiation, *Ecol. Lett.*, **5**, 722-726.

93 McConnell JR, Aristarain AJ, Banta JR, Edwards PR and Simões JC, 2007, 20th-Century doubling in dust archived in an Antarctic Peninsula ice core parallels climate change and desertification in South America, *Proc. Nat. Acad. Sci. USA.*, **104**, 5743– 5748.

94 McLeod A and Keppler F, 2010, Vegetation, in *Methane and Climate Change* eds.: Reay DS, Smith P and van Amstel A, Earthscan, London and Washington, D.C., pp. 74-96.

95 McLeod AR, Fry SC, Loake GJ, Messenger DJ, Reay DS, Smith KA and Yun B-W, 2008, Ultraviolet radiation drives methane emissions from terrestrial plant pectins, *New. Phytol.*, **180**, 124-132.

96 Messenger DJ, McLeod AR and Fry SC, 2009, The role of ultraviolet radiation, photosensitizers, reactive oxygen species and ester groups in mechanisms of methane formation from pectin, *Plant. Cell. Environ.*, **32**, 1-9.

97 Morales LO, Brosché M, Vainonen J, Jenkins GI, Wargent JJ, Sipari N, Strid A, Lindfors AV, Tegelberg R and Aphalo PJ, 2013, Multiple roles for UV RESISTANCE LOCUS8 in regulating gene expression and metabolite accumulation in Arabidopsis under solar ultraviolet radiation, *Plant Physiol.*, **161**, 744-759.

98 Mörsky SK, Haapala JK, Rinnan R, Saarnio S, Suokanerva H, Latola K, Kyrö E, Silvola J, Holopainen T and Martikainen PJ, 2012, Minor long-term effects of ultraviolet-B radiation on methane dynamics of a subarctic fen in Northern Finland, *Biogeochemistry*, **108**, 233-243.

99 Newsham KK and Robinson SA, 2009, Responses of plants in polar regions to UVB exposure: a meta-analysis, *Glob. Change Biol.*, **15**, 2574-2589.

100 Nielsen UN and Wall DH, 2013, The future of soil invertebrate communities in polar regions: different climate change responses in the Arctic and Antarctic?, *Ecol. Lett.*, **16**, 409-419.

101 Pangala SR, Moore S, Hornibrook ERC and Gauci V, 2013, Trees are major conduits for methane egress from tropical forested wetlands, *New. Phytol.*, **197**, 524-531.

102 Parisi AV, Kimlin MG, Wong JCF and Wilson M, 2001, Solar ultraviolet exposures at ground level in tree shade during summer in south east Queensland, *Int. J. Environ. Hlth. Res.*, **11**, 117-127.

103 Parisi AV, Schouten P, Downs NJ and Turner J, 2010, Solar UV exposures measured simultaneously to all arbitrarily oriented leaves on a plant, *J. Photochem. Photobiol. B.*, **99**, 87-92.

104 Parisi AV, Schouten P and Turnbull DJ, 2010, UV dosimeter based on Polyphenylene Oxide for the measurement of UV exposures to plants and humans over extended periods, in *NIWA 2010 UV Workshop: UV radiation and its effects-an update 2010*, Queenstown, New Zealand, pp. 25-26.

105 Parton W, Silver WL, Burke IC, Grassens L, Harmon ME, Currie WS, King JY, Adair EC, Brandt LA, Hart SC and Fasth B, 2007, Global-scale similarities in nitrogen release patterns during long-term decomposition, *Science.*, **315**, 361-364.

106 Paul ND, Moore JP, McPherson M, Lambourne C, Croft P, Heaton JC and Wargent JJ, 2012, Ecological responses to UV radiation: interactions between the biological effects of UV on plants and on associated organisms, *Physiol. Plant.*, **145**, 565-581.

107 Peñuelas J and Staudt M, 2010, BVOCs and global change, *Trends Plant Sci.*, **15**, 133-144.

108 Perlwitz J, 2011, ATMOSPHERIC SCIENCE Tug of war on the jet stream, *Nature Clim. Change*, **1**, 29-31.

109 Possell M and Loreto F, 2013, The role of volatile organic compounds in plant resistance to abiotic stresses: responses and mechanisms, in *Biology, controls and models of tree volatile organic compound emissions* eds.: Niinemets Ü and Monson RK, Springer, Berlin, pp. 209-235.

110 Potosnak MJ, Baker BM, LeStourgeon L, Disher SM, Griffin KL, Bret-Harte MS and Starr G, 2013, Isoprene emissions from a tundra ecosystem, *Biogeosci.*, **10**, 871-889.

111 Purich A and Son SW, 2012, Impact of Antarctic ozone depletion and recovery on Southern Hemisphere precipitation, evaporation, and extreme changes, *J. Climate*, **25**, 3145-3154.

112 Rinnan R, Saarnio S, Haapala JK, Mörsky SK, Martikainen PJ, Silvola J and Holopainen T, 2013, Boreal peatland ecosystems under enhanced UV-B radiation and elevated tropospheric ozone concentration, *Environ. Exp. Bot.*, **90**, 43-52.

113 Rizzini L, Favory JJ, Cloix C, Faggionato D, O'Hara A, Kaiserli E, Baumeister R, Schafer E, Nagy F, Jenkins GI and Ulm R, 2011, Perception of UV-B by the *Arabidopsis* UVR8 Protein, *Science.*, **332**, 103-106.

114 Robinson SA and Erickson III DJ, 2014, Not just about sunburn--the ozone hole's profound effect on climate has significant implications for Southern Hemisphere ecosystems, *Glob. Change Biol.*, DOI: 10.1111/gcb.12739.

115 Robinson SA and Waterman MJ, 2014, Sunsafe bryophytes: photoprotection from excess and damaging solar radiation, *Adv. Photosyn. Resp.*, **37**, 113-130.

116 Rousseaux MC, Julkunen-Tiitto R, Searles PS, Scopel AL, Aphalo PJ and Ballaré CL, 2004, Solar UV-B radiation affects leaf quality and insect herbivory in the southern beech tree *Nothofagus antarctica*, *Oecologia*, **138**, 505-512.

117 Royles J, Ogée J, Wingate L, Hodgson DA, Convey P and Griffiths H, 2012, Carbon isotope evidence for recent climate-related enhancement of CO_2 assimilation and peat accumulation rates in Antarctica, *Glob. Change Biol.*, **18**, 3112-3124.

118 Rozema J, Blokker P, Mayoral Fuertes MA and Broekman R, 2009, UV-B absorbing compounds in present-day and fossil pollen, spores, cuticles, seed coats and wood: evaluation of a proxy for solar UV radiation, *Photochem. Photobiol. Sci.*, **8**, 1233-1243.

119 Ruhland CT, Dyslin MJ and Krenz JD, 2013, Wyoming big sagebrush screens ultraviolet radiation more effectively at higher elevations, *J. Arid. Environ.*, **96**, 19-22.

120 Rutledge S, Campbell DI, Baldocchi D and Schipper LA, 2010, Photodegradation leads to increased carbon dioxide losses from terrestrial organic matter, *Glob. Change Biol.*, **16**, 3065-3074.

121 Sampath-Wiley P and Jahnke LS, 2011, A new filter that accurately mimics the solar UV-B spectrum using standard UV lamps: the photochemical properties, stabilization and use of the urate anion liquid filter, *Plant. Cell. Environ.*, **34**, 261-269.

122 Schade GW, Hofmann RM and Crutzen PJ, 1999, CO emissions from degrading plant matter (I). Measurements, *Tellus Ser. B-Chem. Phys. Meteorol.*, **51**, 889-908.

123 Schreiner M, Mewis I, Huyskens-Keil S, Jansen MAK, Zrenner R, Winkler JB, O'Brien N and Krumbein A, 2012, UV-B-induced secondary plant metabolites - potential benefits for plant and human health, *Crit. Rev. Plant Sci.*, **31**, 229-240.

124 Searles PS, Flint SD and Caldwell MM, 2001, A meta-analysis of plant field studies simulating stratospheric ozone depletion, *Oecologia*, **127**, 1-10.

125 Seckmeyer G, Bais A, Bernhard G, Blumthaler M, Drüke S, Kiedron P, Lantz K, McKenzie R and Riechelmann S, 2010, *Instruments to Measure Solar Ultraviolet Radiation WMO/TD-No. 1538, Part 4: Array Spectroradiometers (vol. No. 191)*, World Meterological Organization, Geneva.

126 Seckmeyer G, Klingebiel M, Riechelmann S, Lohse I, McKenzie RL, Ben Liley J, Allen MW, Siani A-M and Casale GR, 2012, A critical assessment of two types of personal UV dosimeters, *Photochem. Photobiol.*, **88**, 215-222.

127 Selbmann L, Isola D, Zucconi L and Onofri S, 2011, Resistance to UV-B induced DNA damage in extreme-tolerant cryptoendolithic Antarctic fungi: detection by PCR assays, *Fungal Biol.*, **115**, 937-944.

128 Sharkey TD, 2013, Is it useful to ask why plants emit isoprene?, *Plant. Cell. Environ.*, **36**, 517-520.

129 Sharma S and Guruprasad KN, 2012, Enhancement of root growth and nitrogen fixation in *Trigonella* by UV-exclusion from solar radiation, *Plant Physiol. Biochem.*, **61**, 97-102.

130 Singh S, Kumari R, Agrawal M and Agrawal SB, 2011, Modification in growth, biomass and yield of radish under supplemental UV-B at different NPK levels, *Ecotoxicol. Environ. Safety*, **74**, 897-903.

131 Smith WK, Gao W, Steltzer H, Wallenstein MD and Tree R, 2010, Moisture availability influences the effect of ultraviolet-B radiation on leaf litter decomposition., *Glob. Change Biol.*, **16**, 484-495.

132 Song X, Jiang H, Zhang Z, Zhou G, Zhang S and Peng C, 2014, Interactive effects of elevated UV-B radiation and N deposition on decomposition of Moso bamboo litter, *Soil Biol. Biochem.*, **69**, 11-16.

133 Song X, Peng C, Jiang H, Zhu Q and Wang W, 2013, Direct and indirect effects of UV-B exposure on litter decomposition: a meta-analysis, *PLoS ONE*, **8**, e68858.

134 Song X, Zhang H, Jiang H, Donaldson LA and Wang H, 2013, Influence of elevated UV-B radiation on leaf litter chemistry and subsequent decomposition in humid subtropical China, *J. Soils Sediments*, **13**, 846-853.

135 Stocker TF, Qin D, Plattner G-K, Tignor M, Allen SK, Boschung J, Nauels A, Xia Y, Bex V and Midgley PM, 2013, IPCC: Summary for Policymakers. In: Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change Cambridge University Press, Cambridge, UK and New York, NY.

136 Stratmann JW, Stelmach BA, Weiler EW and Ryan CA, 2000, UVB/UVA radiation activates a 48 kDa myelin basic protein kinase and potentiates wound signaling in tomato leaves, *Photochem. Photobiol.*, **71**, 116-123.

137 Suklje K, Antalick G, Coetzee Z, Schmidtke LM, Cesnik HB, Brandt J, du Toit WJ, Lisjak K and Deloire A, 2014, Effect of leaf removal and ultraviolet radiation on the composition and sensory perception of *Vitis vinifera*L. cv. Sauvignon Blanc wine, *Aust. J. Grape Wine Res.*, **20**, 223-233.

138 Sumbele S, Fotelli MN, Nikolopoulos D, Tooulakou G, Liakoura V, Liakopoulos G, Bresta P, Dotsika E, Adams MA and Karabourniotis G, 2012, Photosynthetic capacity is negatively correlated with the concentration of leaf phenolic compounds across a range of different species, *AoB PLANTS*, **2012**, pls025 DOI: 010.1093/aobpla/pls1025.

139 Thomas ER, Bracegirdle TJ, Turner J and Wolff EW, 2013, A 308 year record of climate variability in West Antarctica, *Geophys. Res. Lett.*, **40**, 5492-5496.

140 Thompson DWJ, Solomon S, Kushner PJ, England MH, Grise KM and Karoly DJ, 2011, Signatures of the Antarctic ozone hole in Southern Hemisphere surface climate change, *Nature Geosci.*, **4**, 741-749.

141 Tiiva P, Rinnan R, Faubert P, Räsänen J, Holopainen T, Kyro E and Holopainen JK, 2007, Isoprene emission from a subarctic peatland under enhanced UV-B radiation, *New. Phytol.*, **176**, 346-355.

142 Tsujita H and Plummer CE, 2010, Bovine ocular squamous cell carcinoma, *Vet. Clin. N. Amer. -Food Animal Prac.*, **26**, 511-529.

143 Turnbull JD, Leslie SJ and Robinson SA, 2009, Desiccation protects two Antarctic mosses from ultraviolet-B induced DNA damage, *Funct. Plant Biol.*, **36**, 214-221.

144 Turnbull TL, Barlow A and Adams MA, 2013, Photosynthetic benefits of ultraviolet-A to *Pimelea ligustrina*, a woody shrub of sub-alpine Australia, *Oecologia*, **173**, 375-385.

145 Turner J, Barrand NE, Bracegirdle TJ, Convey P, Hodgson DA, Jarvis M, Jenkins A, Marshall G, Meredith MP, Roscoe H, Shanklin J, French J, Goosse H, Guglielmin M, Gutt J, Jacobs S, Kennicutt Ii MC, Masson-Delmotte V, Mayewski P, Navarro F, Robinson S, Scambos T, Sparrow M, Summerhayes C, Speer K and Klepikov A, 2014, Antarctic climate change and the environment: An update, *Polar Record*, **50**, 237-259.

146 Turner J, Bindschadler RA, Convey P, Di Prisco G, Fahrbach E, Gutt J, Hodgson DA, Mayewski PA and Summerhayes CP, 2009, Antarctic Climate Change and the Environment, SCAR, http://acce.scar.org/wiki/Antarctic_Climate_Change_and_the_Environment accessed November 1, 2014.

147 Turner J and Marshall GJ, 2011, *Climate Change in the Polar Regions*, Cambridge University Press., Cambridge.

148 Turner J, Parisi AV and Turnbull DJ, 2009, Dosimeter for the measurement of plant damaging solar UV exposures, *Agric. Forest Meteorol.*, **149**, 1301-1306.

149 Uselman SM, Snyder KA, Blank RR and Jones TJ, 2011, UVB exposure does not accelerate rates of litter decomposition in a semi-arid riparian ecosystem., *Soil Biol. Biochem.*, **43**, 1254-1265.

150 Verdaguer D, Llorens L, Bernal M and Badosa J, 2012, Photomorphogenic effects of UVB and UVA radiation on leaves of six Mediterranean sclerophyllous woody species subjected to two different watering regimes at the seedling stage, *Environ. Exp. Bot.*, **79**, 66-75.

151 Villalba R, Lara A, Masiokas MH, Urrutia R, Luckman BH, Marshall GJ, Mundo IA, Christie DA, Cook ER, Neukom R, Allen K, Fenwick P, Boninsegna JA, Srur AM, Morales MS, Araneo D, Palmer JG, Cuq E, Aravena JC, Holz A and LeQuesne C, 2012, Unusual Southern Hemisphere tree growth patterns induced by changes in the Southern Annular Mode, *Nature Geosci.*, **5**, 793-798.

152 Virjamo V, Sutinen S and Julkunen-Tiitto R, 2014, Combined effect of elevated UVB, elevated temperature and fertilization on growth, needle structure and phytochemistry of young Norway spruce (*Picea abies*) seedlings, *Glob. Change Biol.*, **20**, 2252-2260.

153 Wang YX and Frei M, 2011, Stressed food - The impact of abiotic environmental stresses on crop quality, *Agric. Ecosyst. Environ.*, **141**, 271-286.

154 Wang ZP, Chang SX, Chen H and Han XG, 2013, Widespread non-microbial methane production by organic compounds and the impact of environmental stresses, *Earth-Sci. Rev.*, **127**, 193-202.

155 Wargent JJ, Elfadly EM, Moore JP and Paul ND, 2011, Increased exposure to UV-B radiation during early development leads to enhanced photoprotection and improved long-term performance in *Lactuca sativa*, *Plant. Cell. Environ.*, **34**, 1401-1413.

156 Wargent JJ and Jordan BR, 2013, From ozone depletion to agriculture: understanding the role of UV radiation in sustainable crop production, *New. Phytol.*, **197**, 1058-1076.

157 Wargent JJ, Nelson BCW, McGhie TK and Barnes PW, 2014, Acclimation to UV-B radiation and visible light in *Lactuca sativa* involves up-regulation of photosynthetic performance and orchestration of metabolome-wide responses, *Plant. Cell. Environ.*, DOI: 10.1111/pce.12392.

158 Williamson CE, Zepp RG, Lucas RM, Madronich S, Austin AT, Ballar. CL, Norval M, Sulzberger B, Bais AF, McKenzie RL, Robinson SA, Häder D-P, Paul ND and Bornman JF, 2014, Solar ultraviolet radiation in a changing climate, *Nature Clim. Change*, **4**, 434-441.

159 Willis KJ, Feurdean A, Birks HJB, Bjune AE, Breman E, Broekman R, Grytnes JA, New M, Singarayer JS and Rozema J, 2011, Quantification of UV-B flux through time using UV-B-absorbing compounds contained in fossil *Pinus sporopollenin*, *New. Phytol.*, **192**, 553-560.

160 WMO, 2011, Scientific Assessment of Ozone Depletion: 2010, Global Ozone Research and Monitoring Project-Report No. 52, Report No., Geneva, Switzerland, p. 516

161 Wu Y, Polvani LM and Seager R, 2013, The importance of the Montreal Protocol in protecting earth's hydrodclimate, *J. Climate*, **26**, 4049-4068.

162 Zavala JA, Mazza CA, Dillon FM, Chludil HD and Ballaré CL, 2014, Soybean resistance to stink bugs (*Nezara viridula* and *Piezodorus guildinii*) increases with exposure to solar UV-B radiation and correlates with isoflavonoid content in pods under field conditions, *Plant. Cell. Environ.*, DOI: 10.1111/pce.12368.

163 Zepp RG, Erickson DJ, Paul ND and Sulzberger B, 2011, Effects of solar UV radiation and climate change on biogeochemical cycling: interactions and feedbacks, *Photochem. Photobiol. Sci.*, **10**, 261-279.

164 Zhang WJ and Björn LO, 2009, The effect of ultraviolet radiation on the accumulation of medicinal compounds in plants, *Fitoterapia*, **80**, 207-218.

Chapter 4: Effects of UV radiation on aquatic ecosystems and interactions with other environmental factors

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Summary

Interactions between climate change and UV radiation are having strong effects on aquatic ecosystems due to feedbacks between temperature, UV radiation, and greenhouse gas concentration. Higher air temperatures and incoming solar radiation are increasing the surface water temperatures of lakes and oceans, with many large lakes warming at twice the rate of regional air temperatures. Warmer oceans are changing habitats and species composition of many marine ecosystems. For some such as corals, the temperatures may become too high. Temperature differences between surface and deep waters are becoming greater. This increase in thermal stratification makes the surface layers shallower and leads to stronger barriers to upward mixing of nutrients necessary for photosynthesis. This also results in exposure to higher levels of UV radiation of surface-dwelling organisms. In Polar and alpine regions decreases in the duration and amount of snow and ice cover on lakes and oceans are also increasing exposure to UV radiation. In contrast, in lakes and coastal oceans the concentration and colour of UV-absorbing dissolved organic matter (DOM) from terrestrial ecosystems is increasing with greater runoff from higher precipitation and more frequent extreme storms. DOM thus creates a refuge from UV radiation that can enable UV-sensitive species to become established. At the same time, decreased UV radiation in such surface waters reduces the capacity of solar UV radiation to inactivate viruses and other pathogens and parasites, and increases the difficulty and price of purifying drinking waters for municipal supplies. Solar UV radiation breaks down the DOM, making it more available for microbial processing, resulting in the release of greenhouse gases into the atmosphere. In addition to screening solar irradiance, DOM, when sunlit in surface water, can lead to the formation of reactive oxygen species (ROS). Increases in carbon dioxide are in turn acidifying the oceans and inhibiting the ability of many marine organisms to form UV-absorbing exoskeletons. Many aquatic organisms use adaptive strategies to mitigate the effects of solar UV-B radiation (280-315 nm), including vertical migration, crust formation, synthesis of UV-absorbing substances, enzymatic and non-enzymatic quenching of ROS.

Whether or not genetic adaptation to changes in the abiotic factors plays a role in mitigating stress and damage has not been determined. This assessment addresses how our knowledge of the interactive effects of UV radiation and climate change factors on aquatic ecosystems has advanced in the past four years.

Introduction

Interactions between climate change, ozone, and ultraviolet (UV) radiation are altering exposure to UV radiation in aquatic ecosystems (see Chapters 1 and 5). Climate change is causing average global air temperature to rise and precipitation patterns to change, with important consequences for UV exposure in aquatic ecosystems. On a regional scale, changes in climate are highly variable in both space and time, leading to widespread floods in wetter regions, more severe droughts in drier regions, and increases in extreme storm events.[70] Climate change is reducing annual snow and ice cover, increasing runoff and concentrations of UV-absorbing dissolved organic matter (DOM) in inland and coastal waters, and increasing the strength of thermal stratification in these systems. Rising atmospheric CO_2 concentration induces ocean acidification and alters seawater chemistry and consequently changes UV protection provided by calcified exoskeletons in many aquatic organisms as well as UV exposure levels in aquatic ecosystems.

The ecosystem services provided by marine and inland waters include food and drinking water for a growing human population, moderating extreme temperature and weather conditions, and regulating important greenhouse gas concentrations such as that of atmospheric CO_2. Freshwater is an indispensible requirement for human existence as well as for all wildlife in terrestrial ecosystems and inland waters. Aquatic ecosystems generate both important regional food supplies as well as stimulate regional economies. Fisheries and aquaculture production have increased faster than the world's human population over the last 50 years but these increases may not be sustainable, constituting an important source of animal protein,[33] and feeding approximately 1 billion people in Asia alone.[159] In the next decade, fish production including that from inland and coastal fish farms is expected to exceed that of other forms of proteins.[33] Aquatic ecosystems provide other ecosystem services including recreation and tourism, with coral reefs alone are estimated to generate 9.6 billion US$ annually.[114] All of these ecosystem services are being influenced by changes in climate and exposure to changing levels of UV radiation.

Here we present an assessment of the advances in our knowledge over the past four years of how interactive effects of climate change and UV radiation are altering aquatic ecosystems, and the critical ecosystem services that they provide.

Consequences of climate change on snow, ice, DOM, and exposure to UV radiation

Melting snow and ice: Aquatic productivity under high solar radiation

Over the last few decades, rising temperatures have reduced the sea and freshwater ice and snow cover with important consequences for underwater exposure to UV radiation. The global ocean temperature has increased by about 1°C over the last 112 years.[38] However, the temperature was almost 2°C above the average from 1951 – 1980 in the Arctic[108] and the warming of the water along the Antarctic Peninsula has been five times faster than the global average over the past 50 years. One of the reasons for the large temperature increase and drop in ice volume at the poles is an effective feedback mechanism. Ice and snow reflect most solar radiation back into space. In contrast, water and soil absorb most of this radiation, which results in a substantial warming and increased penetration of UV radiation into the ocean water. The higher water temperatures have reduced the Arctic ice cover by 49% during the summer compared to the average during the years between 1979 and 2000[171]. The total floating ice volume dropped by about 75% during the same time period. Melting of the Arctic Ocean ice now typically starts in April, 50 days earlier than before the warming,[74] and freezing starts in October, about 1 month later than in the past. In recent years Arctic ozone concentrations have decreased, but it is not clear if this trend will continue. It was the first time the O_3-depleted area was as large as that in the Antarctic.[97] Higher water temperatures resulting in a thinner mixing layer and longer growing season together with increased O_3 depletion all have the potential to increase exposure to UV radiation of aquatic organisms that live in the upper layers of the water column.

Of major concern is how climate and UV radiation will alter phytoplankton biomass in the open oceans. Oceanic phytoplankton biomass is important in explaining variations in UV transparency and constitutes a large sink for atmospheric CO_2 by taking up a comparable amount of CO_2 as all terrestrial ecosystems. Satellite imaging of chlorophyll data shows that phytoplankton concentrations are much higher at polar latitudes than at mid or equatorial regions:[115] e.g., chlorophyll *a* concentrations can exceed 20 mg m^{-3} in the Southern Ocean. Melting ice and snow affect phytoplankton, but local weather and mixing dynamics in the water column contribute differently to the rate and direction of change and are influenced by local weather and mixing dynamics. Judging from 30 years of field studies and satellite chlorophyll fluorescence data, cumulated densities of phytoplankton have decreased by 12% along the West side of the Antarctic Peninsula (Bellingshausen Sea), which has been attributed to increased solar UV-B radiation (280-315 nm) and rapid regional climate change.[103] In the North of the Antarctic Peninsula, however, a lower photosynthetic biomass production is attributed to denser cloud cover and the resulting decreased PAR (photosynthetic active radiation, 400 – 700 nm). In contrast, further south there is less mixing, fewer clouds and consequently lower phytoplankton productivity.[103]

Increasing cloudiness has been found to limit phytoplankton productivity in the Arctic in open water.[11] However, recent research suggests that thinning of the ice is increasing the overall primary productivity and algal biomass in the Arctic. Before recent Arctic warming, the ice cover was about 3 m thick and accumulated over several years, which prevented most light from penetrating into the water below and limited phytoplankton production. Currently the summer ice layer is only about 1 m thick. Pools from meltwater form on the surface, which function as “skylights”. Reduced snowfall further enhances the light availability so that the penetrating solar radiation amounts to about 50% of that incident on the surface.[40] This increased light availability fosters a large growth of ice algae and phytoplankton, which is further supported by nutrients upwelling from below. In 2012 a NASA research cruise (ICESCAPE) to the Chukchi Sea off the coast of Alaska reported an unprecedented huge plankton bloom under the Arctic ice extending down to 50 m,[4] “as dramatic and unexpected as finding a rainforest in the middle of a desert”.[162] This high chlorophyll concentration under the sea ice was not known before and could not be detected by satellite-based remote sensing. Consequently the phytoplankton concentration was among the highest ever recorded extending down to 50 m. Similarly, it was found that these massive blooms occur all over the Arctic Ocean. In the open waters of the Arctic Ocean satellite data have shown a 20% increase in the chlorophyll content between 1998 and 2009.[5]

Very limited information is available on the effects of changing PAR and exposure to UV radiation on the structure of the food web and total system productivity. In contrast to the discovery of high phytoplankton concentrations under the ice, predictions for the future posit a gradual loss of marine ice algae through loss of sea ice, causing a cascade through the higher trophic levels of the food web. Additionally, meltwater from sea ice and glaciers reduces the salinity that negatively affects primary producers and the upper levels of the food web..[28]

The melting sea ice contains about four times more nitrogen than the bulk water,[173] while increasing PAR results in an increase in the carbon to phosphorous ratio in plankton. Therefore reduced sea ice and increased PAR likely mean that phytoplankton food quality is reduced for herbivorous grazers. Changing ice phenology and light and nutrient availability may also affect species composition. Faster melting of sea ice shifts plankton species toward smaller cell types[26] with a better capacity to absorb solar radiation and take up nutrients, which affects the subsequent food web including fish and mammals.

During a 2010 cruise northwest of Svalbard even tropical *Radiolaria* were found in Arctic waters.[15, 66] Out of the 145 taxa identified during the cruise, 98 had come from areas much farther south and tropical species were reproducing in their new habitat. Due to the decreased ice cover phytoplankton productivity has extended further north attracting more fish. For example, in the past, capelin - an important prey for Atlantic cod, had a maximal distribution up to 75°N, but capelin were found up to 78°N in 2012 with cod following them.[123]

Increasing dissolved organic matter and exposure to UV radiation

The increased exposure to PAR and UV radiation, caused by the smaller and thinner ice and O_3 depletion is partially offset in coastal and inland ecosystems by higher runoff from terrestrial dissolved organic matter (DOM), which decreases water transparency. Increases in global temperature and precipitation (in some areas) are accelerating the release of DOM into lakes, rivers, and coastal oceans.[81, 165] Strong inshore-offshore gradients in DOM are common to distances of 20 km or more from the shore in large lakes,[16] and tens to hundreds of km in the Arctic Ocean (Fig. 1). Remote sensing of this DOM[34] provides mechanistic insights into how DOM is changing UV irradiance in coastal and inland waters.

The reasons for the increases in DOM in the Arctic appear to be related primarily to a loss of permafrost. In 2012 a majority of North American and Russian regions reported a 6-10% increase in the depth of soil that thaws annually relative to the average from previous decades.[126] The amount of organic carbon stored in permafrost soils is more than twice that in the atmosphere. Thus, when permafrost thaws, large quantities of DOM stored in the soils can be transported to aquatic ecosystems and outgassed as CO_2 and/or CH_4 after being acted upon by UV radiation and microbes. This DOM is highly photoreactive so that exposure to solar UV radiation and visible light accelerate its breakdown and release to the atmosphere as CO_2.[25] When permafrost thaws, as much as one third of the organic residues can be converted to CO_2 within two weeks.[163] The increases in greenhouse gases in turn increase warming and further thawing of permafrost with important consequences for the global radiative balance.

DOM concentrations have more than doubled in many temperate inland waters in recent decades, and climate change has been suggested to play an important role in these increases,[27] and is expected to lead to a 65% increase in DOM in boreal waters in the future.[81] Increases in precipitation reduce the time that water spends in lakes, which reduces the degradation that occurs when DOM is exposed to UV radiation.[79] The frequency of extreme precipitation events such as hurricanes and summer storms has increased in recent years and dramatically increases the export of UV-absorbing terrestrial DOM to aquatic ecosystems. Up to 63% of the annual DOM may come from the top 10% of precipitation events.[78] A single hurricane can contribute up to 19% of the annual DOM input to receiving waters[31] and increases in DOM associated with a single storm can decrease UV transparency of lake water by a factor of three.[131] Lakes can act as buffers of the seasonal variability in DOM input to streams and rivers, thus moderating DOM increases in downstream regions during high flow periods, and increasing DOM concentrations during base flow conditions.[54] This buffering of extremes does not seem to influence total annual outflow of DOM from the watershed.[94]

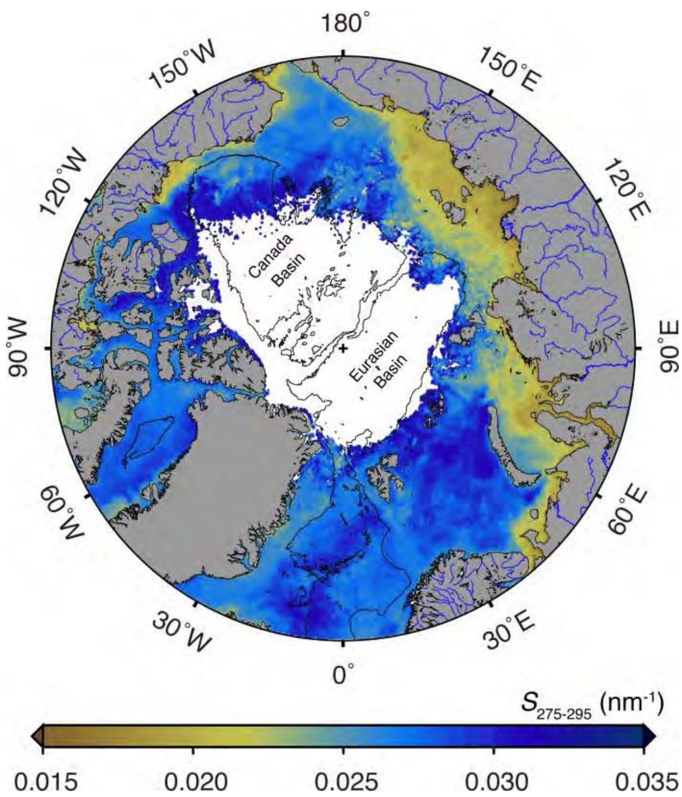

Fig. 1 Image of Earth over the North Pole showing the extent of influence of terrestrial DOM inputs from rivers using an optical metric based on UV absorption - called the spectral slope (the slope of the linear relationship between the natural log of the absorption coefficient and wavelength in the 275-295 nm spectral range, nm^{-1}). Although the satellite cannot detect these shorter wavelengths, algorithms have been developed that lead to an accurate relationship between spectral slope in this range and thus DOM source. Browner colours around the periphery of the Arctic Sea show greater inputs of terrestrial DOM, which is particularly pronounced above Eurasia (from[34]).

At the same time DOM inputs contribute to the role of coastal and inland waters in the global carbon cycle. Inland waters are net sources of CO_2 to the atmosphere, venting carbon fixed by terrestrial land plants that have subsequently died and decomposed.[155] Metabolism and UV-dependent photolysis of terrestrial DOM may have important consequences on greenhouse gas emissions from lakes and for global climate. Inland waters emit large amounts of CH_4, a greenhouse gas that is more than 20 times as potent as CO_2. The quantity of methane emitted from the world's inland waters is estimated to be equivalent to 25% of the global terrestrial carbon sink[8] making inland waters important players in the climate-UV interactions, despite comprising only a fraction (1%) of the total water on Earth.

In addition to the concentration of DOM, the radiation it absorbs influences exposure to UV radiation of inland and coastal waters. Changes in iron (Fe) concentrations, pH, and land-use patterns modify DOM optical characteristics, degradation, and absorption of UV radiation. While the precise reasons for Fe increase are still not completely understood, there is evidence that waters with high concentrations of soluble Fe are feeding into the surface waters[80] and contributing to higher UV absorbance of DOM. Photodegradation of DOM is higher at low pH and high Fe concentrations.[119] Peatlands have higher DOM export than do agricultural watersheds and some agricultural landscapes may export more DOM than forested ecosystems.[23] The susceptibility of DOM to degradation by UV radiation and visible light (photoreactivity) and microbial decomposition (bioreactivity) varies with the source of the DOM. The DOM from agricultural watersheds is less photoreactive than is DOM from forested lands, but these two types of DOM may be similar in their bioreactivity.[95] When exposed to artificial UV lamps in the lab, DOM in water collected from the Chesapeake Bay during base-flow conditions is more photoreactive than that collected during snowmelt in tributaries, but land-use (urban *vs* agriculture *vs* forested) made little difference. [96] These data collectively suggest that land-use patterns may alter not only the amount of DOM in aquatic ecosystems, but also its quality, UV-absorptivity, and subsequent breakdown rates by UV radiation and microbial decomposition to CO_2 and CH_4.

Apart from reducing the underwater UV radiation and visible light zone, increases in terrestrial DOM alter aquatic food webs via changes in ratios between different basal carbon and nutrient sources. In situ mesocosm studies have demonstrated that increases in nutrient-poor DOM inputs to Arctic lakes will decrease primary productivity and increase heterotrophy (uptake of organic material, in contrast to autotrophy, light driven photosynthesis) within the lake.[39] In contrast, addition of DOM with a higher nutrient content to a nutrient-poor alpine lake can stimulate autotrophy more than heterotrophy.[77] Increasing DOM also traps heat closer to the surface of aquatic ecosystems, increasing surface temperatures, decreasing the depth of the surface mixed layer and decreasing temperatures in deeper waters. These patterns collectively lead to stronger thermal stratification.[122] Vertical mixing in the water column largely reduces the UV-induced inhibition of photosynthesis dependent on the relative changes in mixing depth versus UV transparency. Further evidence shows that exposure of DOM to solar radiation can lead to the formation of ROS.[73, 135] Increases in DOM may alter aquatic community structure by altering the temperature of inland and coastal waters, decrease exposure to UV radiation, and ameliorate effects of toxic metals and organic pollutants on fish and other aquatic organisms.[143]

Collectively these data indicate that climate change-induced inputs of DOM cause severe change in UV transparency and functioning of inland and coastal waters. While DOM provides a refuge from damaging UV radiation for many ecologically and economically important aquatic organisms, it also has the potential to increase the survival of pathogens.[113] Higher concentrations of DOM reduce the effectiveness of natural UV radiation on disinfection of drinking water supplies as well as increase its cost and potential for production of carcinogenic disinfection byproducts.[57] Understanding the role of interactive effects of DOM, ROS concentrations, UV radiation and climate change in aquatic ecosystems will thus be important for sustaining structure and function of the aquatic ecosystem, for example, through fisheries production and potential to use the water as a drinking water resource.

Thermal stratification and exposure to UV radiation

Many aquatic organisms, such as zoo- and phytoplankton, are restricted to the upper mixed layer (UML), the lower boundary of which is the thermocline. Temperate latitudes are characterised by seasonal changes in temperature and irradiance, which are reflected in seasonal cycles of abundance and species composition.[12, 167]

Tropical waters typically exhibit stable thermal stratification.[47] In contrast to polar waters, where the UML can exceed 100 m, in tropical waters it is usually limited to the upper 10 – 35 m. Across latitudes, nutrient concentrations are higher in deeper layers, but the transport into the mixing zone is limited. As a consequence, these two clearly separated layers shelter distinctly different organisms. At higher latitudes, the input of freshwater from melting ice increases stratification because freshwater is less dense than saltwater.[144]

Global climate change results in ocean warming, which makes stratification more pronounced and decreases the depth of the UML, causing organisms through all trophic levels to be exposed to increased visible and UV radiation.[47, 158] In addition, it further limits the transport of nutrients from deeper waters because the lower boundary is more stable.[150] Changes in wind speeds are also altering the depth of the UML in many water bodies. Higher temperatures mitigate the inhibitory effects of UV-B radiation by enhancing enzyme-mediated photo-repair as well as photosynthetic carbon fixation and quantum yield.[61, 64] The molecular mechanism of this enhancement is based on a significantly higher gene expression and activity at 25°C compared to 20°C as well as augmented enzyme-driven repair._ENREF_124 The mitigating effects of elevated temperatures can reduce the UV stress as has been shown in the South China Sea where the photosynthetic carbon fixation was less inhibited by UV-B radiation in the summer than in the winter.[85, 167] The respiration index (log of oxygen to carbon dioxide pressure), which may increase with ocean acidification and changes in multiple climate change stressors, could affect photosynthetic production.[46] In contrast, higher temperatures can impair the cell cycle resulting in lower growth rates.[152]

Vertical mixing in the water column largely reduces the UV-induced inhibition of photosynthesis in dependence of the mixing frequency and depth, since phytoplankton are constantly moved from the surface to the thermocline and back. Being at the bottom of the UML allows organisms to repair damage that they encounter at the surface, e.g., phytoplankton communities in a coral reef ecosystem where an increased mixing rate and depth results in less UV-B-induced reduction of photosynthetic_ENREF_24 carbon incorporation.[84] UV-A radiation (315-400 nm) can have positive effects on the growth of larger phytoplankton cells under mixing conditions, since this radiation is used by the enzyme photolyase to split UV-B-induced cyclobutane pyrimidine dimers (CPDs). UV-A radiation also contributes to harvesting of photosynthetic energy.[85, 87]

When stratification becomes more pronounced and the mixing layer shallower, hypoxic (low oxygen) areas in inland and coastal waters expand.[75]_ENREF_121 Harmful algal blooms (dinoflagellates and cyanobacteria) can increase in intensity and frequency in both freshwater and marine habitats due to increasing nutrient availability from terrestrial runoff, rising temperatures and increased stratification.[62] These organisms are not very sensitive to solar UV-B radiation.

In summary, the increased water temperature due to global climate change reduces the depth of the UML and the organisms dwelling in this layer are exposed to higher UV radiation (Fig. 2). Damage from UV-B radiation encountered at the surface is mitigated by repair processes, which are activated when the organisms are passively transported to the lower boundary of the UML. Higher temperatures favour enzyme-mediated repair of damage by UV radiation.

Ocean acidification and exposure to UV radiation

The pH of seawater is in the range of 7.5 to 8.4 and is relatively stable due to buffering capacity. However, increasing atmospheric CO_2 concentrations have lowered this value by about 0.1 units, which corresponds to an increase in the H^+ concentration by 30%.[125] Assuming increasing CO_2 emissions (IPCC A1F1 scenario), an atmospheric concentration of 800 – 1,000 ppmv is predicted by 2100, which will correspond to a pH reduction by 0.3 – 0.4 in the ocean, an increase in H^+ ions in surface waters by 100 – 150% [47].

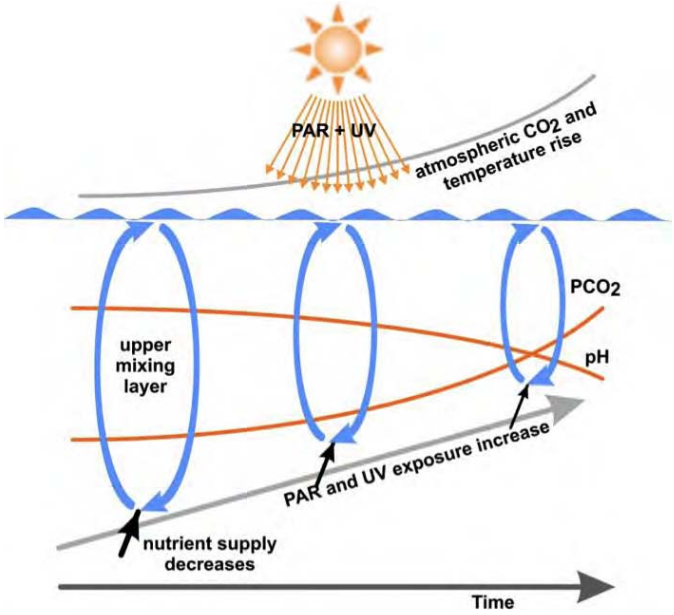

Fig. 2 Combined effects of anthropogenic changes in the environmental condition in marine ecosystems, including UV, CO_2, and temperature. Increasing atmospheric and water CO_2 concentrations reduce the calcifying abilities of many organisms. Increasing water temperatures and incoming solar radiation decrease the depth of the mixing layer (exposing organisms to higher irradiances) and increase the temperature difference between surface and deeper layers. This temperature difference limits the exchange of materials such as nutrients between layers (modified from[47]).

Ocean acidification in conjunction with UV-B radiation affects enzymatic and other biochemical processes in several aquatic organisms, such as phytoplankton, macroalgae and many animals, such as mollusks and corals.[9, 65, 151] Phytoplankton may serve as a partial remedy to the problem, since they sequester CO_2 through photosynthetic carbon fixation.[26] While many higher plants benefit from increased atmospheric CO_2 concentration, this does not support higher growth rates in phytoplankton.[47, 48] The red tide microalga, *Phaeocystis,* showed a much lower growth rate under elevated UV-B which was more pronounced under elevated CO_2, indicating that increasing ocean acidification and UV-B act synergistically to reduce photochemical performance_ENREF_47.[24]

Zooplankton seem to be little affected by water acidification, although acclimation leads to higher respiration and increased grazing rates.[88] Their shells are mainly composed of chitin, which is not affected by acidification. In contrast, those organisms with outer skeletons of calcium carbonate are affected. Increasing acidity affects calcification in phytoplankton,_ENREF_238 calcified macroalgae[49]_ENREF_158 and animals with exo- or endoskeletons such as corals, depriving these organisms of some defense against solar UV-B radiation.[2]_ENREF_190 UV-B radiation strongly impairs the photosynthetic apparatus in coccolithophorides, while UV-A radiation inhibits calcification.[55] The calcified outer scales form a protective exoskeleton[168] Cells grown at high calcium concentrations are more resistant to UV radiation than under limited calcium concentrations.[168]_ENREF_229

In Polar regions, dissolution of CO_2 from the air into seawater differs from that in low latitude areas. Low sea surface temperature means that more CO_2 is dissolved than in low latitude waters. Changes in carbonate chemistry of seawater in the high-latitude oceans are already becoming negatively affecting some species. Consequently, it is projected that within decades, large parts of the Polar oceans will become corrosive to the shells of calcareous marine organisms.[22] The shells of pteropods, small marine snails (sea butterflies), that are key species in the food web, are already dissolving in parts of the Southern Ocean surrounding Antarctica.[10] Ocean acidification has effects not only on biological processes but also on the uptake and availability of iron[134] and ammonium.[12]

Degrees of sensitivity of aquatic organisms

Mechanisms of UV radiation damage

In the upper photic zone, aquatic organisms are exposed to solar UV radiation. Although the UV-B irradiance amounts to only a few percent of the total solar radiation, this wavelength band can be hazardous since it affects biomolecules and cellular structures (Fig. 3) and may block enzymatic reactions and interfere with physiological responses such as motility and orientation.[125] UV-B radiation can either directly alter biomolecules or induce the formation of reactive oxygen species (ROS) inside the cell such as singlet oxygen ($^1O_2$).[139, 172] Formation of ROS is augmented by increasing temperatures.[104]

Photosynthesis is specifically prone to damage by solar UV-B radiation. In addition to other targets, radiation damages the D1 protein in the electron transport chain of photosystem II (PS II), which is subsequently removed and during repair replaced with a newly synthesized protein.[59] Higher water temperatures enhance the repair process, while limited nutrient supply impairs the repair mechanisms.[89] An unexpected finding was that UV-B radiation damages phytoplankton more by impairing repair mechanisms than by directly damaging the protein.[166] In addition, solar UV-B radiation affects the accessory pigments that funnel solar energy to the reaction centres. The blue pigments, phycobilins, in cyanobacteria and red algae are especially sensitive to damage.[138]

Another main target of solar UV-B radiation is the DNA in both prokaryotic (bacteria) and eukaryotic (organisms with a cell nucleus) organisms. In addition to single- and double strand breaks and the formation of 6-4 photoproducts (and their Dewar valence isomers), the most frequent lesion induced by UV-B radiation is the induction of CPDs.[124] Repair mechanisms for DNA damage include several mechanisms (such as excision repair, mismatch repair and SOS response), but above all the photoactivated CPD photolyase is engaged to break the dimers using the energy of UV-A radiation or blue light photons.[124]

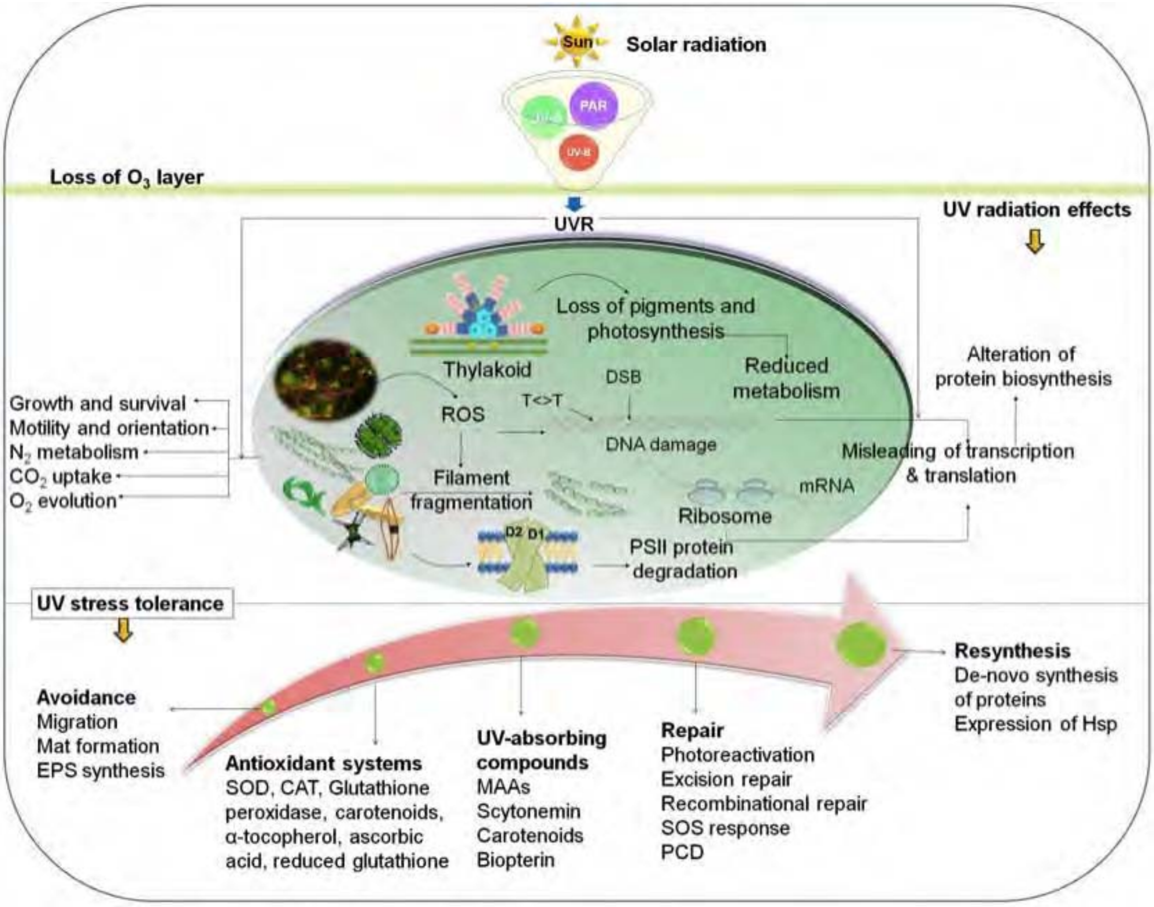

Fig. 3 Effects of solar UV radiation on biomolecules, cellular components and physiological responses as well as mitigating strategies and repair mechanisms (for details see text).

Mechanisms to avoid or moderate UV-B radiation-induced damage include vertical migration to move out of zones of excessive radiation found in zooplankton and phytoplankton or by mat formation.[7] With the exception of very small cells (picoplankton), many aquatic organisms produce UV-absorbing compounds to prevent solar UV-B radiation from damaging the central regions of the cell such as the nucleus. Cyanobacteria synthesize scytonemin to diminish the impact of UV radiation.[121] In addition, phytoplankton and macroalgae produce several mycosporine-like amino acids (MAAs).[93] UV-B radiation-induced reactive oxygen species are removed by enzymatic reactions and non-enzymatic quenchers including carotenoids.[136, 172] Animals such as zooplankton are not capable of synthesizing MAAs, but may take up these substances with their food and use them for protection from solar UV radiation.

Several factors make accurate assessment and measurement of the effects of UV radiation on organisms in natural ecosystems very challenging. These factors include the wide variation among organisms in the mechanisms of defense against damage by UV radiation, the need to allow organisms adequate time to adapt to sudden highly elevated UV radiation levels, and assuring accurate measurements of UV radiation. Laboratory experiments with artificial sources of UV radiation often use excessive short wavelength UV-

B irradiance levels that are more damaging and have little ecological significance to natural solar radiation due to inappropriate balance in the spectral composition (see Chapter 3).

UV radiation exposure levels in aquatic ecosystems exhibit strong gradients over time (daily to annual), depth, and distance from the shore. Different natural populations may vary in their sensitivity to UV radiation over time and may acclimate to the radiation, resulting in some adaptation.

Parasites and pathogens

UV radiation plays an important role in the ecology of many infectious diseases of aquatic organisms, particularly when there is a pronounced difference in the UV radiation tolerance of the host and pathogen or parasite. For example, *Metchnikowia* is a fungal parasite that is lethal to the important freshwater zooplankton grazer, *Daphnia*. Relative to its host, the parasite is extremely sensitive to UV radiation and longer wavelength sunlight. Thus in more UV radiation transparent water bodies, outbreaks of this parasite are suppressed and delayed until later in the autumn after incident solar UV radiation has subsided.[113] Natural solar radiation is also highly effective at reducing viral infections in some aquatic organisms including fish and harmful algal blooms (HABs). Some experiments that have manipulated natural sunlight reveal a million-fold decrease in the infectious hematopoietic necrosis virus (HNV) in Atlantic salmon in treatments exposed to sunlight versus dark controls for just 3 hours.[50] Viruses may be responsible for more than half of the mortality of aquatic cyanobacteria, which has led to interest in using cyanophages to control HABs of toxic cyanobacteria.[71] The extreme sensitivity of many viruses to UV radiation damage suggests that knowing more about the changing underwater UV radiation environment may lead to new insights into the potential role of viruses in controlling HAB of cyanobacteria.[71]

Trematodes are some of the most common parasites in intertidal systems. Their larvae are free-living for short periods of time between hosts that range from snails to other invertebrates and birds. During this short, free-living period in very shallow aquatic environments the larvae may be exposed to high levels of solar UV radiation. Recent UV radiation exposure experiments in the laboratory showed that UV radiation caused DNA damage and oxidative stress in the larvae and no evidence of photoprotective MAAs or photoenzymatic repair.[145] Similar experiments also demonstrated negative effects of UV-B as well as UV-A radiation exposure on the survival of larvae. In addition, susceptibility to infection of the amphipod secondary host increased when the host was exposed to UV radiation.[146] Further experiments on this trematode parasite system revealed significant interaction effects between UV radiation and temperature, with greater UV radiation effects at 20°C *vs* 30°C.[147]

Parasites may also play some role in altering the exposure to UV radiation of infected fish hosts. Three-spined sticklebacks undertake daily vertical migration and are generally deeper in the water column during the day than during the night. However, individuals captured in the surface waters during the day have a higher parasite load than those captured at night, which increases the potential for this parasite to be transmitted to its definitive host - fish eating birds.[120] Increasing evidence is accumulating for the direct and indirect effects of exposure to UV radiation on several marine fish species. Melanosis and melanoma skin cancer rates of up to 15% have been reported in coral trout in the Great Barrier Reef of Australia (Fig. 4).[149] The role of UV radiation in the induction of this high prevalence is unknown. In shallow, UV-transparent aquatic ecosystems, such as coral reef flats, photobleaching may lead to destruction of corals and may result in further negative effects when UV radiation and interactions with multiple stressors occurs.[63]

Bacteria and viruses
Heterotrophic bacteria and viruses are more affected by UV radiation than phytoplankton since they do not synthesize UV-absorbing pigments (but they can repair UV induced damage). Their small dimensions would require extremely large concentrations of these substances to effectively protect them from excessive short-wavelength radiation.[170] These organisms respond to UV radiation with adaptive processes such as increased frequency of division, but exposure to UV radiation results in significant changes in species composition due to a varying UV sensitivity of different bacteria taxa.[98] Acclimation to long-term UV exposure has also been found in natural sub-Antarctic phytoplankton communities.

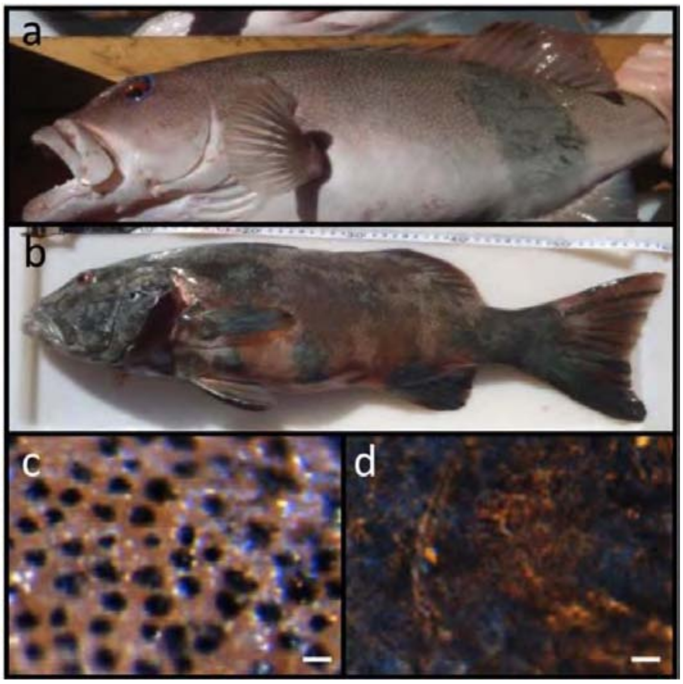

Fig. 4 Cancer lesions on Coral Trout from the Great Barrier Reef observed in up to 15% the natural population and thought to be due to exposure to solar UV radiation. Shown are individuals with only partial (a) and almost full body (b) lesions as well as close-up photographs taken under a microscope of healthy skin (c) and skin lesions (d). Scale bars are 20 µm (from [149]).

Inland and coastal waters are rich in bacterioplankton, which feed on the high concentrations of humic substances.[127] Bacteria are under pressure from UV-B and UV-A radiation component of sunlight, but recover when the solar radiation decreases during the daily cycle. The highest bacterioplankton activity has been found between 5 and 10 m, below the depths of high solar UV-B radiation exposure. Inhibitory effects of UV radiation on bacterial growth are mitigated by water mixing.[13] Different strains have different sensitivity to higher temperatures and UV radiation, leading to selection of more resistant strains and species. Whether or not also genetic adaptation may mitigate the effects of altered stress parameters needs to be examined.[53]

Phytoplankton
The amount of solar UV and visible radiation determines the species composition of phytoplankton blooms. Large-celled diatoms are less affected by solar UV-B radiation and can utilise high light irradiances.[76] In contrast, small-celled phytoplankton such as the

ecologically important cyanobacteria and small eukaryotes experience more UV-B-induced damage than larger cells.[90]

In oligotrophic waters (waters with low nutrient contents) solar radiation induces a higher kill rate in marine picoplankton than in larger cyanobacteria and eukaryotic phytoplankton.[91] The main driver for mortality is UV-B radiation since filtering out this short wavelength radiation significantly enhances survival. Surface samples are more resistant to solar UV-B radiation than samples collected at depth. Exposing phytoplankton samples experimentally at a fixed depth inhibits photosynthesis more than under natural conditions, where the organisms are moved within the mixing layer.[72] The mitigation of the UV-induced inhibition of photosynthetic carbon fixation depends on the mixing rate and depths as shown in tropical coral reef phytoplankton assemblages.[84]

Phytoplankton of the same taxonomic groups can have significant different sensitivities toward solar UV-B radiation depending on their geographical origin such as tropical, temperate and Antarctic habitats. In contrast to UV-B radiation, even the highest applied doses of UV-A radiation did not cause growth inhibition. After periods of excessive UV radiation some phytoplankton species, such as the marine diatom *Phaeodactylum tricornutum*, show a higher growth rate which partially compensates for prior UV-induced growth reductions. Photosynthesis in phytoplankton is damaged by UV-B radiation mainly at the D1 protein but with higher temperatures increasing the repair rate.[89]

Primary production in freshwater systems is, in contrast to that in marine systems, often limited by phosphorus. Because of this, effects of UV radiation on phosphorus metabolism can be important in freshwater aquatic ecosystems. For example, in a high mountain mesocosm experiment, heterotrophic microorganism biomass (bacteria and flagellates) increased when phosphorus addition was reduced by 80% if UV radiation was excluded.[101] Sereda et al. investigated how ambient UV radiation affects the phosphorus metabolism of plankton communities from 18 lakes in Ontario and Saskatchewan.[133] The turn-over time for phosphorus and the steady state phosphate concentration increased when the organisms were exposed to UV radiation.

The concentration of phytoplankton strongly depends on the pressure by grazers. For example, the seasonal abundance and feeding patterns of copepods in a pelagic food web in the White Sea showed that up to 85% of the daily phytoplankton biomass was consumed by calanoid copepods.[100] Exposure to UV radiation affects the quality of phytoplankton in terms of food for zooplanktonic grazers.[105] Therefore the level of UV-B radiation is an important modulator of the phytoplankton standing crop.

Mitigation of UV-induced damage by UV-absorbing substances

Phytoplankton use a number of effective repair mechanisms as well as UV-absorbing substances (mostly MAAs) to mitigate UV-B-induced damage of DNA and the photosynthetic apparatus. Samples from phytoplankton blooms under the ozone 'hole' counterintuitively show significantly less inhibition of the photosynthetic quantum yield by UV-B radiation than those from outside the ozone-depleted areas, indicating the protective role of their higher MAA concentration.[21, 112] Another reason for these findings may be that large-size cells occur inside the blooms while outside the blooms smaller cells prevail, which, due to their small size, cannot take advantage of the MAA protection. Ryan et al. experimentally measured the effects of UV-B radiation on sea-ice algae in Antarctica[130] and concluded that brine channel communities were better protected from UV-B radiation.. They speculate that the high tolerance to UV-B radiation in the brine communities could be due to production of MAAs.

Concentrations of UV-absorbing compounds such as MAAs increase with higher exposure to solar radiation in phytoplankton and macroalgae and decrease under experimental conditions without UV.[137] In parallel, inhibition by UV radiation of growth and photosynthesis is mitigated with increased contents of MAAs_ENREF_34. Higher levels of nitrate result in higher contents of MAAs, while phosphate limitation did not affect the MAA content.[169] In addition to their UV-absorbing properties, MAAs serve as antioxidants scavenging ROS.[92]

MAAs are produced in algal cells and protect against UV-B radiation. The production depends on species, degree of impairment, and locality.[56] Large differences have been found in MAA production that correlated with differences in species composition and sensitivity to UV-B radiation. Phytoplankton in inland and coastal waters are generally less tolerant to UV radiation than open ocean assemblages. This is probably because they need less protection and therefore have developed lower MAA concentrations as a consequence of the lower transparency of the water.[6] UV-B radiation can impair growth and development, morphology, photosynthesis and nutrient uptake in coastal phytoplankton species.[37]

In the tropics UV-absorbing MAAs within phytoplankton cells show the same concentration year round, while in temperate waters MAA concentrations are lower in winter than in summer in surface waters <50 m.[93] MAA expression is linearly related with the UV irradiance at the surface. In the tropics, phytoplankton is under considerable UV-B radiation stress on sunny days. On cloudy days microplankton (>20 µm) use UV-A radiation as an energy source for photosynthesis, while pico- and nanoplankton are impaired.[86] Cloud patterns and density affect the level of UV radiation, but this has rarely been studied in detail. Along a 13,000 km meridional transect (from 52°N to 45°S) the highest MAA concentrations were found in the south (>40° S) and in the north subtropical region.[93]

Interacting stress factors

Satellite monitoring of the oceans, shows that phytoplankton concentrations have been declining at about 1% per year over the past 50 years.[19] Laufkoetter et al.[82] calculated a different number for the decrease (6.5% during the period 1960-2006), simulating phytoplankton net primary production on a global scale with large spatial resolution. However, there are large areas of uncertainty: even though the external factors of temperature, pH, CO_2 supply, nutrients, PAR and UV irradiances and mixing depths are known to be primary variables driving photosynthesis and production, their interactions have not been thoroughly investigated.[47] This interacting web can only be disentangled by multifactorial analysis and modelling.[20, 58] In order to reveal the effects in nature with its fast changing temperature, solar radiation and nutrient availability, large scale, long-term studies are needed in the relevant ecosystems.[47] This is difficult and time-consuming because of the vast areas to be covered, the diversity of organisms and ecosystems and the low concentrations of cells especially in open ocean waters. The effects of the many possible feedback mechanisms on marine primary producers are largely unknown. For example, do higher temperatures of the oceans result in denser cloud cover? This could result in lower exposure of the phytoplankton to solar UV radiation and PAR, favouring taxa that are more sensitive to UV radiation.[67] Feedbacks have the potential to change the species composition of future assemblages of primary producers with large consequences for inland and marine food webs.

Feedbacks between UV radiation and inland and coastal ecosystem organisms also have the potential to moderate climate. For example, phytoplankton and macroalgae produce dimethylsulfoniopropionate (DMSP),[129] that acts as an osmolytic substance or as an antioxidant. DMSP is excreted and broken down to dimethylsulfide (DMS), which enters the atmosphere and down-regulates global warming and reduces UV-B radiation from reaching Earth. In temperate shelf areas, the key phytoplankton species, UV irradiance and nutrient concentrations determine the seasonal cycle of DMS. Ocean acidification reduces DMS accumulation, enhancing global warming, but the role of UV radiation on the production of DMS has not been investigated.[140]

Increasing environmental pollution, such as crude oil spills affect algae and bacteria especially in the Arctic shallow-water marine habitats. Pyrene is a component of crude oil and accumulates in the sediment where it exerts a synergistically negative effect with increased solar UV-B radiation.[116] Pyrene is taken up by and concentrated in the cells where it reduces growth rate. In the Greenland Current and Arctic Ocean persistent organic pollutants (POP) accumulate in phytoplankton as documented during the ATOS-ARCTIC cruise on board the R/V Hespérides.[45]

Exposure to solar UV radiation alters the fatty acid concentration in several phytoplankton groups[117] and affects enzyme activity and nitrogen assimilation in both eukaryotic and prokaryotic phytoplankton. However, the sensitivity of phytoplankton species to UV-B radiation is modified by the light history indicating some short-term acclimation to UV-B radiation stress.[60] Comparable levels of solar UV-B radiation caused the same degree of growth inhibition in phytoplankton in coastal and offshore surface waters of the South China Sea under clear skies by about 28%. In contrast, inhibition by UV-A radiation was higher in open water samples (13%) than in coastal water samples (4%).[87] Due to terrestrial runoff, coastal ecosystems often have higher nutrient concentrations than open ocean systems. In some taxa, such as dinoflagellates, higher nutrient supply (N and P) augments the quantum yield resulting in a different species composition than in open oceanic waters.[3] For example, dinoflagellates may outcompete diatoms when rivers deliver larger nutrient loads to coastal waters.[141] High nutrient concentrations in coastal waters often induce blooms of toxic phytoplankton (e.g., dinoflagellates), which enter the food chain and can be poisonous to humans. However, solar UV-B radiation does not seem to impair these red tide phytoplankton species.[62]

The toxicity of many pollutants increases with exposure to UV radiation. Inland and coastal marine environments are under stress from these interactions between UV radiation and pollutants such as polycyclic aromatic hydrocarbons (PAHs), which form from combustion engines, and water-soluble fractions of heavy oil that affect plankton communities. Toxicity of PAHs is enhanced by solar UV radiation as shown with natural phytoplankton communities from the Mediterranean Sea, Atlantic, Arctic and Southern Ocean.[32] Natural phytoplankton communities pre-stressed with UV-B radiation are more susceptible to pollutants, such as atrazine, tributyltin or crude oil, which enter coastal waters from terrestrial drainage or maritime traffic, than those grown under UV radiation-free conditions.

Benthic organisms

Several studies have demonstrated the response of benthic (bottom-dwelling) organisms and communities to solar UV radiation in shallow aquatic habitats. In combined laboratory and field experiments freshwater snails were found to have several mechanisms to avoid damage from UV radiation including behavioural avoidance, photorepair, increased shell thickness, pigmentation and body size.[1, 111] Juvenile benthic marine polychaetes showed reduced growth and development of tentacles when fed detritus derived from diatoms pre-exposed to artificial UV-B radiation from lamps versus diatoms that were not pre-exposed to UV-B radiation.[106] Ostracods, small crustaceans that thrive in shallow benthic habitats, have shells that block 60-80% of UV radiation, as opposed to the exoskeleton of more planktonic *Daphnia* that block only 35% of UV radiation.[161] In a four month-long field experiment on tidal flats where the benthic community was followed when ambient UV-B or UVB+UVA radiation was excluded, the only structural change was a doubling of Ostracod biomass under UV radiation compared to PAR only treatments.

Seaweeds are an important group of benthic organisms for coastal ecosystems. In addition to being primary producers, seaweeds shape local environments that are important for many animals including fish larvae. Seaweeds are located in fixed positions and need sunlight for photosynthesis and thus cannot escape exposure to high UV radiation. A substantial species-dependent variation in sensitivity to UV radiation correlates with vertical zonation; and smaller and juvenile seaweeds are generally the most sensitive.[14] Seaweeds have several life stages of which some are motile (zoospores and gametes) and important for the expansion of the species to new locations. These stages may also be sensitive to DNA damage by solar UV-B radiation as they have only one gene copy.[109]

The seafloor also harbours benthic communities in the form of invertebrates, bacteria, fungi and microalgae. An experimental study examined the effects of different radiation regimes on the development of these benthic communities in Spitsbergen.[41] A total of 17 algal and invertebrate taxa were analysed. No detrimental effects were found from UV radiation (relative to PAR only); although in some species the abundance increased, especially under UV-A radiation. This indicates that at the community level the effects of exposure to UV radiation are dependent on species composition and successional stage. A recent study on the impact of multiple stressors, including UV radiation, temperature and ocean acidification on molluscan development[30] showed that the embryos developed significantly better at 26°C than at 22°C. Mortality was significantly higher at 22°C and pH of 7.6. UV radiation had no significant impact on the embryonic development.

Zooplankton

Changes in species composition resulting from climate change[160] may favour species that have different UV tolerances. Species that routinely experience high levels of UV radiation are better protected than those that are used to low levels of UV radiation, as was demonstrated by the differences in the UV absorbance of carapaces of *Daphnia* originating from high UV alpine and low UV boreal lakes.[107] In a field survey in Argentina, the relative abundance of more UV-tolerant copepods versus less UV-tolerant *Daphnia* increased with the distance from the turbid input of a glacier, suggesting UV radiation as a possible regulator of zooplankton community structure, although a role for other factors that changed along the gradient cannot be ruled out.[68]

The response of species to UV radiation varies and is related to the extent of their ability to use various UV avoidance or protection strategies. Evidence confirms that exposure to UV radiation plays an important role in stimulating downward migration of zooplankton during the day in highly transparent waters. These observations have recently been integrated with past studies to develop a more comprehensive theory of daily vertical migration (DVM).[164] Some of the strongest evidence for the importance of UV radiation in DVM comes from alpine lakes that lack the visually feeding fish that are often implicated in DVM. For example, in high elevation lakes in Northern Italy[153] and Poland,[118] crustacean zooplankton migrate to deeper depths during the day in spite of the lack of fish or other visual predators. In the Italian lakes the abundance of crustacean zooplankton in the surface waters of 13 lakes during the day was found to be similar in those lakes with and without fish, suggesting that it is not fish predation that excludes zooplankton from the surface waters of these lakes.[154] In temperate lakes of glacial origin *in situ* experimental manipulation of fish and UV radiation in 15 m deep mesocosms similarly revealed that UV radiation induced stronger downward migration than did the presence of fish.[128] In this same study, *Daphnia* were found to migrate upward in the water column during daylight following a strong storm event that reduced water transparency to UV radiation and visible light. In some marine systems copepods may occur deep enough in the water column that UV radiation plays little or no role in DVM.[68] Collectively these observations suggest that changes in water transparency due to climate change are likely to influence the vertical distribution and abundance of zooplankton, a critical link in both freshwater and marine food webs.

The importance of the sublethal effects of UV radiation on both freshwater and marine zooplankton has become increasingly recognized. Sublethal effects of UV radiation on marine copepods include reduced egg quality and survival of larvae.[68] In a series of laboratory experiments marine copepods grazed at higher rates on algae that had previously been exposed to elevated levels of UV radiation.[35]

Further advances have been made in understanding defense mechanisms against UV radiation in freshwater and marine zooplankton, including the trade-offs among multiple defenses and pressures from visual predators and other environmental factors. A recent meta-analysis shows that copepods from freshwater ecosystems have more carotenoids than marine copepods, but that the two groups have similar amounts of MAAs.[68] Repair and antioxidant enzymes may similarly provide defense against UV radiation and visual predators simultaneously. Following exposure to artificial UV radiation, freshwater calanoid copepods rapidly activated enzyme systems that reduce peroxidation, cell death, and damage to neurotransmitters.[142] Freshwater copepods challenged by simultaneous exposure to fish predation and potentially damaging UV radiation can exhibit trait compensation wherein they increase anti-oxidant enzymes and decrease pigmentation, thus reducing damage by both threats.[69] Higher concentrations of carotenoid photoprotective pigments have been observed in copepods in shallow turbid lakes with lower water transparency, apparently due to the lack of aquatic plants and increase in wind-driven turbulence that exposes the copepods to surface UV radiation.[132]

Fish, amphibians and mammals

Recent evidence indicates that changes in the underwater UV radiation environment may play an important role in regulating invasive fish in cold, clear-water lakes. Studies of two species of invasive warm-water fish (bluegill and largemouth bass) and one native (Lahontan redside) fish in Lake Tahoe, California-Nevada, have demonstrated strong differences in tolerance to UV radiation between native and invasive species. Warm temperatures in shallow near-shore habitats are necessary for the invasive species to breed. High UV transparency in these near-shore habitats prevents the warm-water invasive species from successfully breeding due to the low tolerance to UV radiation of their larvae. Climate change and other disturbances that reduce UV transparency of waters in the warmer shallow shoreline habitat can open an invasion window that permits the invasive warm-water species to become established and reduces native species population sizes through competition and predation.[156] The differences in tolerance to UV radiation between invasive and native species can be used in fisheries management to exclude the warm-water invasive species by developing minimum UV attainment thresholds and maintaining high UV transparency of the shoreline breeding habitats.[157] Histological studies have demonstrated that species of fish native to highly UV transparent lakes are also more tolerant of simultaneous exposure to solar UV radiation and pollutants such as polycyclic aromatic hydrocarbons (PAHs) than are invasive warm-water species found in characteristically less UV transparent lakes.[52] UV radiation and PAHs exposure experiments confirmed these results as well as those showing that the native species have more melanin for coping with high UV radiation levels than do the invasive species.[51]

Other recent studies have demonstrated both behavioural avoidance as well as other indirect and direct damaging effects of UV radiation on fish. Experiments that manipulated natural UV radiation with filter foils demonstrated that the survival of freshwater yellow perch larvae is more negatively influenced by UV-A radiation and longer wavelength UV-B and UV-A radiation than by the shorter wavelength UV-B.[17] Experimental studies manipulated exposure of two species of salmon fry to solar UV-B radiation in outdoor rearing tanks and tagged smolts using acoustic transmitters to examine their growth rates during rearing as well as subsequent survival rates in the marine environment.[102] Exposure to UV-B radiation led to a decrease in early growth of Coho salmon, but had no effects on early survival of either species in the oceans. Exposure of European sea bass larvae to even low levels of artificial UV radiation in the laboratory led to behavioural avoidance, reduced ability to osmoregulate, as well as increased mortality.[148] Atlantic cod larvae subjected to prior exposure to artificial UV lamps showed subsequent reductions in the ability to escape suction predators, but not tactile predators;[43] feeding rates were also reduced compared to unexposed controls.[42] While these studies suggest reductions in feeding will translate to reduced survival under natural conditions,[42] this speculation is in contrast to a prior study with largemouth bass larvae under more natural conditions in lakes, where the presence of UV radiation stimulated feeding on zooplankton.[83] An analysis of the relationship between brown trout biomass and DOM in 168 lakes in Southern Norway revealed a unimodal relationship with a peak in fish biomass at intermediate DOM levels;[36] UV radiation was hypothesized to play a role in decreased biomass at low DOM levels.

In a comprehensive assessment of exposure to UV-B radiation in amphibian breeding habitats, UV-B radiation levels were estimated to be high enough to seriously threaten wood frogs breeding in northern Minnesota vernal pools.[110] Reductions in forest canopy cover due to timber harvest as well as changes in water transparency or pool depth related to climate change may further alter exposure to UV radiation in these amphibian breeding habitats.

Marine mammals are being influenced not only by direct damage from exposure to solar UV radiation, but also indirectly through pollution of coastal marine habitats by anthropogenic sunscreen chemicals (sun-tan lotions). They contribute to the bleaching of corals by promoting viral infections and may change the sex of fish.[29] Methods for identifying UV-induced skin damage in humans based on real time PCR and mitochondrial DNA (mtDNA) biomarkers have been recently modified and applied to whales.[18] Individuals of three different whale species showed significant variations in mtDNA damage in the skin using these techniques. Different species of whales vary in their strategies for coping with exposure to UV radiation. Blue whales, which have relatively pale skin, vary their melanin production seasonally as UV radiation levels vary with their migrations across latitudes; the inverse relationship between melanin and levels of damage from UV radiation suggest that melanin is an effective defense against UV radiation in these cetaceans.[99] Sperm whales, which spend more time in the high UV radiation environments at the surface of the ocean all year long, have more melanocytes than blue whales, but similar amounts of melanin.[99] The widely used human sunscreen compound, octocrylene, has recently been found in the liver of dolphins off the coast of Brazil.[44] Thus it could also have effects on humans.

Gaps in knowledge

While the response of aquatic biomass producers to solar UV-B radiation and global climate change have been characterized to some extent, the effects of interacting stress factors on natural assemblages and ecosystems needs to be further investigated. How the changes in phytoplankton species composition, due to differential sensitivity of individual species caused by UV radiation and interaction with other environmental factors such as temperature, will affect the subsequent food web including fish and mammals also needs to be quantified. There are limited records on the dynamics of overall effects of UV radiation on physical, chemical, and biological attributes of oligotrophic biomass changes.

Ocean acidification due to increased atmospheric CO_2 concentrations alters the marine chemical environment, which in turn interferes with UV radiation-protecting calcification in many aquatic organisms including phytoplankton, macroalgae and animals such as molluscs and corals. Multifactorial effects including UV-B radiation and ocean acidification on diverse organisms as well as ecosystems should to be studied in order to understand the impacts of future ocean climate changes.

Aquatic organisms employ several lines of defense mechanism to mitigate the damaging effects of UV radiation. A number of ecologically and economically important organisms need to be screened for the presence of photoprotective compounds and molecular mechanisms of repair.

There is limited knowledge on the cumulative effects of UV radiation-climate change interactions on the nature and type of invasive species and its impact on native populations in aquatic ecosystems.

References

1 Ahlgren J, Yang X, Hansson L-A and Brönmark C, 2013, Camouflaged or tanned: plasticity in freshwater snail pigmentation, *Biol. Lett.*, **9**, 20130464.

2 Anthony KRN, Maynard JA, Diaz-Pulido G, Mumby PJ, Marshall PA, Cao L and Hoegh-Guldenberg O, 2011, Ocean acidification and warming will lower coral reef resilience, *Glob. Change Biol.*, **17**, 1798-1808.

3 Arndt S, Lacroix G, Gypens N, Regnier P and Lancelot C, 2011, Nutrient dynamics and phytoplankton development along an estuary–coastal zone continuum: a model study, *J. Mar. Syst.*, **84**, 49-66.

4 Arrigo KR, Perovich DK, Pickart RS, Brown ZW, van Dijken GL, Lowry KE, Mills MM, Palmer MA, Balch WM, Bahr F, Bates NR, Benitez-Nelson C, Bowler B, Brownlee E, Ehn JK, Frey KE, Garley R, Laney SR, Lubelczyk L, Mathis J, Matsuoka A, Mitchell BG, Moore GWK, Ortega-Retuerta E, Pal S, Polashenski CM, Reynolds RA, Schieber B, Sosik HM, Stephens M and Swift JH, 2012, Massive phytoplankton blooms under Arctic sea ice, *Science.*, **336**, 1408

5 Arrigo KR and van Dijken GL, 2011, Secular trends in Arctic Ocean net primary production, *J. Geophys. Res. Oceans*, **116**, 160-168.

6 Ayoub LM, Hallock P, Coble PG and Bell SS, 2012, MAA-like absorbing substances in Florida Keys phytoplankton vary with distance from shore and CDOM: Implications for coral reefs, *J. Exp. Mar. Biol. Ecol.*, **420**, 91-98.

7 Barnes BB, Hu C, Cannizzaro JP, Craig SE, Hallock P, Jones DL, Lehrter JC, Melo N, Schaeffer BA and Zepp R, 2014, Estimation of diffuse attenuation of ultraviolet light in optically shallow Florida Keys waters from MODIS measurements, *Rem. Sens. Environ.*, **140**, 519-532.

8 Bastviken D, Tranvik LJ, Downing JA, Crill PM and A. Enrich-Prast A, 2011, Freshwater methane emissions offset the continental carbon sink, *Science.*, **331**, 50.

9 Beaufort L, Probert I, De Garidel-Thoron T, Bendif EM, Ruiz-Pino D, Metzl N, Goyet C, Buchet N, Coupel P, Grelaud M, Rost B, Rickaby REM and de Vargas C, 2011, Sensitivity of coccolithophores to carbonate chemistry and ocean acidification, *Nature*, **476**, 80-83.

10 Bednaršek N, Tarling GA, Bakker DCE, Fielding ZS, Jones EM, Venables HJ, Ward P, Kuzirian A, Lézé B, Feely RA and Murphy EJ, 2012, Extensive dissolution of live pteropods in the Southern Ocean, *Nature Geosci.*, **5**, 881-885.

11 Bélanger S, Babin M and Tremblay J-E, 2013, Increasing cloudiness in Arctic damps the increase in phytoplankton primary production due to sea ice receding, *Biogeosci.*, **10**, 4087-4101.

12 Beman JM, Chow C-E, King AL, Feng Y, Fuhrman JA, Andersson A, Bates NR, Popp BN and Hutchins DA, 2011, Global declines in oceanic nitrification rates as a consequence of ocean acidification, *Proc. Nat. Acad. Sci. USA.*, **108**, 208–213.

13 Bertoni R, Jeffrey WH, Pujo-Pay M, Oriol L, Conan P and Joux F, 2011, Influence of water mixing on the inhibitory effect of UV radiation on primary and bacterial production in Mediterranean coastal water, *Aquat. Sci.*, **73**, 377-387.

14 Bischof K and Steinhoff FS, 2012, Impacts of stratospheric ozone depletion and solar UVB radiation on seaweeds, in *Seaweed Biology,* **Vol. 219**, Springer Berlin Heidelberg, pp. 433-448.

15 Bjørklund KR, Kruglikova SB and Anderson OR, 2012, Modern incursions of tropical Radiolaria into the Arctic Ocean, *J. Micropalaeontol.*, **31**, 139-158.

16 Bocaniov SA, Barton DR, Schiff SL and Smith REH, 2013, Impact of tributary DOM and nutrient inputs on the nearshore ecology of a large, oligotrophic lake (Georgian Bay, Lake Huron, Canada), *Aquat. Sci.*, **75**, 321-332.

17 Boily V, Bertolo A, Magnan P, Martinoli M-G and Thérien H-M, 2011, The effects of UVR irradiance and spectral composition on yellow perch (*Perca flavescens*) larvae survival, *Aquat. Sci.*, **73**, 345-354.
18 Bowman A, Martinez-Levasseur LM, Acevedo-Whitehouse K, Gendron D and Birch-Machin MA, 2013, The simultaneous detection of mitochondrial DNA damage from sun-exposed skin of three whale species and its association with UV-induced microscopic lesions and apoptosis, *Mitochondrion*, **13**, 342-349.
19 Boyce DG, Lewis MR and Worm B, 2010, Global phytoplankton decline over the past century, *Nature*, **466**, 591-596.
20 Boyd PW, 2011, Beyond ocean acidification, *Nature Geosci.*, **4**, 273-274.
21 Bracher AU and Wiencke C, 2000, Simulation of the effects of naturally enhanced UV radiation on photosynthesis of Antarctic phytoplankton, *Mar. Ecol. Prog. Ser.*, **196**, 127-141.
22 Broadgate W, Riebesell U, Armstrong C, Brewer P, Denman K, Feely R, Gao K, Gattuso J-P, Isensee K and Kleypas J, 2013, Ocean acidification summary for policymakers–Third symposium on the ocean in a high-CO_2 world.
23 Caverly E, Kaste JM, Hancock GS and Chambers RM, 2013, Dissolved and particulate organic carbon fluxes from an agricultural watershed during consecutive tropical storms, *Geophys. Res. Lett.*, **40**, 5147-5152.
24 Chen S and Gao K, 2011, Solar ultraviolet radiation and CO_2-induced ocean acidification interacts to influence the photosynthetic performance of the red tide alga *Phaeocystis globosa* (Prymnesiophyceae), *Hydrobiologia.*, **675**, 105-117.
25 Cory RM, Crump BC, Dobkowski JA and Kling GW, 2013, Surface exposure to sunlight stimulates CO_2 release from permafrost soil carbon in the Arctic *Proc. Nat. Acad. Sci. USA.*, **110**, 3429-3434.
26 Coupel P, Jin HY, Joo M, Horner R, Bouvet HA, Sicre M-A, Gascard J-C, Chen JF, Garçon V and Ruiz-Pino D, 2012, Phytoplankton distribution in unusually low sea ice cover over the Pacific Arctic, *Biogeosci.*, **9**, 4835-4850.
27 Couture S, Houle D and Gagnon C, 2012, Increases of dissolved organic carbon in temperate and boreal lakes in Quebec, Canada, *Environ. Sci. Poll. Res.*, **19**, 361-371.
28 Cui S, He J, He P, Zhang F, Ling C and Ma Y, 2012, The adaptation of Arctic phytoplankton to low light and salinity in Kongsfjorden (Spitsbergen), *Adv. Polar Sci.*, **23**, 19-24.
29 Danovaro R, Bongiorni L, C. C, Giovannelli D, Damiani E, Astolfi, P., Greci L and Pusceddu A, 2008, Sunscreens cause coral bleaching by promoting viral infections, *Environ. Health Perspect.*, **116**, 441-447.
30 Davis AR, Coleman D, Broad A, Byrne M, Dworjanyn SA and Przeslawski R, 2013, Complex responses of intertidal molluscan embroys to a warming and acidifying ocean in the presence of UV radiation, *PLoS ONE*, **8**, e55939.
31 Dhillon GS and Inamdar S, 2013, Extreme storms and changes in particulate and dissolved organic carbon in runoff: Entering uncharted waters?, *Geophys. Res. Lett.*, **40**.
32 Echeveste P, Agustí S and Dachs J, 2011, Cell size dependence of additive versus synergetic effects of UV radiation and PAHs on oceanic phytoplankton, *Environ. Pollut.*, **159**, 1307-1316.
33 FAO, 2012, *The State of World Fisheries and Aquaculture 2012*, FAO, Rome.
34 Fichot CG, Kaiser K, Hooker SB, Amon RM, Babin M, Bélanger S, Walker SA and Benner R, 2013, Pan-Arctic distributions of continental runoff in the Arctic Ocean, *Sci. Rep.*, **3**, 1053.
35 Fields DM, Durif CMF, Bjelland RM, Shema SD, Skiftesvik AB and Browman HI, 2011, Grazing rates of *Calanus finmarchicus* on *Thalassiosira weissflogii* cultured under different levels of ultraviolet radiation, *PLoS One*, **6**.
36 Finstad AG, Helland IP, Ugedal O, Hesthagen T and Hessen DO, 2014, Unimodal response of fish yield to dissolved organic carbon, *Ecol. Lett.*, **17**, 36-43.
37 Fiorda Giordanino M, Strauch SM, Villafañe VE and Helbling EW, 2011, Influence of temperature and UVR on photosynthesis and morphology of four species of cyanobacteria, *J. Photochem. Photobiol. B.*, **103**, 68-77.
38 Fischetti M, 2013, Deep heat threatens marine life, *Sci. Am.*, **308**, 92.
39 Forsstrom L, Roiha T and Rautio M, 2013, Responses of microbial food web to increased allochthonous DOM in an oligotrophic subarctic lake, *Aquat. Microb. Ecol.*, **68**, 171-184.
40 Frey KE, Perovich DK and Light B, 2011, The spatial distribution of solar radiation under a melting Arctic sea ice cover, *Geophys. Res. Lett.*, **38**, L22501.
41 Fricke A, Molis M, Wiencke C, Valdivia N and Chapman AS, 2011, Effects of UV radiation on the structure of Arctic macrobenthic communities, *Polar Biol.*, **34**, 995-1009.
42 Fukunishi Y, Browman HI, Durif CMF, Bjelland RM, Shema SD, Fields DM and Skiftesvik AB, 2013, Sub-lethal exposure to ultraviolet radiation reduces prey consumption by Atlantic cod larvae (*Gadus morhua*), *Mar. Biol.*, **160**, 2591-2596.

43 Fukunishi Y, Browman HI, Durif CMF, Bjelland RM and Skiftesvik AB, 2012, Effect of sub-lethal exposure to ultraviolet radiation on the escape performance of atlantic cod larvae (*Gadus morhua*), *PLoS ONE*, **7**, e35554.

44 Gago-Ferrero P, Alonso MB, Bertozzi CP, Mango J, Barbosa L, Cremer M, Secchi ER, Domit C, Azevedo A, Lailson-Brito J, Torres JPM, Malm O, Eljarrat E, Diaz-Cruz MS and Barcelo D, 2013, First determination of UVf filters in marine mammals. Octocrylene levels in Franciscana dolphins, *Environ. Sci. Technol.*, **47**, 5619-5625.

45 Galbán-Malagón CJ, Cabrerizo A, Berrojálbiz N, Ojeda MJ and Dachs J, 2012, Air-water exchange and phytoplankton accumulation of persistent organic pollutants in the Greenland current and Arctic Ocean, http://132.246.11.198/2012-ipy/pdf-all/ipy2012arAbstract00801.pdf, accessed August, 2014.

46 Gao K and Campbell D, 2014, Photophysiological responses of marine diatoms to elevated CO_2 and decreased pH: a review, *Funct. Plant Biol.*, **41**, 449-459.

47 Gao K, Helbling EW, Häder D-P and Hutchins DA, 2012, Responses of marine primary producers to interactions between ocean acidification, solar radiation, and warming, *Mar. Ecol. Prog. Ser.*, **470**, 167–189

48 Gao K, Xu J, Gao G, Li Y, Hutchins DA, Huang B, Zheng Y, Jin P, Cai X, Häder D-P, Li W, Xu K, Liu N and Riebesell U, 2012, Rising carbon dioxide and increasing light exposure act synergistically to reduce marine primary productivity, *Nature Clim. Change*, **2**, 519–523.

49 Gao K and Zheng Y, 2010, Combined effects of ocean acidification and solar UV radiation on photosynthesis, growth, pigmentation and calcification of the coralline alga *Corallina sessilis* (Rhodophyta), *Glob. Change Biol.*, **16**, 2388-2398.

50 Garver KA, Mahony AAM, Stucchi D, Richard J, Van Woensel C and Foreman M, 2013, Estimation of parameters influencing waterborne transmission of infectious Hematopoietic Necrosis Virus (IHNV) in Atlantic Salmon (*Salmo salar*), *PLoS ONE*, **8**, e82296.

51 Gevertz AK and Oris JT, 2014, Microscopic examination of skin in native and nonnative fish from Lake Tahoe exposed to ultraviolet radiation and fluoranthene, *Aquat. Toxicol.*, **147**, 151-157.

52 Gevertz AK, Tucker AJ, Bowling AM, Williamson CE and Oris JT, 2012, Differential tolerance of native and nonnative fish exposed to ultraviolet radiation and fluoranthene in Lake Tahoe (California/Nevada), USA, *Environ. Toxicol. Chem.*, **31**, 1129-1135.

53 Goldman RP and Travisano M, 2011 Experimental evolution of ultraviolet radiation resistance in *Escherichia coli*, *Evolution*, **65**, 3486-3498.

54 Goodman KJ, Baker MA and Wurtsbaugh WA, 2011, Lakes as buffers of stream dissolved organic matter (DOM) variability: Temporal patterns of DOM characteristics in mountain stream-lake systems, *J. Geophys. Res. Biogeosci.*, **116**, G00N02.

55 Guan W and Gao K, 2010, Impacts of UV radiation on photosynthesis and growth of the coccolithophore *Emiliania huxleyi* (Haptophyceae), *Environ. Exp. Bot.*, **67**, 502-508.

56 Ha SY, Kim YM, Park MO, Kang SH, Kim HC and Shin KH, 2012, Production of mycosporine-like amino acids of in situ phytoplankton community in Kongsfjorden, Svalbard, Arctic, *J. Photochem. Photobiol. B.*, **114**, 1-14.

57 Haaland S, Hongve D, Laudon H, Riise G and Vogt RD, 2010, Quantifying the drivers of the increasing colored organic matter in boreal surface waters, *Environ. Sci. Technol.*, **44**, 2975-2980.

58 Häder D-P, 2011, Does enhanced solar UV-B radiation affect marine primary producers in their natural habitats?, *Photochem. Photobiol.*, **87**, 263–266.

59 Häder D-P, Helbling EW, Williamson CE and Worrest RC, 2011, Effects of UV radiation on aquatic ecosystems and interactions with climate change, *Photochem. Photobiol. Sci.*, **10**, 242-260.

60 Häder D-P, Richter P, Villafañe VE and Helbling EW, 2014, Influence of light history on the photosynthetic and motility responses of *Gymnodinium chlorophorum* exposed to UVR and different temperatures, *J. Photochem. Photobiol. B.*, **in press**.

61 Halac SR, Villafañe VE and Helbling EW, 2010, Temperature benefits the photosynthetic performance of the diatoms *Chaetoceros gracilis* and *Thalassiosira weissflogii* when exposed to UVR, *J. Photochem. Photobiol. B.*, **101**, 196−205.

62 Hallegraeff GM, 2010, Ocean climate change, phytoplankton community responses, and harmful algal blooms: a formidable predictive challenge, *J. Phycol.*, **46**, 220−235.

63 Harborne AR, 2013, The ecology, behaviour and physiology of fishes on coral reef flats, and the potential impacts of climate change, *J. Fish Biol.*, **83**, 417-447.

64 Helbling EW, Buma AG, Boelen P, Van der Strate HJ, Fiorda Giordanino MV and Villafañe VE, 2011, Increase in Rubisco activity and gene expression due to elevated temperature partially counteracts ultraviolet radiation-induced photoinhibition in the marine diatom *Thalassiosira weissflogii*, *Limnol. Oceanogr.*, **56**, 1330-1342.

65 Hoegh-Guldberg O, 2010, Dangerous shifts in ocean ecosystem function?, *The ISME Journal* **4**, 1090–1092.

66 http://earth.columbia.edu, http://earth.columbia.edu/articles/view/2993, accessed

67 Huertas IE, Rouco M, López-Rodas V and Costas E, 2011, Warming will affect phytoplankton differently: evidence through a mechanistic approach, *Proc. R. Soc. B. Biol. Sci.*, **278**, 3534−3543.

68 Hylander S, Grenvald JC and Kiorboe T, 2014, Fitness costs and benefits of UVR exposure in marine pelagic copepods, *Funct. Ecol.*, **28**, 149-158.

69 Hylander S, Souza MS, Balseiro E, Modenutti B and Hansson LA, 2012, Fish-mediated trait compensation in zooplankton, *Funct. Ecol.*, **26**, 608-615.

70 IPCC, 2013, Summary for Policymakers: Climate Change 2013 - The Physical Science Basis, Report No., pp. 1-38

71 Jassim SAA and Limoges RG, 2013, Impact of external forces on cyanophage-host interactions in aquatic ecosystems, *World J. Micrbiol. Biotech,*, **29**, 1751-1762.

72 Jin P, Gao K, Villafañe V, Campbell D and Helbling W, 2013, Ocean acidification alters the photosynthetic responses of a coccolithophorid to fluctuating ultraviolet and visible radiation, *Plant Physiol.*, **162**, 2084-2094.

73 Kadir K and Nelson KL, 2014, Sunlight mediated inactivation mechanisms of *Enterococcus faecalis* and *Escherichia coli* in clear water versus waste stabilization pond water, *Water Res.*, **50**, 307–317.

74 Kahru M, Brotas V, Manzano-Sarabia B and Mitchell BG, 2010, Are phytoplankton blooms occurring earlier in the Arctic?, *Glob. Change Biol.*, **17**, 1733-1739.

75 Keeling RF, Körtzinger A and Gruber N, 2010, Ocean deoxygenation in a warming world, *Ann. Rev. Mar. Sci.*, **2**, 199-229.

76 Key T, McCarthy A, Campbell DA, Six C, Roy S and Finkel ZV, 2010, Cell size trade-offs govern light exploitation strategies in marine phytoplankton, *Environ. Microbiol.*, **12**, 95-104.

77 Kissman CEH, Williamson CE, Rose KC and Saros JE, 2013, Response of phytoplankton in an alpine lake to inputs of dissolved organic matter through nutrient enrichment and trophic forcing., *Limnol. Oceanogr.*, **58**, 867-880.

78 Knoll LB, 2011, *Linking watershed-scale features and processes to carbon, nitrogen, and phosphorus fluxes*, PhD thesis, Miami University (Oxford, OH).

79 Kohler SJ, Kothawala D, Futter MN, Liungman O and Tranvik L, 2013, In-lake processes offset increased terrestrial inputs of dissolved organic carbon and color to lakes, *PLoS ONE*, **8**, e70598.

80 Kritzberg ES and Ekström S, M, 2012, Increasing iron concentrations in surface waters - a factor behind brownification?, *Biogeosci.*, **9**, 1465-1478.

81 Larsen S, Andersen T and Hessen D, 2011, Climate change predicted to cause severe increase of ogranic carbon in lakes, *Glob. Change Biol.*, **17**, 1186-1192.

82 Laufkoetter C, Vogt M and Gruber N, 2013, Trends in marine plankton composition and export production in a CCSM-BEC hindcast (1960-2006), in *EGU General Assembly Conference Abstracts,* **Vol. 15**, p. 11917.

83 Leech DM, Boeing WJ, Cooke SL, Williamson CE and Torres L, 2009, UV-enhanced fish predation and the differential migration of zooplankton in response to UV radiation and fish, *Limnol. Oceanogr.*, **54**, 1152-1161.

84 Li G, Che ZW and Gao K, 2013, Photosynthetic carbon fixation by tropical coral reef phytoplankton assemblages: a UVR perspective, *Algae*, **28**, 281-288.

85 Li G and Gao K, 2012, Variation in UV irradiance related to stratospheric ozone levels affects photosynthetic carbon fixation of winter phytoplankton assemblages from surface coastal water of the South China Sea, *Mar. Biol. Res.*, **8**, 670-676.

86 Li G and Gao K, 2013, Cell size-dependent effects of solar UV radiation on primary production in coastal waters of the South China Sea, *Estuaries Coasts*, **36**, 728-736.

87 Li G, Gao K and Gao G, 2011, Differential impacts of solar UV radiation on photosynthetic carbon fixation from the coastal to offshore surface waters in the South China Sea, *Photochem. Photobiol.*, **87**, 329-334.

88 Li W and Gao KS, 2012, A marine secondary producer respires and feeds more in a high CO_2 ocean, *Mar. Poll. Bull.*, **64**, 699-703.

89 Li Y, Gao K, Villafañe V and Helbling E, 2012, Ocean acidification mediates photosynthetic response to UV radiation and temperature increase in the diatom *Phaeodactylum tricornutum*, *Biogeosci. Discuss.*, **9**, 7197-7226.

90 Llabrés M, Agustí S, Alonso-Laita P and Herndl G, 2010, *Synechococcus* and *Prochlorococcus* cell death induced by UV radiation and the penetration of lethal UVR in the Mediterranean Sea, *Mar. Ecol. Prog. Ser.*, **399**, 27-37.

91 Llabrés M, Agustí S, Fernández M, Canepa A, Maurin F, Vidal F and Duarte CM, 2013, Impact of elevated UVB radiation on marine biota: a meta-analysis, *Global Ecol. Biogeogr.*, **22**, 131-144.

92 Llewellyn CA and Airs RL, 2010, Distribution and abundance of MAAs in 33 species of microalgae across 13 classes, *Mar. Drugs*, **8**, 1273-1291.

93 Llewellyn CA, White DA, Martinez-Vincente V, Tarran G and Smyth TJ, 2012, Distribution of mycosporine-like amino acids along a surface water meridional transect of the Atlantic, *Micro. Ecol.*, **64**, 320-333.

94 Lottig NR, Buffam I and Stanley EH, 2013, Comparisons of wetland and drainage lake influences on stream dissolved carbon concentrations and yields in a north temperate lake-rich region, *Aquat. Sci.*, **75**, 619-630.

95 Lu YH, Bauer JE, Canuel EA, Yamashita Y, Chambers RM and Jaffe R, 2013, Photochemical and microbial alteration of dissolved organic matter in temperate headwater streams associated with different land use, *J. Geophys. Res. Biogeosci.*, **118**, 566-580.

96 Macdonald MJ and Minor EC, 2013, Photochemical degradation of dissolved organic matter from streams in the western Lake Superior watershed, *Aquat. Sci.*, **75**, 509-522.

97 Manney GL, Santee ML, Rex M, Livesey NJ, Pitts MC, Veefkind P, Nash ER, Wohltmann I, Lehmann R, Froidevaux L, Poole LR, Schoeberl MR, Haffner DP, Davies J, Dorokhov V, Gernandt H, Johnson B, Kivi R, Kyrö E, Larsen N, Levelt PF, Makshtas A, McElory CT, Nakajima H and Parrondo MC, 2011, Unprecedented Arctic ozone loss in 2011, *Nature*, **478**, 469-475.

98 Manrique JM, Calvo AY, Halac SR, Villafañe VE, Jones LR and Helbling EW, 2012, Effects of UV radiation on the taxonomic composition of natural bacterioplankton communities from Bahía Engaño (Patagonia, Argentina), *J. Photochem. Photobiol. B.*, **117**, 171-178.

99 Martinez-Levasseur LM, Birch-Machin MA, Bowman A, Gendron D, Weatherhead E, Knell RJ and Acevedo-Whitehouse K, 2013, Whales use distinct strategies to counteracts solar ultraviolet radiation, *Sci. Rep.*, **3**, 2386.

100 Martynova DM, Kazus NA, Bathmann UV, Graeve M and Sukhotin AA, 2011, Seasonal abundance and feeding patterns of copepods *Temora longicornis*, *Centropages hamatus* and *Acartia* spp. in the White Sea (66°N), *Polar Biol.*, **34**, 1175-1195.

101 Medina-Sanchez M, Delgado-Molina JA, Bratbak J, Bullejos GJ, Villar-Argaiz F and Carrillo M, 2013, Maximum in the middle: Nonlinear response of microbial plankton to ultraviolet radiation and phosphorus, *PLoS ONE*, **8**.

102 Melnychuk MC, Walters CJ, Christensen V, Bothwell ML and Welch DW, 2012, Effects of solar ultraviolet radiation exposure on early ocean survival and fry-to-smolt growth of juvenile salmon, *Mar. Ecol. Prog. Ser.*, **457**, 251-264.

103 Montes-Hugo M, Doney SC, Ducklow HW, Fraser W, Martinson D, Stammerjohn SE and Schofield O, 2009, Recent changes in phytoplankton communities associated with rapid regional climate change along the Western Antarctic Peninsula, *Science.*, **323**, 1470-1473.

104 Muller R, Desel C, Steinhoff FS, Wiencke C and Bischof K, 2012, UV-radiation and elevated temperatures induce formation of reactive oxygen species in gametophytes of cold-temperate/Arctic kelps (Laminariales, Phaeophyceae), *Phycol. Res.*, **60**, 27-36.

105 Nahon S, Charles F, Lantoine F, Vétion G, Escoubeyrou K, Desmalades M and Pruski AM, 2010, Ultraviolet radiation negatively affects growth and food quality of the pelagic diatom *Skeletonema costatum*, *J. Exp. Mar. Biol. Ecol.*, **383**, 164–170.

106 Nahon S, Pruski AM, Duchene JC, Mejanelle L, Vetion G, Desmalades M and Charles F, 2011, Can UV radiation affect benthic deposit-feeders through biochemical alteration of food resources? An experimental study with juveniles of the benthic polychaete *Eupolymnia nebulosa*, *Mar. Environ. Res.*, **71**, 266-274.

107 Nevalainen L and Rautio M, 2013, Cladoceran carapace absorbance as a new method for inferring past UV radiation exposure of aquatic biota, *Quatern. Sci. Rev.*, **84**, 109-115.

108 New M, Liverman D, Schroder H and Anderson K, 2011, Four degrees and beyond: the potential for a global temperature increase of four degrees and its implications, *Philos. Trans. Roy. Soc. Lond. A.*, **369**, 6-19.

109 Olischläger M and Wiencke C, 2013, Seasonal fertility and combined effects of temperature and UV-radiation on *Alaria esculenta* and *Laminaria digitata* (Phaeophyceae) from Spitsbergen, *Polar Biol.*, **36**, 1019-1029.

110 Olker JH, Johnson LB, Axler RP and Johnson CM, 2013, Factors influencing ultraviolet radiation dose to developing frogs in northern vernal pools, *Can. J. Fish. Aquat. Sci.*, **70**, 1531-1541.

111 Olson MH and Barbieri NE, 2013, Mechanisms of ultraviolet radiation tolerance in the freshwater snail *Physa acuta*, *Freshwater Sci.*, **33**, 66-72.

112 Oubelkheir K, Clementson LA, Moore GF and Tilstone GH, 2013, Production of mycosporine-like amino acids by phytoplankton under ultraviolet radiation exposure in the Sub-Antarctic Zone south of Tasmania, *Mar. Ecol. Prog. Ser.*, **494**, 41-63.

113 Overholt EP, Hall SH, Williamson CE, Meikle CK, Duffy MA and Cáceres CE, 2012, Solar radiation decreases parasitism in *Daphnia*, *Ecol. Lett.*, **15**, 47-54.

114 Parisi AV and Kimlin MG, 2004, Personal solar UV exposure measurements employing modified polysulphone with an extended dynamic range, *Photochem. Photobiol.*, **79**, 411-415.

115 Parry W, 2011, Arctic's Spring Phytoplankton Blooms Arrive Earlier, http://www.livescience.com/13082-arctic-plankton-blooms-ocean-climate-change.html, accessed

116 Petersen DG and Dahllöf I, 2007, Combined effects of pyrene and UV-light on algae and bacteria in an Arctic sediment, *Ecotoxicol.*, **16**, 371-377.

117 Piepho M, Arts MT and Wacker A, 2012, Species-specific variation in fatty acid concentrations of four phytoplankton species: Does phosphorus supply influence the effect of light intensity or temperature?, *J. Phycol.*, **48**, 64-73.

118 Pietrzak B, Bednarska A, Markowska M, Rojek M, Szymanska E and Slusarczyk M, 2013, Behavioural and physiological mechanisms behind extreme longevity in *Daphnia*, *Hydrobiologia.*, **715**, 125-134.

119 Porcal P, Dillon PJ and Molot LA, 2014, Interaction of extrinsic chemical factors affecting photodegradation of dissolved organic matter in aquatic ecosystems, *Photochem. Photobiol. Sci.*, **13**, 799-812.

120 Quinn TN, Kendall NW, Rich Jr. HB and Chasco BE, 2012, Diel vertical movements, and effects of infection by the cestode *Schistocephalus solidus* on daytime proximity of three-spined sticklebacks *Gasterosteus aculeatus* to the surface of a large Alaskan lake, *Oecologia* **168**, 43–51.

121 Rastogi RP, Sinha RP and Incharoensakdi A, 2013, Partial characterization, UV-induction and photoprotective function of sunscreen pigment, scytonemin from *Rivularia* sp. HKAR-4, *Chemosphere*, **93**, 1874-1878.

122 Read JS and Rose KC, 2013, Physical responses of small temperate lakes to variation in dissolved organic carbon concentrations, *Limnol. Oceanogr.*, **58**, 921-931.

123 Renaud P, Berge J, Varpe Ø, Lønne O, Nahrgang J, Ottesen C and Hallanger I, 2012, Is the poleward expansion by Atlantic cod and haddock threatening native polar cod, Boreogadus saida?, *Polar Biol.*, **35**, 401-412.

124 Richa, Sinha RP and Häder D-P, 2014, Physiological aspects of UV-excitation of DNA, in *Photoinduced Phenomena in Nucleic Acids* eds.: Barbatti B, Borin AC and Ullrich AC, Springer, Berlin Heidelberg, pp. 1-46.

125 Richa, Sinha RP and Häder D-P, 2014, Phytoplankton productivity in a changing global climate, in *Phytoplankton: Biology, Classification and Environmental Impacts* ed.: Sebastiá MT, Nova Science Publishers, New York, pp. 1 – 35.

126 Romanovsky VE, Smith SL, Christiansen HH, Shiklomanov NI, Streletskiy DA, Drozdov DS, Oberman NG, Kholodov AL and Marchenko SS, 2013, Permafrost, NOAA Report No., pp. 131-136. http://www.arctic.noaa.gov/reportcard

127 Romera-Castillo C, Sarmento H, Álvarez-Salgado XA, Gasol JM and Marrasé C, 2011, Net production and consumption of fluorescent colored dissolved organic matter by natural bacterial assemblages growing on marine phytoplankton exudates, *Appl. Environ. Microbiol.*, **77**, 7490-7498.

128 Rose KC, Williamson CE, Fischer JM, Connelly SJ, Olson M, Tucker AJ and Noe DA, 2012, The role of UV and fish in regulating the vertical distribution of *Daphnia*, *Limnol. Oceanogr.*, **57**, 1867-1876.

129 Ruiz-González C, Galí M, Sintes E, Herndl GJ, Gasol JM and Simó R, 2012, Sunlight effects on the osmotrophic uptake of DMSP-sulfur and leucine by Polar phytoplankton, *PLoS ONE*, **7**, e45545.

130 Ryan KG, McMinn A, Hegseth EN and Davy SK, 2012, The effects of ultraviolet radiation on Antarctic sea-ice algae, *J. Phycol.*, **48**, 74-84.

131 Sandro S and J.M. M, 2012, The effect of an extreme rain event on the biogeochemistry and ecosystem metabolism of an oligotrophic high-elevation lake, *Arctic Antarctic Alpine Res.*, **44**, 222-231.

132 Schneider T, Herzig A, Koinig KA and Sommaruga R, 2012, Copepods in turbid shallow soda lakes accumulate unexpected high levels of carotenoids, *PLOS ONE*, **7**, e43063.

133 Sereda JM, Vandergucht DM and Hudson JJ, 2012, n situ UVA exposure modulates change in the uptake of radiophosphate in size-fractionated plankton assemblages following UVR exposure, *Micro. Ecol.*, **63**, 751-760.

134 Shi D, Xu Y, Hopkinson BM and Morel FMM, 2010, Effect of ocean acidification on iron availability to marine phytoplankton, *Science.*, **327**, 676-679.

135 Silverman A, Peterson BM, Boehm AB, McNeill K and Nelson KL, 2013 Sunlight inactivation of human viruses and bacteriophages in coastal waters containing natural photosensitizers, *Environ. Sci. Technol.*, **47**, 1870-1878.
136 Singh G, Babele PK, Sinha RP, Tyagi MB and Kumar A, 2013, Enymatic and non-enzymatic defense mechanisms against ultraviolet-B radiation in two *Anabaena* species, *Process Biochem.*, **48**, 796-802.
137 Singh SP, Ha S-Y, Sinha RP and Häder D-P, 2014, Photoheterotrophic growth unprecedentedly increases the biosynthesis of mycosporine-like amino acid shinorine in the cyanobacterium *Anabaena* sp., isolated from hot springs of Rajgir (India), *Acta. Physiol. Plant.*, **36**, 389-397.
138 Singh SP, Häder D-P and Sinha RP, 2010, Cyanobacteria and ultraviolet radiation (UVR) stress: mitigation strategies, *Ageing Res. Rev.*, **9**, 79-90.
139 Singh SP, Rastogi RP, Sinha RP and Häder D-P, 2014, Temporal dynamics of ROS biogenesis under simulated solar radiation in the cyanobacterium *Anabaena variabilis* PCC 7937, *Protoplasma* **251**, 1223-1230.
140 Six KD, Kloster S, Ilyina T, Archer SD, Zhang K and Maier-Reimer E, 2013, Global warming amplified by reduced sulphur fluxes as a result of ocean acidification, *Nature Clim. Change*, **3**, 975-978.
141 Skinner MP, Lewis RJ and Morton S, 2013, Ecology of the ciguatera causing dinoflagellates from the Northern Great Barrier Reef: Changes in community distribution and coastal eutrophication, *Mar. Poll. Bull.*, **77**, 210-219.
142 Souza MS, Hansson LA, Hylander S, Modenutti B and Balseiro E, 2012, Rapid enzymatic response to compensate UV radiation in copepods, *PLoS ONE*, **7**, e32046.
143 Stasko AD, Gunn JM and Johnston TA, 2012, Role of ambient light in structuring north-temperate fish communities: potential effects of increasing dissolved organic carbon concentration with a changing climate, *Environ. Rev.*, **20**, 173-190.
144 Steinacher M, Joos F, Froelicher TL, Bopp L, Cadule P, Cocco V, Doney SC, Gehlen M, Lindsay K, Moore JK, Schneider B and Segschneider J, 2010, Projected 21st century decrease in marine productivity: a multi-model analysis, *Biogeosci.*, **7**, 979-1005.
145 Studer A, Cubillos VM, Lamare MD, Poulin R and Burritt DJ, 2012, Effects of ultraviolet radiation on an intertidal trematode parasite: An assessment of damage and protection, *Int. J. Parasitol.*, **42**, 453-461.
146 Studer A, Lamare MD and Poulin R, 2012, Effects of ultraviolet radiation on the transmission process of an intertidal trematode parasite, *Parasitology.*, **139**, 537-546.
147 Studer A and Poulin R, 2013, Cercarial survival in an intertidal trematode: a multifactorial experiment with temperature, salinity and ultraviolet radiation, *Parasitol. Res.*, **112**, 243-249.
148 Sucre E, Vidussi F, Mostajir B, Charmantier G and Lorin-Nebel C, 2012, Impact of ultraviolet-B radiation on planktonic fish larvae: Alteration of the osmoregulatory function, *Aquat. Toxicol.*, **109**, 194-201.
149 Sweet M, Kirkham N, Bendall M, Currey L, Bythell J and Heupel M, 2012, Evidence of melanoma in wild marine fish populations, *PLoS ONE*, **7**, e41989.
150 Taylor GT, Muller-Karger FE, Thunell RC, Scranton MI, Astor Y, Varela R, Ghinaglia LT, Lorenzoni L, Fanning KA and Hameed S, 2012, Ecosystem responses in the southern Caribbean Sea to global climate change, *Proc. Nat. Acad. Sci. USA.*, **109**, 19315-19320.
151 Terrado R, Scarcella K, Thaler M, Vincent WF and Lovejoy C, 2013 Small phytoplankton in Arctic seas: vulnerability to climate change, *Biodiver. Conser.*, **14**, 2-18.
152 Thyssen M, Ferreyra G, Moreau S, Schloss I, Denis M and Demers S, 2011, The combined effect of ultraviolet B radiation and temperature increase on phytoplankton dynamics and cell cycle using pulse shape recording flow cytometry, *J. Exp. Mar. Biol. Ecol.*, **406**, 95-107.
153 Tiberti R and Barbieri M, 2011, Evidences of zooplankton vertical migration in stocked and never-stocked alpine lakes in Gran Paradiso National Park (Italy), *Oceanolog. Hydrobiol. Stud.*, **40**, 36-42.
154 Tiberti R and Iacobuzio R, 2013, Does the fish presence influence the diurnal vertical distribution of zooplankton in high transparency lakes?, *Hydrobiologia.*, **709**, 27-39.
155 Tranvik LJ, Downing J, Cotner JB, Loiselle S, Striegl R, Ballatore TJ, Dillon P, Finlay K, Fortino K, Knoll LB, Korelainen PL, Kutser T, Larsen S, Laurion I, Leech DM, McCallister SL, McKnight D, Melack J, Overholt E, Porter JA, Prairie Y, Renwick W, Roland F, Sherman BS, Schindler DE, Sobek S, Tremblay A, Vanni MJ, Verschoor AM, Wachenfeldt Ev and Weyhenmeyer GA, 2009, Lakes and reservoirs as regulators of carbon cycling and climate, *Limnol. Oceanogr.*, **54**, 2298-2314.
156 Tucker AJ and Williamson CE, 2014, The invasion window for warmwater fish in clearwater lakes: the role of ultraviolet radiation and temperature, *Div. Distrib.*, **20**, 181-192.

157 Tucker AJ, Williamson CE and Oris JT, 2012, Development and application of a UV attainment threshold for the prevention of warmwater aquatic invasive species, *Biological Invasions*, **14**, 2331-2342.
158 Turner J, Barrand NE, Bracegirdle TJ, Convey P, Hodgson DA, Jarvis M, Jenkins A, Marshall G, Meredith MP, Roscoe H, Shanklin J, French J, Goosse H, Guglielmin M, Gutt J, Jacobs S, Kennicutt II MC, Masson-Delmotte V, Mayewski! P, Navarro F, Robinson S, Scambos T, Sparrow M, Summerhayes C, Speer K and Klepikov A, 2013, Antarctic Climate Change and the Environment: An Update, Cambridge University Press Report No., Cambridge, pp. 1-23
159 UNEP, 2006, Marine and coastal ecosystems and human well-being: a synthesis report based on the findings of the millennium ecosystem assessment, *UNEP Report*, Nairobi.
160 Vadadi-Fulop C, Sipkay C, Meszaros G and Hufnagel L, 2012, Climate change and freshwater zooplankton: what does it boil down to?, *Aquat. Ecol.*, **46**, 501-519.
161 Van Den Broecke L, Martens K, Pieri V and Schön I, 2012, Ostracod valves as efficient UV protection, *J. Limnol.*, **71**.
162 Viñas MJ, 2012, NASA discovers unprecedented blooms of ocean plant life, *NASA Science News*.
163 Vonk JE, Mann PJ, Davydov S, Davydova A, Spencer RGM, Schade J, Sobczak WV, Zimov N, Zimov S, Bulygina E, Eglinton TJ and Holmes RM, 2013, High biolability of ancient permafrost carbon upon thaw, *Geophys. Res. Lett.*, **40**, 2689-2693.
164 Williamson CE, Fischer JM, Bollens SM, Overholt EP and Breckenridge JK, 2011, Toward a more comprehensive theory of zooplankton diel vertical migration: Integrating ultraviolet radiation and water transparency into the biotic paradigm, *Limnol. Oceanogr.*, **56**, 1603-1623.
165 Wilson HF, Saiers JE, Raymond PA and Sobczak WV, 2013, Hydrologic drivers and seasonality of dissolved organic carbon concentration, nitrogen content, bioavailability, and export in a forested New England stream, *Ecosystems*, **16**, 604-616.
166 Wu D, Hu Q, Yan Z, Chen W, Yan C, Huang X, Zhang J, Yang P, Deng H and Wang J, 2012, Structural basis of ultraviolet-B perception by UVR8, *Nature*, **484**, 214-219.
167 Wu Y, Gao K, Li G and Helbling EW, 2010, Seasonal impacts of solar UV radiation on photosynthesis of phytoplankton assemblages in the coastal waters of the South China Sea, *Photochem. Photobiol.*, **86**, 586-592.
168 Xu K, Gao K, Villafañe V and Helbling E, 2011, Photosynthetic responses of *Emiliania huxleyi* to UV radiation and elevated temperature: roles of calcified coccoliths, *Biogeosci.*, **8**, 1441-1452.
169 Xu Z and Gao K, 2009, Impacts of UV radiation on growth and photosynthetic carbon acquisition in *Gracilaria lemaneiformis* (Rhodophyta) under phosphorus-limited and replete conditions, *Funct. Plant Biol.*, **36**, 1057-1064.
170 Yuan X, Yin K, Harrison PJ and Zhang J, 2011, Phytoplankton are more tolerant to UV than bacteria and viruses in the northern South China Sea, *Aquat. Microb. Ecol.*, **65**, 117-128.
171 Zhang J, Lindsay R, Schweiger A and Steele M, 2013, The impact of an intense summer cyclone on 2012 Arctic sea ice retreat, *Geophys. Res. Lett.*, **40**, 720-726.
172 Zhang Y, Jiang H-B and Qiu B-S, 2013, Effects of UVB radiation on competition between the bloom-forming cyanobacterium *Microcystis aeruginosa* and the chlorophyceae *Chlamydomonas microsphaera*, *J. Phycol.*, **49**, 318-328.
173 Zhuang Y, Jin H, Chen J, Wang B, Li H, Chen F, Liu Y and Xu J, 2012, Nutrient status and phytoplankton-pigments response to ice melting in the Arctic Ocean, *Adv. Polar Sci.*, **24**, 151-158.

Chapter 5. Effects of stratospheric ozone depletion, solar UV radiation, and climate change on biogeochemical cycling: Interactions and feedbacks

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Summary

Climate change modulates the effects of solar UV radiation on biogeochemical cycles in terrestrial and aquatic ecosystems, particularly for carbon cycling, resulting in UV-mediated positive or negative feedbacks on climate. Possible positive feedbacks discussed in this assessment include: (i) Enhanced UV-induced mineralisation of above ground litter due to aridification; (ii) Enhanced UV-induced mineralisation of photoreactive dissolved organic matter (DOM) in aquatic ecosystems due to changes in continental runoff and ice melting; (iii) Reduced efficiency of the biological pump due to UV-induced bleaching of coloured dissolved organic matter (CDOM) in stratified aquatic ecosystems, where CDOM protects phytoplankton from the damaging solar UV-B radiation. Mineralisation of organic matter results in the production and release of CO_2, whereas the biological pump is the main biological process for CO_2 removal by aquatic ecosystems. This paper also assesses the interactive effects of solar UV radiation and climate change on the biogeochemical cycling of aerosols and trace gases other than CO_2, as well as of chemical and biological contaminants. Interacting effects of solar UV radiation and climate change on biogeochemical cycles are particularly pronounced at terrestrial-aquatic interfaces.

Introduction

The Montreal protocol has been successful in phasing out ozone-depleting CFCs and, as a consequence, stratospheric ozone concentrations are recovering at low and mid-latitudes[145, 236] (see Chapter 1). However, springtime ozone depletion is expected to continue at polar latitudes for many decades,[8, 138] largely due to climate change. A major consequence of stratospheric ozone change is altered intensity of solar UV-B radiation which in turn affects the biogeochemical cycling of carbon and other chemical elements. Terrestrial and aquatic biogeochemical cycles are discussed here in the context of their possible interactions with UV radiation and climate change (Fig. 1).

The intensity of solar UV radiation reaching the Earth's surface is also controlled by climate-related variables such as cloud cover and aerosols. In addition, the penetration of UV-B radiation into water bodies largely depends on the concentration and the optical properties of chromophoric dissolved organic matter (referred to as coloured dissolved organic matter, CDOM, hereafter). Climate-change related effects on terrestrial and aquatic ecosystems, e.g., desertification, ocean acidification and stratification, as well as land use change interact in various ways with solar UV radiation, resulting in UV-mediated feedbacks on climate. Feedbacks, combined effects and interactions of solar UV radiation and climate change on biogeochemical cycles are discussed and assessed, and gaps in knowledge identified.

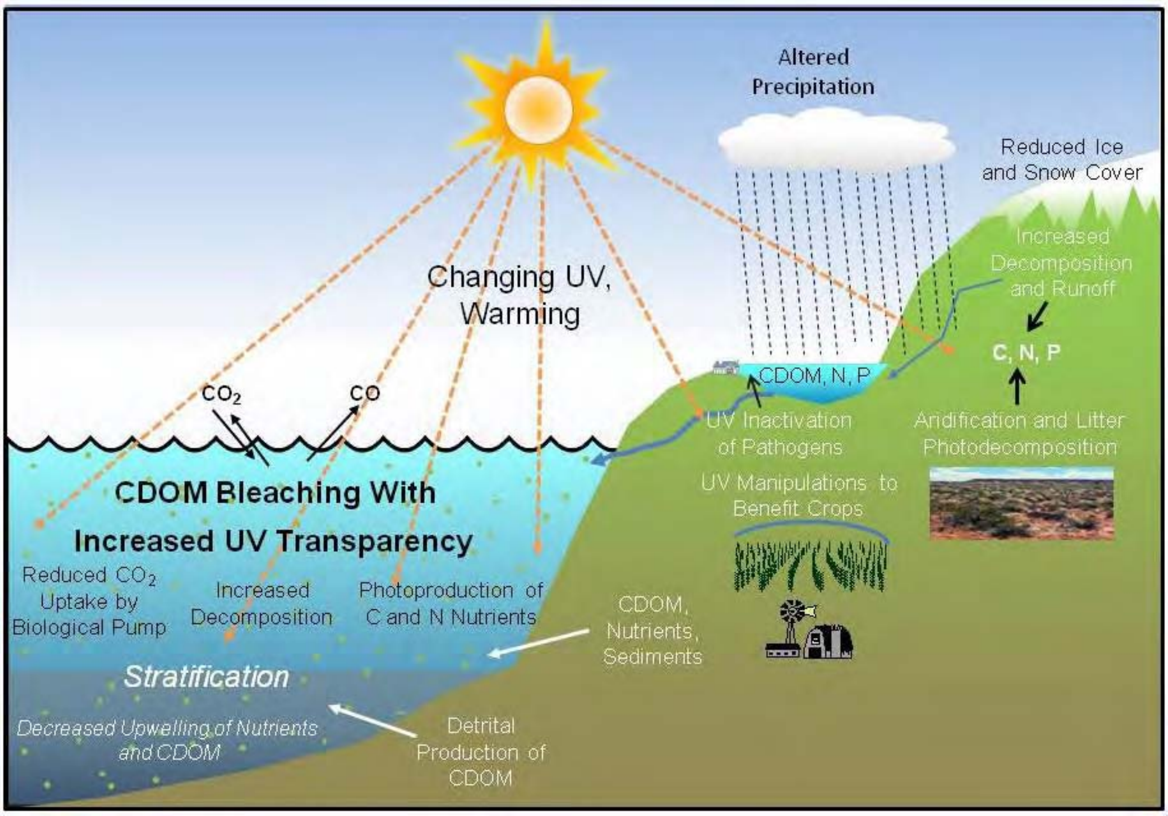

Fig. 1 Conceptual model of aquatic and terrestrial processes that are possibly influenced by interactions between UV radiation and climate change. Recent findings on these interactions are discussed in more detail in this assessment. Reprinted from Williamson et al.[234], with permission from Macmillan Publishers Ltd: Nature Climate Change, copyright 2014.

Interactive effects of stratospheric ozone depletion and climate change on terrestrial and aquatic ecosystems

We include a section that summarises some important issues of climate change, since climate change modulates the effects of solar UV radiation of biogeochemical cycles. Climate change also affects the stratospheric ozone concentration and thus the intensity of solar UV radiation reaching the Earth's surface.

Climate change and polar stratospheric ozone depletion

Some chemistry-climate models and observations predict that an ozone 'hole' may still be present in the Antarctic spring in 2100.[8] A large loss of stratospheric ozone, comparable to that in the Antarctic ozone 'hole', was also observed over the Arctic in spring 2011[138] due, in part, to the extremely cold stratospheric Arctic winter 2010/2011.[204] In spring 2011 increased levels of solar UV radiation were observed at Arctic and sub-Arctic ground stations.[16] The Arctic stratosphere is particularly affected by radiative cooling due to Arctic amplification (enhanced warming in high northern latitudes relative to the northern hemisphere).[193] There are several reasons for the fast response of the Arctic to global warming, including increased advection of water from the Atlantic to the Arctic,[167, 209] and reduced albedo due to sea ice melting and vegetation shifts.[165] Hence, increasing attention is being paid to Arctic tipping points.[129] The term "tipping point" is used for systems (e.g., Arctic ecosystems), where a small change in forcing could potentially cause a large change in future ecosystems. Further detail on climate change and polar stratospheric ozone depletion is given in Chapter 1.

Ice melting: effects on local climates

Global warming has dramatically enhanced melting of glaciers, ice caps, and sea ice in both hemispheres, with the largest present rates of melting in the Northern Hemisphere.[100, 198, 229] The Arctic sea ice, whose extent usually reaches a minimum each year in September, is particularly affected[100, 229] (Fig. 2) (also see Fig. 1 in Chapter 4). Melting of Greenland and Antarctic sea ice is mainly due to warmer ocean temperatures.[106] Increasing meltwater ponds on the surface of polar ice reduce albedo and allow more solar radiation, both UV and photosynthetically active radiation (PAR), to enter the water column through the ice[63] (see Chapter 1). Screen and Simmonds[193] suggest that positive ice-temperature feedbacks occur in the Arctic due to increases in atmospheric water vapour content that enhances warming in the lower part of the atmosphere, especially in high northern latitudes. Sea ice melting at high latitudes could also be due to the transformation of solar UV-B radiation into heat by planktonic microorganisms in a cyclic reaction consisting of photooxidation of water at 300 nm that yields H_2O_2 with subsequent decomposition of H_2O_2 by catalase.[152]

The decline in Arctic sea ice affects local climates, particularly in North America, Europe, and East Asia with large impacts on biogeochemical cycles. For example, changes in rates of primary production and respiration in terrestrial and aquatic ecosystems may occur as a consequence of droughts and enhanced runoff of terrestrially derived organic carbon, respectively (see below). These effects on local climates can be summarised as follows: The melting of Arctic sea ice results in increased air temperatures due to evaporation and condensation of surface water, changes in the turbulent heat fluxes and, as a consequence, in increased geopotential height over the Arctic.[194] As a result, the jet stream is transformed into Rossby waves that are characterised by cold air moving to the north and warm air moving to the south.[61, 62] The higher the amplitude of Rossby waves, the slower they move from west to east, resulting in more frequent episodes of blocking of weather patterns and therefore in longer lasting extreme weather events such as droughts, flooding, cold spells, and heat.[61, 62, 79, 133, 218]

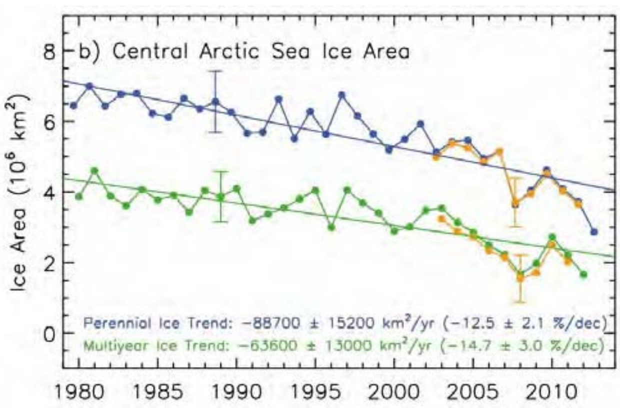

Fig. 2 Arctic sea ice loss from 1979 to 2012 as derived from satellite passive microwave data. The yellow lines (after 2002) are from AMSR-E data. (Panel b) of Fig. 4.4 from Chapter 4 "Observations: Cryosphere" of the IPCC Report 2013, Working Group I: Climate Change 2013: The Physical Science Basis).[100]

Further impacts of land and sea ice melting are sea level rise,[100] increases in freshwater input and hence changes in ocean circulation and reduced surface albedo[99] (see Chapter 1), and enhanced exposure of organisms in aquatic ecosystems and on land surfaces such as tundra to solar UV radiation (this assessment and Chapter 4). Over the period 1901-2010, global mean sea level rose by 0.19 (0.17 to 0.21) m and the IPCC WGI Report 2013 (summary for policymakers)[100] states with *high confidence* that the "rate of sea level rise since the mid-19th century has been larger than the mean rate during the previous two millennia."

Interacting effects of stratospheric ozone depletion and climate change on ecosystems

The interplay between stratospheric ozone depletion and climate change affects atmospheric circulation, the speed and direction of winds, and, as a consequence, ocean mixing. There is a global trend of increasing values of surface and higher level wind speed, linked, in part, to stratospheric ozone depletion.[126, 161, 241] Causes of this phenomenon have been reported more than ten years ago in a key paper by Gillet and Thompson.[67] Based on observations and modeling results, these investigators found falling geopotential heights at constant pressure (500-hPa) at high southern latitudes from 1979-2000 due to Antarctic stratospheric ozone depletion and thus decreasing temperatures. Concomitantly, 500-hPa heights were rising in the middle southern latitudes, due to increasing greenhouse gas concentrations and thus increasing temperatures. This interplay between Antarctic stratospheric ozone depletion and climate change results in an upward trend of the Southern Annular Mode (SAM).[140, 141, 161] Positive SAM indices result in mean high values of the westerly polar vortexes and a poleward shift of the westerly wind belts at the Earth's surface.[108, 126] As a consequence, net uptake of carbon dioxide in the Southern Ocean, believed to be a major sink for atmospheric CO_2,[75, 101] may be reduced by enhanced wind-driven upwelling of carbon-rich deepwater.[128, 232] Paleo-oceanographic studies suggest that a Southern Ocean CO_2 ventilation event might have caused glacial-interglacial changes in the atmospheric CO_2 concentration.[30, 180, 202, 220] Changes in atmospheric and ocean circulation due to the combined effects of Antarctic stratospheric ozone depletion and climate change alter Southern Hemisphere weather. These alterations potentially include increased incidence of extreme events, floods, droughts, and wildfires.[177]

Ocean warming, stratification, acidification, and deoxygenation

Global warming results in increased sea-surface temperatures (SST) and, in turn, in thermal stratification. Another effect of increasing SST is ocean deoxygenation as a consequence of reduced oxygen solubility. Furthermore, increasing CO_2 concentrations result in ocean acidification.[75] Ocean acidification lowers the saturation state of calcite and aragonite (Fig. 3) and thus the ability of calcifiers such as coccolithophores and corals to produce and maintain their shells of calcite and aragonite.[66, 75]

Framework building corals are also sensitive to ocean warming because of the breakdown of the symbiosis with symbiotic algae (zooxanthellae), resulting in coral bleaching.[34, 75, 83, 163, 205] Algae that no longer live in symbiosis with corals are less protected from solar UV-B radiation. Furthermore, iron stress of zooxanthellae has been shown to reduce their photosynthetic efficiency and to alter the pigment composition at elevated temperatures.[201] The combined effects of increasing SST, ocean acidification and stratification, and solar UV radiation on marine ecosystems are likely to reduce the rate of primary production by phytoplankton (see below). Based on a Biogeochemical Elemental Cycling model, Laufkoetter et al.[123] reported a decrease in global net primary production of phytoplankton with increasing SST from 1960-2006. An excellent review article on these topics has been published by Gruber.[75]

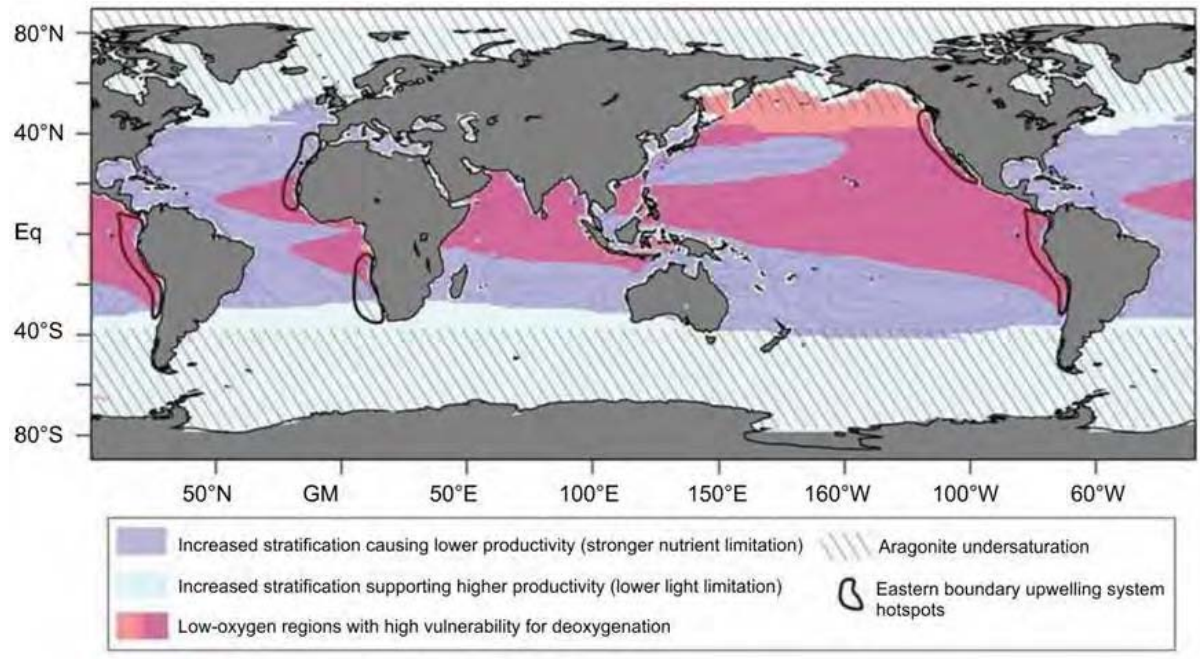

Fig. 3 Global map showing oceanic regions of particular vulnerability to climate-change effects (see legend above). Reprinted from Gruber[75] with permission from The Royal Society: Philosophical Transactions A, copyright 2011.

Changes in hydroclimatic conditions and continental runoff

The interplay between global warming and stratospheric ozone depletion affects precipitation patterns in space and time and enhances the intensity of precipitation extremes.[3, 51, 108, 147, 162] Cooling of the Antarctic stratosphere due to ozone depletion causes circulation cells to shift polewards, resulting in wetter conditions in the southern subtropics in the austral summer and drier conditions around 40°S.[51, 108] On the other hand, strong El Niño/Southern Oscillation (ENSO) events, potentially due to global warming, cause the South Pacific convergence zone to shift towards the Equator with concomitant changes in hydroclimatic conditions resulting in more frequent weather events such as droughts, floods, and tropical cyclones.[31] In the Northern Hemisphere, the intensity of heavy precipitation events has increased over much of the land area due to warming.[43, 117, 147] Changes in hydroclimatic conditions may result in an enhanced input of terrestrial organic matter into aquatic systems[12, 77, 210, 243] with consequences for the rate of UV-induced mineralisation of organic carbon (see below).

Changes in continental runoff of CDOM have consequences for the transmission of solar UV radiation into water bodies and thus for the protection of phytoplankton against the damaging UV-B radiation (see below). Remote sensing studies have provided new information on the extent of CDOM runoff and its impact on the penetration depth of UV radiation in the biologically-rich waters and coral reefs of South Florida (Fig. 4).

Vegetation shifts, droughts, fires, and tipping points

Climate related changes in the spatial distribution and regional intensities of precipitation and temperatures extremes, among other variables, drive vegetation shifts, droughts and the occurrence and extent of fires. This results in changes in the biogeochemical cycles that are initiated by UV interactions with the terrestrial biosphere and fire-scarred continental surfaces. Solar UV radiation also impacts the oxidative state of the atmosphere, in both the gas and aerosol phases, further influencing greenhouse gases concentrations and budgets.[14] This section seeks to provide heuristic linkages between climate related drivers such as wild fires, droughts and how UV fluxes, and changes and trends in UV fluxes, interact may push terrestrial ecosystems up to and over tipping points in ecosystem health.

Intensification of agriculture and the evolution of natural landscapes and ecosystems to managed ecosystems have increased rapidly over the past 50 years.[80, 87, 165] Changes in plant species also occur in regions that are undergoing large climate-related ecosystem shifts.[169] Climate-related changes in some of the Earth's largest terrestrial ecosystems are being detected.[45, 70] Droughts, for example, are reducing terrestrial primary production and are increasing in many regions of the Earth.[13, 37, 192, 246] UV radiation interacts extensively with the biogeochemical cycles that are shifting with changing land surface characteristics. The interactions of vegetation with the changing UV fluxes result in altered trace gas emission to the atmosphere including volatile organic carbon compounds (VOCs) (see below and Chapter 3). These UV-induced trace gas emissions include both direct emission of VOCs from plants, thought to be weakly sensitive to changes in UV radiation, and UV interactions with burned and/or modified litter. It is, however, difficult to separate changes in ecosystems due to ecosystem maturation and those due to climate change.[18]

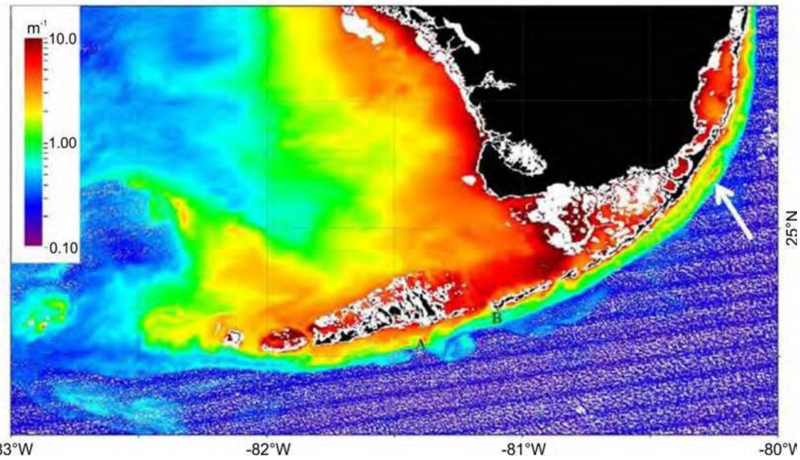

Fig. 4 Image showing UV attenuation caused by runoff of colored dissolved organic matter in coastal regions of South Florida. Results were derived from satellite measurements (MODIS/A) on 9 January 2009 using a model described by Barnes et al.[11] Land is masked in black. White indicates coastline, clouds or algorithm failure. Figure modified from Barnes et al.[11]

As ozone, aerosols and trace gases change and evolve in the atmosphere, the UV radiation at the surface changes, as well as the characteristics of the surface itself.[231] UV radiation-mediated release of trace gases and aerosols from the terrestrial biosphere then changes as a result of the altered make-up of the land surface. Fires have emerged as an important component of such land surface change.[112, 230] Not only do fires input massive amounts of chemicals and aerosols to the atmosphere, altering atmospheric UV radiation and chemistry, but they also leave charred substrate behind. Charcoal can persist for long periods in terrestrial systems. As a result, increasing amounts of black carbon, an important constituent of charred substrate, are entering rivers and flowing into lakes and the ocean where photochemical transformations are important sinks.[48, 102, 142, 213] The intent of this section is to highlight and draw attention to the often ignored interactions between UV radiation, atmospheric chemistry and surface land characteristics that are dependent on the extant ecosystems. The way in which these interacting systems are changing at the same time, often at different rates, is also addressed.

Terrestrial biosphere tipping points occur due to the complex interactions between UV radiation, drought-induced aerosol distributions, anthropogenic pollution and column ozone depletion over specific areas.[16, 27] UV radiation changes could represent the final source of variability that pushes/pulls the terrestrial biosphere over tipping points with large impacts on global biogeochemical cycles. Even with the general success of the Montreal protocol, there are still large areas with high UV radiation reaching the Earth's surface due to column ozone depletion.[16] Tipping points in biogeochemical cycles may be traversed by strong gradients in surface UV radiation. Biogeochemical cycles are occurring over large regions of similar ecosystem make-up and experience large differences in UV flux due to atmospheric chemistry and physical climate variables such as clouds. As in the purely physical climate system, extreme events often have a greater impact on biogeochemical cycles than a change in the mean state.[25, 134] There are direct feedbacks where the processes of afforestation lead to changes in the general circulation of the atmosphere resulting in changes in precipitation.[217] Extreme events, physical climate system shifts, fires and droughts all may contribute to UV initiation of tipping points in both terrestrial and aquatic biogeochemical cycles. For example, extensive increases in melting snow and ice cover lead to increases in the exposure of aquatic ecosystems to UV and PAR,[63] which have the potential to create tipping points - shifts in photosynthetic *vs* heterotrophic organisms where community as well as ecosystem structure and function are fundamentally altered.[38].

As ecosystems change due to climate change, fire and droughts, the chemicals released (i.e. hydrocarbon, CO_2, CH_4, aerosols) alter atmospheric chemistry. These biogeochemical changes have, in turn, implications for the residence times of greenhouse gases that are modulated by UV photochemistry. These interactions and biogeochemical cycling aspects of the Earth system often fall outside of traditional boundaries of scientific specialization and are only now becoming more fully appreciated.

Interactive effects of solar UV radiation and climate change on the carbon cycle

Carbon exchange between ocean and atmosphere

Air-sea CO_2 fluxes vary locally and seasonally and depend on the partial pressure of CO_2 and, in turn, on ocean temperature, mixing, and biology.[175, 195] The main biological process that controls the uptake of CO_2 by the ocean is the so-called biological pump (CO_2 binding in photosynthesis by phytoplankton and export of dead particulate organic matter to the ocean sediment) (Fig. 5).

Rates of primary production depend on various factors including light and nutrient availability, temperature, and the species composition of phytoplankton. Also phytoplankton performance is important for efficient CO_2 uptake and may be negatively affected by solar UV-B radiation.[78, 242] Evidence has continued to mount that the concentration of CDOM controls the penetration of UV and short-wavelength visible

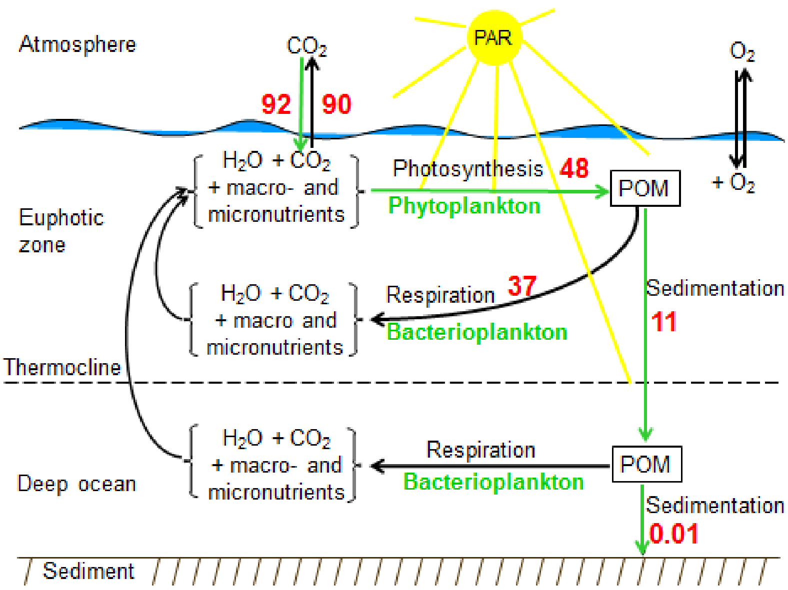

Fig. 5 Schematic representation of the biological pump, indicated by the green arrows. The efficiency of the biological pump depends on the rates of both photosynthesis (primary production) with photosynthetic active radiation (PAR) and the formation and sedimentation of particulate organic matter (POM). Numbers in red are from Houghton[96] and correspond to approximate global mean fluxes in Pg C yr^{-1}.

radiation into lakes and the coastal ocean.[11, 78, 158, 208, 242] CDOM effectively protects aquatic ecosystems from harmful UV-B radiation while permitting PAR to be transmitted into the water column. The degradation of CDOM by photochemical and biological processes leads to a loss of colour and reduced UV absorbance, both in the UV-B and UV-A regions.[26, 69, 74, 85, 197, 216, 239] As a consequence of CDOM photobleaching, the penetration depths of solar UV radiation into water bodies increase, thereby increasing the exposure of phytoplankton to damaging solar UV-B radiation (also see Chapter 4). CDOM photobleaching is particularly evident in thermally stratified waters bodies.[23, 85, 239] Stratification results in a shallower mixing depth, which in addition leads to a greater exposure of phytoplankton to UV-B radiation.[226] Enhanced stratification, due to increasing sea surface temperatures, occurs mainly in low latitude marine environments where it also hinders the transport of nutrients to the euphotic zone from deeper water layers and hence negatively affects primary production.[21, 123] Stratification has also been observed in ice-free Arctic marine regions due to increased meltwater input.[32] Cai et al.[32] predict that an ice-free Artic Ocean will not become a larger CO_2 sink due, in part, to an inefficient biological pump as a consequence of negative effects of solar UV radiation on phytoplankton.

CDOM in aquatic systems originates from several sources. In the coastal ocean, continental runoff of CDOM plays an important role (see also above).[57, 73, 158, 173, 197, 208] In the open ocean and large lakes, CDOM is a by-product of biological degradation of dead phytoplankton.[157, 158, 216] Thus, a reduced concentration of phytoplankton will drive decreased CDOM production, further increasing transmission of UV radiation into the ocean. The observed reductions in chlorophyll concentration that have been attributed to increasing sea surface temperatures[21] are probably caused by a combination of increased exposure to UV radiation and reduced nutrient upwelling.[50]

An important part of the biological pump is the export production, i.e. the formation and sedimentation of particulate organic matter (POM) stemming from dead phytoplankton and zooplankton material. The export production has decreased by 8% from 1960-2006 globally with strong spatial variability, based on model calculations.[123] One reason for this decline may be a global decrease in the biomass of small phytoplankton and diatoms in the period 1960-2006 (8.5% and 3%, respectively[123]). Ocean acidification may further reduce the biomass of coccolithophores, small calcifying phytoplankton, and hence the production of $CaCO_3$ “ballast” that enhances sinking rates of carbonate-rich POM.[75, 88, 89, 123] Overall, the interaction of solar UV radiation with climate-change effects such as ocean stratification is likely to decrease the efficiency of the biological pump and to cause UV-mediated, positive feedbacks on atmospheric CO_2 (see also below).

Carbon exchange between terrestrial ecosystems and atmosphere

The uptake of CO_2 by terrestrial ecosystems via photosynthesis of plants and the release of CO_2 to the atmosphere via decomposition of senescent plant material (litter) are affected both positively and negatively by solar UV radiation and climate change.[10, 242] Climate change, and in particular the intensity and frequency of droughts in terrestrial ecosystems could negatively impact primary production by plants and crops and thus CO_2 uptake by terrestrial ecosystems.[13, 100, 246] At the same time, changes in climate that decrease cloudiness and increase UV radiation at the terrestrial surface may increase losses of carbon from terrestrial ecosystems due to increased photochemical degradation of plant material.[7]

A part of the CO_2 fixed by plants may be sequestered in forests or long-lived plant soil components such as woody tissue or peat in soil organic matter, thus increasing its residence time in organic pools. Plant litter on the soil surface is, however, subject to rapid degradation, which results in emissions of CO_2 and other greenhouse gases to the atmosphere.[24, 82, 184, 242] The release of CO_2 from terrestrial ecosystems by microbial degradation of soil organic matter is strongly affected by temperature and moisture.[19, 135, 206] In addition, there is increasing evidence of abiotic decomposition of above ground litter due to UV radiation, particularly in arid and semiarid regions with low soil biotic activity.[6, 7, 24, 42, 53, 64, 113, 125, 135, 143, 184, 206] Rates of plant litter photodegradation due to exposure to UV radiation depend on various factors, including: (i) plant cover,[7] (Fig. 6), (ii) the intensity of solar UV radiation (altitude, latitude), (iii) exposure of litter mass to solar radiation due to differences in litter area to mass ratio, and (iv) chemical composition of plant litter[6, 113] (Figure 7, also see Chapter 3).

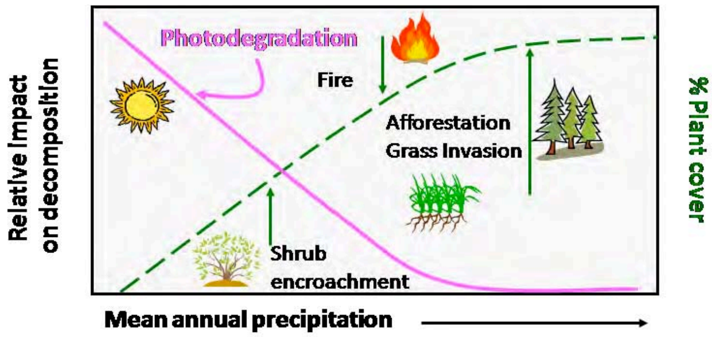

Fig. 6 Hypothesized effect of plant cover on photodegradation in terrestrial ecosystems. Plant cover is a key factor which will affect the degree of exposure to UV radiation and impacts of photodegradation as a vector of carbon loss in arid and semiarid ecosystems. As precipitation increases, primary production and resulting plant cover increase, thereby reducing the relative importance of photodegradation in mesic and humid ecosystems. Global changes such as shrub encroachment, increased fire frequency, invasion of non-native annual species and afforestation will all affect plant cover and consequently the relative impact of photodegradation on decomposition in these ecosystems. Red line shows the importance of photodegradation as rainfall increases, the dashed line is changes in plant cover. Green arrows indicate the direction of change in plant cover with global change. Figure modified from Austin.[7]

Recent information regarding the role of litter chemistry in determining the rate of UV-induced litter degradation has identified the importance of lignin in the process of photodegradation. Several studies have shown a decrease in litter lignin content with exposure to solar or UV-B radiation[59, 86] and that lignin content of litter is *positively* correlated with higher rates of mass loss (Fig. 7, Austin and Ballaré[6]). The latter can be explained in terms of a higher percentage of aromatic components in lignin and thus a higher rate of light absorption in the UV and visible range.[6, 53, 64, 215] Although abiotic photodegradation increases with the lignin content, the rate of microbial degradation tends to decrease with increasing lignin content, due to the bio-recalcitrant nature of lignin[6] (Fig. 7). Finally, there is some evidence that exposure of plant litter to solar UV-radiation can increase the bioavailability of some compounds to soil microorganisms,[24, 42, 53, 64] although the mechanistic basis of this stimulation has not been established.

The direct and indirect effects of UV radiation on decomposition of plant litter are likely to become a much more significant global pathway for terrestrial organic matter decomposition in the future. Aridification due to land use and/or climate change could amplify photodegradative losses from senescent plant litter, with large potential impacts on the carbon balance of terrestrial ecosystems. Particular attention needs to be paid to Arctic terrestrial ecosystems. The Arctic region is experiencing rapid warming and its land area, including the tundra, has large stores of carbon that are likely to be rapidly converted to GHGs with warming. For example, losses from plant litter may be enhanced due to the thawing of permafrost[42] and Arctic tundra wildfires,[136] (see also above). All of these global changes have potential to affect plant cover (Fig. 6)[7] and hence increase the importance of photodegradation in these modified ecosystems.

The terrestrial-aquatic interface

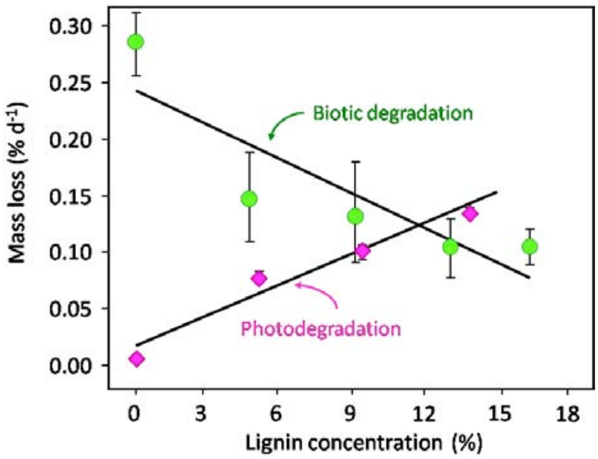

Fig. 7 Effects of lignin concentration on biotic decomposition and photodegradation. While biotic degradation of plant litter is inhibited by high lignin concentrations, lignin serves as a light absorbing compound facilitating photodegradation and carbon release from decomposing plant litter. Green circles indicate material of varying lignin concentrations which was decomposed in shaded conditions in contact with soil (biotic decomposition) while red diamonds indicate identical material of varying lignin concentrations that was isolated from the soil surface and exposed to full solar radiation. Figure modified from Austin and Ballaré.[6]

Terrestrial and aquatic ecosystems are largely linked via the biogeochemical cycling of carbon. Runoff and leaching of plant litter is a major source of CDOM in aquatic environments, especially in freshwaters. In coastal marine environments, a large fraction of organic carbon originates from terrestrial ecosystems that is transported to coastal oceans (i) via rivers,[54, 56, 68, 130, 155, 210] and (ii) fluxes from wetlands, particularly from mangrove swamps[15] (Fig. 4). Terrestrial organic matter (tDOM), in particular its CDOM fraction, more strongly attenuates solar UV radiation than organic matter produced within lakes and the sea due to its relatively high aromatic content,[57, 74, 159, 173, 197, 211, 242] where the optical properties of terrigenous CDOM arise primarily from partially oxidised lignins originating from vascular plant sources[22] (see also above). UV-induced photodegradation occurs more readily with terrestrially derived CDOM than with microbial CDOM[74, 105, 179, 211, 242] where microbial CDOM is derived from autochthonous organic sources in the ocean and lakes such as dead phytoplankton cells. In the Arctic Ocean, continental runoff is a major source of terrigenous organic material and nutrients, thereby influencing water column stratification, gas exchange, light attenuation, surface heating, biological productivity, and carbon sequestration. A remote sensing study of the pan-Arctic distribution of tDOM and continental runoff in the surface Arctic Ocean indicated a correspondence between climate-driven changes in river discharge and tDOM inventories in the Kara Sea.[57]

The major carbon substances resulting from UV-induced photodegradation of CDOM are inorganic species: dissolved inorganic carbon (DIC) and to a lesser extent carbon monoxide (CO)[173, 197, 233] (see Fig. 8). Photochemical DIC formation may strongly impact carbon cycling in seawater and other natural waters. For example, the annual photodegradation of CDOM exceeded the annual terrestrial input of photoreactive CDOM to the Baltic Sea, indicating that photochemical transformation is a major sink for terrestrial CDOM in such coastal systems.[1] Other mechanistic studies of the efficiencies of CDOM photodegradation have shown that DIC photoproduction rates are up to 30 times greater than CO photoproduction[173, 197, 233] (Fig. 8). Although not precise, these estimates suggest that CO_2 photoproduction rates are comparable to other oceanic CO_2 production terms, e.g., microbial respiration.

UV-induced and the microbial degradation of DOM (respiration, see Fig. 5) result in production of CO_2. The rate of this process is largely controlled by the availability of DOM to heterotrophic bacteria, which in turn depends on the chemical composition of DOM.[41, 178, 210, 215] UV-induced transformations generally decrease the bioavailability of microbial CDOM and enhance the bioavailability of terrigenous CDOM.[41, 215, 242] Such a UV-induced enhancement also has been observed in the case of terrestrial plant litter where the term “photochemical priming” has been used to describe this enhancement (see Chapter 3).

Climate change can influence the UV-induced degradation of CDOM through effects on its sources. For examples, melting of glaciers, ice sheets, and thawing permafrost heightens the input of microbial DOM into aquatic systems[46, 52, 164] and this source of CDOM generally becomes less biodegradable when transformed by solar UV radiation. Furthermore, both changes in continental hydrology and land use change may increase fluxes of tDOM from land to ocean[150, 174, 210, 222, 243] thereby enhancing UV-induced CO_2 production via mineralisation of tDOM.[130] According to Regnier et al.[174], the carbon flux to inland waters from soils has risen by 1.0 Pg C per year since preindustrial times. Also land use changes can affect sources of CDOM. For example, disturbance of peatlands has resulted in a 32% increase in fluvial organic flux from southeast Asia[150] and this source of tDOM likely is photodegradable. Arctic aquatic ecosystems are particularly affected by increased input of DOM due to changes in rainfall, melting of ice, snow, and the permafrost. Depending on its source, DOM in Arctic aquatic ecosystems is subject to UV-induced or microbial mineralisation, where photochemical priming plays an important role.[219]

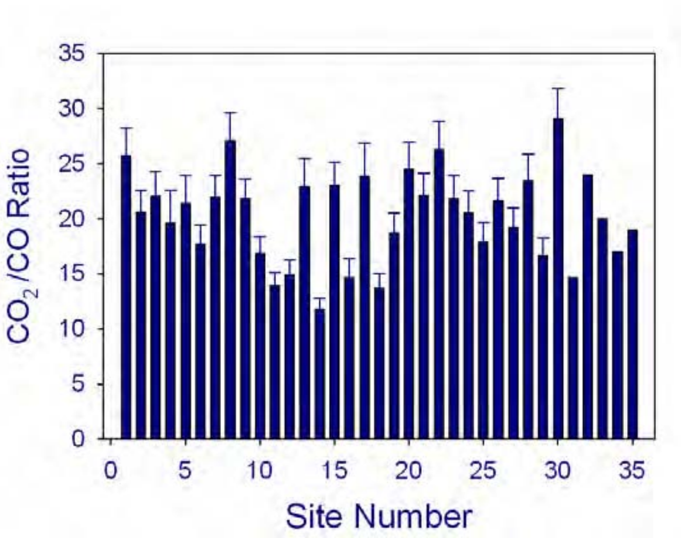

Fig. 8 Measured ratios of sunlight-induced CO_2/CO photoproduction in oceanic water samples collected from a variety of locations and times. The average ratio is close to 20 in marine systems but somewhat lower in freshwaters.[173, 197, 233]

Links between carbon and nutrient cycles

In aquatic ecosystems, CO_2 fixation in photosynthesis by phytoplankton (primary production) plays a key role in linking the carbon and nutrient cycles. The rate of primary production depends, in part, on the concentration and bioavailability of macro- and micronutrients present in the euphotic zone. Many nutrients are transported into the euphotic zone from deeper water layers.[104] However, ocean stratification due to increasing sea-surface temperatures (SST) hinders the upwelling of nutrients and, as a consequence, negatively affects primary production and hence the biological pump[21, 50, 123](see above). Micronutrients (essential trace metals including Fe, Cu, Zn, Mn, Co, and Cd) may co-limit phytoplankton growth and primary production in marine environments.[110, 111, 127, 201] The biological availability of essential trace metals depends on their chemical speciation. In general, only dissolved and weakly-bound or unchelated metals are available to phytoplankton.[4, 151, 238] For this reason, oxidation and mainly reduction processes (redox reactions) induced by solar UV radiation play an important role in the formation of bioavailable metal species.[84] Increased vertical mixing of water bodies reduces rates of UV-induced redox cycling of essential metals. For example, sea-ice loss in the western Antarctic Peninsula is hypothesised to reduce iron bioavailability because of greater vertical mixing in winters with little sea ice.[225]

Iron plays a key role as a micronutrient and co-limits phytoplankton growth particularly in the so-called high-nutrient-low chlorophyll (HNLC) oceanic regions.[110, 111] In oxygenated marine environments, Fe (III) is largely present in the form of solid Fe(III) phases, with low solubility. In the Southern Ocean, for example, dissolved iron concentrations range between 0.4 and 1.5 nmol L^{-1}.[189] However, these solid iron phases can undergo UV-induced dissolution yielding dissolved iron species[20, 109] and this photochemical process has been shown to occur at pH-values of marine waters.[20]

Ocean acidification (see above) can result in reduced availability of essential trace metals such as Fe, Zn, and Cd to phytoplankton, either via changes in the chemical speciation of metals or by decreasing the effectiveness of the enzymatic reduction of metals.[199, 238] For example, the uptake rate of iron bound to the siderophore desferrioxamine B by a model diatom was by a factor of ~2 lower in seawater samples with pH 7.8 as compared to samples with pH 8.7.[199] Ocean acidification also slows down nitrogen uptake by phytoplankton under low iron conditions by lowering the efficiency of N_2 fixation.[200]

Combined effects of solar UV radiation and climate change on the biogeochemistry of trace gases and aerosols

Terrestrial and aquatic environments are important atmospheric sources and sinks of trace gases and aerosols. Recent research on the air-sea exchange of trace gases has provided further evidence that these sources are strongly influenced by interactions between solar UV radiation and climate change.

Methane

Methane is an important greenhouse gas that is stored in various reservoirs in the terrestrial, aquatic and atmospheric systems. UV radiation is involved in the release and exchange of CH_4 between these reservoirs as well as atmospheric chemical processes in the troposphere and stratosphere.[49, 90, 156] Temperature, water vapour, stratospheric ozone, biomass burning, and lightning NO_x are the dominant sources of inter-annual changes in methane lifetime.[90] UV radiation plays a critical role in determining the effectiveness of each of these sources in inter-annual changes in methane lifetime which is ~9 yr.[149] The linkages and inferences of this section revolve around the UV-mediated atmospheric chemistry, ozone, OH etc. that drive atmospheric methane concentrations, and how CH_4 release and uptake from land, aquatic and atmospheric reservoirs is influenced by UV radiation and biogeochemical cycles in general.

New satellite and airborne data assimilation techniques allow high-resolution, global estimates of the sources and sinks of atmospheric methane.[97] These emerging technologies allow quantification and evaluation of the wild-fire production of atmospheric methane, an increasing source due to the climate related increased occurrence of wildfires.[181, 224] UV radiation plays a critical role in the atmospheric chemistry of methane as well as modulating its production in soils and other components of the terrestrial biosphere,[235, 245] although Morsky et al. [154] find its role in methane production in a sub-arctic fen was more modest. The release of methane to the atmosphere from land surfaces is dependent upon climate change in the terrestrial biosphere as well as heat and UV supply to specific methane reservoirs such as permafrost regions.

Methane fluxes from the Arctic Ocean are strong and occurred mainly in areas of open water between sea-ice (leads) and fractional sea-ice up to 82° N.[118] Additional sources from submarine permafrost regions have also been reported.[196] Such oceanic regions are likely to become increasing sources of atmospheric methane in the future due to climate-related changes in sea-ice cover. Warming has also been shown to affect the emission of methane in Western Siberian lakes with implications for atmospheric chemistry and UV interactions.[168] We posit that as climate changes, ocean sea-ice coverage changes and often decreases, resulting in new and increased distributions of air-sea methane flux. The resultant methane releases will change and will be occurring simultaneously with the evolving atmospheric UV radiation budget.

Carbon monoxide

Carbon monoxide (CO) is widely produced through interactions of solar UV radiation with organic substances in aquatic and terrestrial systems. The average ratio of measured CO_2/CO fluxes from various marine environments is close to 20 (Fig. 8). CO participates in chemical reactions that change air quality and it is one of the most important sinks for atmospheric hydroxyl radicals (•OH). Due to its significant effects on •OH, CO also indirectly influences the concentrations of methane, halocarbons and other gases in the troposphere (see above). Recent research has provided further evidence that UV-induced processes as well as abiotic thermal processes involving tDOM in aquatic systems and plant litter on land are significant sources of CO to the atmosphere.[55, 113, 173, 197, 207, 212, 233, 240, 244] tDOM generally is a more efficient source of CO (higher apparent quantum yields) than microbial CDOM derived from marine sources such as algal detritus. For example, CO photoproduction efficiencies in the Tyne estuary were highest for high CDOM riverine samples and almost an order of magnitude lower for low CDOM coastal seawater samples.[212] One exception to this general observation is the unusually high efficiency of CO photoproduction from CDOM within floating Sargassum colonies[197]. There are also significant CO microbial sinks in aquatic and terrestrial systems and the competition between these sources and sinks often results in diurnal fluctuations in the net exchange of CO between biosphere and atmosphere.[190, 240, 244]

An extensive study of the sea to air exchange of CO_2 in the sub-arctic estuarine water body, the Canadian St. Lawrence estuary system, showed that the rates of photoproduction and microbial consumption of CO are approximately balanced.[244] Other findings are that the photochemical efficiency for CO production from DOM in aquatic systems decreases with increasing salinity across the freshwater-marine mixing zone.[207, 233, 237, 245]

Studies of terrestrial plants have provided additional evidence that exposure to UV radiation leads to production of CO from dead plant matter (litter) and that production rates depend on the litter traits.[125] Studies of the effects of changing wavelength on CO photoproduction from litter are uncommon but one study showed that UV radiation induces CO production from *Sequoia dendrongiganteum* litter. CO emissions were strongly reduced in the absence of oxygen as compared to air.[47] Other studies have shown that living plant leaves also photoproduce CO,[29] although the production efficiency generally is much lower than for senescent or dead vegetation.

Nitrogen compounds

Among nitrogen-containing gases, nitrogen oxides (NO_x = NO + NO_2) play an important role in atmospheric chemistry, and many nitrogen gases have important interactions with UV radiation. In the troposphere, NO_x enhances the formation of O_3 via UV-induced reactions (see Chapter 6). In the stratosphere, the opposite is the case, where NO_x destroys O_3 by the following reaction: $NO + O_3 \rightarrow NO_2 + O_2$, where NO_2 acts as a catalyst in stratospheric O_3 destruction.[170] Furthermore, the reaction of NO_2 with ClO yields $ClONO_2$, a reservoir of reactive chlorine that continues to play an important role in polar stratospheric ozone depletion in the Arctic and Antarctic spring. Given these important interactions, changes in the atmospheric concentrations of nitrogen oxides due to climate change or other human activity may indirectly affect ozone recovery and the amount of UV radiation reaching the Earth´s surface.

Anthropogenic NO_x emission from combustion of fossil fuel, is an important source of NO_x to the atmosphere. Additionally, nitric oxide (NO) from natural sources is produced mainly by anaerobic bacteria that reduce nitrate (NO_3^-) to nitrogen gas N_2;[166] NO is also a by-product of the oxidation of ammonium (NH_4^+) to nitrate by ammonia-oxidising soil bacteria.[160, 166] Nitrous acid (HONO) emissions from ammonia-oxidising bacteria are comparable with emissions of NO.[160, 214]. Since soil emissions of both NO and HONO depend on the soil water content,[160] increasing soil dryness, due to climate change, may increase the emission of NO and HONO from soils. UV-induced photolysis of HONO is a major source of the hydroxyl radical (HO•) (up to ~30% of production in the lower atmosphere[214]). In addition to soil emissions of NO_x from biotic processes, UV-induced photolysis of

NO_3^- (photodenitrification) is an important source of NO_x to the atmosphere.[153, 176] This abiotic process has been shown recently to occur on the surface of nitrate-containing snow in the Arctic,[153] and in sea salt particles containing Cl^- and Br^-.[176]

Another key nitrogen-containing gas is nitrous oxide (N_2O), an important greenhouse and stratospheric ozone depleting gas. The surface emission of N_2O approximately balances the stratospheric N_2O loss[170] via formation of the ozone destroying NO [$N_2O + O^* \rightarrow 2\ NO$, where O* is produced via photolysis of ozone: $O_3 + h\nu \rightarrow O^* + O_2$]. In terrestrial ecosystems, N_2O is formed by denitrifying soil bacteria that reduce NO_3^- to N_2.[166] N_2O formation in soils depends on soil water content (SWC) and temperature and occurs at higher SWC than soil emission of HONO and NO.[28, 160] Van Groenigen et al.[223] predict that rising levels of CO_2 will result in increased emissions of N_2O from upland soil due to reduced plant respiration and thus higher SWC. In addition, more frequent precipitation events, due to climate change, that increase SWC could thus enhance the N_2O flux from soils.[28]

In aquatic ecosystems, ammonia is produced by the UV-induced degradation of DOM[184] and N_2O by both denitrifying bacteria and ammonia oxidising archaea.[188] N_2O formation is particularly efficient in suboxic and hypoxic oceanic regions (~10% of the ocean volume).[39, 228] The area of such regions is likely to expand (Fig. 3) due to the following factors: (i) eutrophication of coastal waters, (ii) decreasing O_2 solubility with warmer water temperatures, and (iii) shifts in respiration towards the upper oceanic water column because of reduced sinking velocity of particles in the ocean[39, 88, 227] (see also above). Furthermore, it has been shown that during storms, N_2O rich subsurface water is mixed upwards[228] suggesting that more frequent storm events, due to climate change, may result in increased emission of N_2O from marine environments. In addition, sea-ice retreat has been suggested to decrease the residence time of N_2O in the surface water of the Arctic Ocean and thus could enhance the sea-air flux of N_2O.[115, 172] Geoengineering via fertilisation of marine regions with iron could enhance marine N_2O production,[103] (also see Chapter 1).

Halogen compounds

Biogenic processes in terrestrial and aquatic ecosystems are important sources of halocarbons other than CFC (e.g., the methyl halides CH_3Br, CH_3Cl, and CH_3I) to the atmosphere.[17, 65, 81, 121, 132] In aquatic ecosystems, phytoplankton is involved in the formation of these halocarbons, particularly pico-sized phytoplankton,[121] and to a lesser extent bacteria belonging to *Erythrobacter* or *Pseudomonas*.[65] The rate of halocarbon production in aquatic ecosystems also depends on the chemical composition of dissolved organic matter (DOM), with tDOM playing an important role in the formation of halocarbons such as bromoform ($CHBr_3$) and dibromomethane (CH_2Br_2).[132] Hence increased fluxes of tDOM from land to ocean, due to climate change, may enhance the formation of halocarbons, particularly in eutrophic coastal waters. In addition to the biotic production of halocarbons, abiotic UV-induced processes could also be involved in the formation of CH_2ClI, and CH_2I_2 in seawater.[121]

In the atmosphere, halocarbons are transformed into reactive halogen species (RHS, e.g., the radicals Br• and BrO•), where the hydroxyl radical (HO•$^{\cdot}$, formed in reactions induced by solar UV radiation) acts as the oxidant.[93, 214] In the troposphere, RHS react with ozone[186, 187] and other gases, e.g., gaseous elemental mercury (Hg^0)[171] (see also below). Halocarbons can reach the lowermost stratosphere and undergo UV radiation-induced transformations yielding RHS, particularly $BrO^{\cdot}$, that participate in stratospheric ozone depletion.[93, 94] Models suggest that the loading of the stratosphere with reactive bromine species will increase in the future due to climate change[92] and thus the destruction of ozone in the stratosphere by RHS represents a positive feedback on solar UV radiation. This feedback could be enhanced by climate-change related processes, particularly by increased input of tDOM into coastal zones[132] and by increases in ocean mixing and thus transport of CH_3Br to the lower stratosphere.[93]

Aerosols

Atmospheric aerosols play an important role in the biogeochemistry of greenhouse gases, atmospheric circulation trends due to changes in climate and atmospheric chemistry.[137] The surfaces of atmospheric aerosol particles provide reactive multi-phase regions for chemical transformations in the atmosphere. Surfaces, as well as the liquid phase portions inside the aerosols, interact with UV radiation to process chemicals critical to climate and atmospheric chemistry in general. Aerosol distributions and trends in distributions due to climate change alter UV fluxes to Earth's surface. This is due to direct blocking of UV radiation by aerosols in the atmosphere and the fact that the distributions and the radiative and chemical make–up of the aerosols are evolving as climate changes.

Aerosols affect circulation directly via interactions with radiation with attendant thermal gradient impacts.[122, 148] This means that strong feedbacks exist between aerosol distributions, UV radiation, and the circulation that influence precipitation and atmospheric transport.[44] Changes in the distribution of atmospheric aerosols are occurring at the same time as shifts in terrestrial and aquatic and marine ecosystems.[191] UV radiation is involved in and affected by biogeochemical feedbacks that result from chemical exchanges at the Earth surface, physical circulation changes and human-induced modification of the environment. UV interactions with the liquid phase of marine aerosol particles result in trace gas production, which alter the oxidation state of the atmosphere. Fe compounds have recently been implicated in these aerosol multiphase interactions.[139] Aerosols not only scatter and absorb atmospheric UV radiation they influence and change atmospheric gas and liquid phase chemistry.

Urbanisation and managed agriculture have resulted in changing patterns of atmospheric dust distributions and deposition.[120] These dust aerosols, which affect the transparency of the troposphere, have a concurrent impact on UV flux to aquatic and terrestrial ecosystems. Non-Asian sources are a significant source of dust to the North Pacific[98] and will likely result in significant changes in the supply of nutrients, as organically bound Fe and P is transported atmospherically from continental regions to ocean ecosystems.[107, 150, 191] Information from studies of the impacts of volcanic supplies of aerosols are being used to predict the impact of future aerosol distributions on the carbon cycle.[182]

There is an emerging realisation that liquid phase UV-driven aerosol chemistry can influence biogeochemical cycling of atmospheric greenhouse gases.[131] This means that not only do atmospheric aerosols modulate surface UV fluxes via their distribution in the atmospheric column, but also the multi-phase chemical processes that occur on/in aerosols affect the oxidative state of the atmosphere. An example of this multi-phase chemistry is the Fe chemistry in aerosols that influences atmospheric radicals, oxidative state and lifetimes of greenhouse gases[139]. These newly identified biogeochemical cycles assist in understanding some of the interactions between UV radiation, aerosol chemistry and atmospheric greenhouse gas distributions.

Combined effects of solar UV radiation and climate change on chemical and biological contaminants

Organics

Global climate change and interactions with solar ultraviolet radiation will potentially influence chemical fate and bioaccumulation in terrestrial and aquatic environments.[71, 91] Reviews and modeling studies have particularly focused on the Arctic and persistent organic pollutants (POPs)[5, 72, 221] and predict the following effects: (1) Increased ambient temperatures could lead to increased emissions of chemicals through passive volatilisation from materials and stockpiles; (2) Increased emissions of

POPs are predicted as a result of changing land-use patterns and changes in global agricultural practices, such as pesticide formulations and application rates; (3) Changes in energy use will affect use and release of chemicals; (4) Increases in the frequency of forest fires will increase the emissions of polycyclic aromatic hydrocarbons and other combustion by-products such as charcoal and black carbon.

Although POPs are chemicals such as chlorinated compounds that are resistant to biodegradation and/or to photodegradation through direct absorption of sunlight, these chemicals can be transformed by indirect photoreactions that involve natural substances such as tDOM (or related natural organic substances that were isolated from soils or natural waters), peroxides, nitrate or certain trace metals. Most of the recent examples of indirect photoreactions involve participation of tDOM.[35, 36, 72, 76, 183] Chemicals having a wide variety of structural features participate in these indirect photoreactions including chlorinated contaminants,[72, 183] antibiotics,[76] beta-blockers,[36] and other drugs.[35]

One manner through which environmental variables influenced by global climate change could affect contaminant toxicity involves direct effects of the variable on chemical characteristics. The toxicity of polycyclic aromatic hydrocarbons (PAHs), for example, can be photoactivated by solar UV radiation.[91] The intensity and wavelength distribution of UV radiation, key factors in determining PAH phototoxicity, are likely to be affected by variables altered by climate change. For example, these variables could include decreases in pH that can increase water clarity, thereby increasing exposure of aquatic animals to UV radiation, and increased inputs of CDOM or particulate carbon to aquatic systems, which would effectively reduce UV penetration. Hence, specific influences of climate change on UV intensity in aquatic systems are likely to be site- and situation-specific.

Although increased UV-B radiation can negatively affect the growth and viability of many organisms in aquatic food webs, sensitivity to UV radiation has the beneficial effect of disinfecting pathogens.[1, 58, 144, 203] This process is facilitated by climate and UV-induced changes that alter exposure of surface-dwelling organisms through increased water transparency and stratification, and reduced ice and snow cover. For example, human pathogenic viruses, which are frequently found in rivers, lakes and drinking water, are sensitive to solar UV radiation[203] and disinfection by solar UV irradiation (SODIS) is becoming a widely-used tool for purification of drinking water in developing countries.[144] The observed increases in CDOM in aquatic environments can have opposing effects on pathogen levels. On the one hand, the increases in CDOM reduce UV exposure and thus disinfection by direct photoinactivation of parasites and pathogens. On the other hand, photoinactivation of pathogens can be enhanced through photosensitisation by CDOM.[203]

Inorganics: Mercury

Mercury (Hg) is one of the inorganic priority pollutants and its biological availability and thus toxicity is strongly affected by solar UV radiation and climate change. Mercury is not an essential metal and is toxic at very low concentrations. Most mercury released to the atmosphere is in the form of gaseous elemental mercury (Hg^0), which can be transported over long distances and is deposited mainly in the oxidised form as divalent mercury (Hg^{II}).[40] In the oxidation process, the radicals BrO• and Br•, that are formed in UV-induced reactions, play a key role.[171] In addition, UV-induced re-reduction of Hg^{II} occurs in the troposphere, however, at a lower rate than Hg^0 oxidation.[40] Following deposition to terrestrial and aquatic ecosystems, Hg^{II} undergoes methylation yielding methylmercury (MeHg), the toxic form of mercury. In sunlit surface waters MeHg may undergo UV-induced decomposition, a process that is enhanced by DOM.[243]

Climate change may amplify effects of solar UV radiation on the biogeochemical cycling of mercury. For example, ocean warming increases the sea-air flux of Hg^0.[119] As a consequence, the rate of oxidation of Hg^0 to Hg^{II} (via UV-induced formation of reactive radicals, see above) can be expected to increase since the oxidation rate depends on the concentration of both reactive radicals and Hg^0. Hence it is likely that the combined effects of ocean warming and solar UV radiation on the biogeochemical cycling of mercury result in increased formation of the toxic form of mercury.

Nanomaterials

In addition to organic contaminants and mercury, new chemicals are coming into global markets that require initial assessment. Inorganic and organic engineered nanomaterials (ENMs) and their composites with polymers and coatings (also see Chapter 7) are being introduced into the environment through widespread use in consumer products. Concerns about their health and safety have stimulated research on their persistence and toxicity. UV-induced photoreactions are important environmental processes for ENMs such as nanosilver, nano-titanium dioxide, fullerenes, carbon nanotubes and graphene oxide. These photoreactions are sensitised by tDOM in some cases. For example, nanosilver can be readily formed by the tDOM-induced photoreduction of ionic silver,[2, 95] a sunlight-induced process that helps reverse toxicity associated with oxidation of nanosilver. UV-induced processes initiate the environmental release of ENMs from polymer nanocomposites by photodegradation of the polymer matrix.[114]

Gaps in knowledge

Our understanding of the interacting effects of solar UV radiation and climate change on the biogeochemical cycling of carbon, nitrogen and halogen compounds, essential and toxic metals, and on the fate of organic pollutants has increased in the four years since our last assessment. However, there remain important gaps in knowledge. For example, climate models generally do not include effects of solar UV radiation on biogeochemical cycles. To do this would be important for predicting trends in the net CO_2 sink strength of terrestrial and aquatic ecosystems.

Terrestrial and aquatic ecosystems are currently net CO_2 sinks on a global average, where the CO_2 uptake corresponds to ca 30% and 25%, respectively, of anthropogenic CO_2 emission.[9, 33] However, the CO_2 sink strength of terrestrial and aquatic ecosystems may decrease due to climate change[123, 124, 146] and interactions between solar UV radiation and climate change could accelerate this decline. Based on a biogeochemical elemental cycling model (without taking into account effects of solar UV radiation), Laufkoetter et al.[123] simulated a decrease in phytoplankton net primary production by 6.5% within 50 years (1960-2006) on a global average, due to various climate-change related factors, including ocean stratification. A decrease in net primary production by phytoplankton is likely to reduce the efficiency of the biological pump and thus the CO_2 sink strength of aquatic ecosystems. Even without a decrease in the global CO_2 sink strength of terrestrial and aquatic ecosystems; their capacity to take up CO_2 does not keep pace with increasing atmospheric CO_2 concentrations.[9, 116, 185]

As discussed earlier, an important effect of solar UV-radiation in aquatic ecosystems is photobleaching of CDOM, resulting in increased transmission of the damaging solar UV-B radiation into water bodies with negative effects on photosynthetic organisms (organisms such as phytoplankton that transform CO_2 into organic matter). The enhancement of UV-induced bleaching of CDOM due to stratification of water bodies therefore represents a UV-mediated, positive feedback on climate. In terrestrial ecosystems a positive feedback on climate is increased UV-induced decomposition and mineralisation of above ground litter (under release of CO_2) due to aridification and decreased plant cover from human activity.

Important greenhouse gases other than CO_2 are nitrous oxide (N_2O) and methane (CH_4). Climate change, via changing precipitation and temperature distributions and extreme events, can have large impacts on the emission of these gases. For example, N_2O and CH_4 emissions from plants may be increased through temperature effects, indirectly due to rising CO_2 levels. UV-induced inhibition of microbial processes in aquatic systems can also influence trace gas exchange such as CO and N_2O to air. Interactions in atmospheric chemistry also exist via UV-induced reactions involving N_2O resulting in the formation of ozone destroying compounds.

Halocarbons such as methyl bromide (CH_3Br), which are emitted by phytoplankton, are other gases that undergo UV-induced transformations to highly reactive species and thus also have the potential to cause stratospheric ozone depletion. Changes in oceanic phytoplankton distributions and community structure due to climate change is expected to alter rates of emission of these trace gases. Highly reactive species formed in UV-induced transformations of halocarbons also react with tropospheric pollutants, e.g., gaseous elemental mercury yielding the precursor of the bioavailable and thus toxic form of mercury. While there exists a large body of literature on the effects of climate change or of solar UV radiation on the fate of mercury, the interactive effects of climate change and solar UV radiation on the biogeochemical cycling of mercury have, to our knowledge, not yet been extensively studied.

Levels of organic pollutants and pathogens in aquatic environments are affected by interactions with changing climate and solar UV radiation. For example, UV radiation can inactivate pathogenic viruses by direct pathways and also by indirect pathways that involve sensitisation by CDOM. CDOM, a climate-sensitive component of most aquatic environments, can also modulate pathogen levels by screening out the UV component of sunlight.

The combined effects of solar UV radiation and climate change on biogeochemical cycles are likely to be particularly pronounced in the Arctic due to Arctic Amplification that also hinders the recovery of the stratospheric ozone concentration in Arctic spring. As a consequence of Arctic stratospheric ozone depletion, increased levels of solar UV radiation reach Artic terrestrial and aquatic ecosystems. Negative effects of solar UV-B radiation on phytoplankton and thus on the biological pump are expected in ice-free Arctic marine regions, particularly in combination with stratification due to increasing melt-water input. Based on a radiation transfer model, Fountoulakis et al.[60] predict that up to 10 times higher levels of solar UV irradiance will enter large parts of the Arctic Ocean by 2100, compared to the 1950s, mainly due to Arctic sea-ice melting. Furthermore, increased emissions of CO_2 via mineralisation of organic matter due to thawing permafrost and Arctic tundra wildfires as well as decreased albedo due to vegetation shifts,[165] have large effects on carbon cycling in the Arctic[219] and together can act as a positive feedback on global warming. Therefore, more attention needs to be paid to Arctic tipping points.

References

1 Aarnos H, Ylostalo P, Vahatalo AV, 2012, Seasonal phototransformation of dissolved organic matter to ammonium, dissolved inorganic carbon, and labile substrates supporting bacterial biomass across the Baltic Sea, *J. Geophys. Res. Biogeosci.*, **117**, G01004.

2 Adegboyega NF, Sharma VK, Siskova K, Zboril R, Sohn M, Schultz BJ, Banerjee S, 2013, Interactions of Aqueous Ag+ with Fulvic Acids: Mechanisms of Silver Nanoparticle Formation and Investigation of Stability, *Environ. Sci. Technol.*, **47**, 757-764.

3 Allan RP, 2011, Human influence on rainfall, *Nature*, **470**, 340-341.

4 Aristilde L, Xu Y, Morel FMM, 2012, Weak organic ligands enhance zinc uptake in marine phytoplankton, *Environ. Sci. Technol.*, **46**, 5438-5445.

5 Armitage J, Quinn C, Wania F, 2011, Global climate change and contaminants—an overview of opportunities and priorities for modelling the potential implications for long-term human exposure to organic compounds in the Arctic, *J. Environ. Monit.*, **13**, 1352-1546.

6 Austin AT, Ballare CL, 2010, Dual role of lignin in plant litter decomposition in terrestrial ecosystems, *Proc. Nat. Acad. Sci. USA.*, **107**, 4618-22.

7 Austin AT, 2011, Has water limited our imagination for aridland biogeochemistry?, *Trends. Ecol. Evol.*, **26**, 229-35.

8 Austin J, Struthers H, Scinocca J, Plummer DA, Akiyoshi H, Baumgaertner AJG, Bekki S, Bodeker GE, Braesicke P, Bruehl C, Butchart N, Chipperfield MP, Cugnet D, Dameris M, Dhomse S, Frith S, Garny H, Gettelman A, Hardiman SC, Joeckel P, Kinnison D, Kubin A, Lamarque JF, Langematz U, Mancini E, Marchand M, Michou M, Morgenstern O, Nakamura T, Nielsen JE, Pitari G, Pyle J, Rozanov E, Shepherd TG, Shibata K, Smale D, Teyssedre H, Yamashita Y, 2010, Chemistry-climate model simulations of spring Antarctic ozone, *J. Geophys. Res. Atmos.*, **115**.

9 Ballantyne AP, Alden CB, Miller JB, Tans PP, White JWC, 2012, Increase in observed net carbon dioxide uptake by land and oceans during the past 50 years, *Nature*, **488**, 70.

10 Ballare CL, Caldwell MM, Flint SD, Robinson A, Bornman JF, 2011, Effects of solar ultraviolet radiation on terrestrial ecosystems. Patterns, mechanisms, and interactions with climate change, *Photochem. Photobiol. Sci.*, **10**, 226-241.

11 Barnes BB, Hu C, Cannizzaro JPSE, Craig SEP, Hallock P, Jones DL, Lehrter JCN, Melo N, Schaeffer BA, Zepp R, 2014, Estimation of diffuse attenuation of ultraviolet light in optically shallow Florida Keys waters from MODIS measurements, *Rem. Sens. Environ.*, **140**, 519-532.

12 Bass AM, Bird MI, Liddell MJ, Nelson PN, 2011, Fluvial dynamics of dissolved and particulate organic carbon during periodic discharge events in a steep tropical rainforest catchment, *Limnol. Oceanogr.*, **56**, 2282-2292.

13 Beer C, Reichstein M, Tomelleri E, Ciais P, Jung M, Carvalhais N, Roedenbeck C, Arain MA, Baldocchi D, Bonan GB, Bondeau A, Cescatti A, Lasslop G, Lindroth A, Lomas M, Luyssaert S, Margolis H, Oleson KW, Roupsard O, Veenendaal E, Viovy N, Williams C, Woodward FI, Papale D, 2010, Terrestrial Gross Carbon Dioxide Uptake: Global Distribution and Covariation with Climate, *Science.*, **329**, 834-838.

14 Bekki S, Rap A, Poulain V, Dhomse S, Marchand M, Lefevre F, Forster PM, Szopa S, Chipperfield MP, 2013, Climate impact of stratospheric ozone recovery, *Geophys. Res. Lett.*, **40**, 2796-2800.

15 Bergamaschi BA, Krabbenhoft DP, Aiken GR, Patino E, Rumbold DG, Orem WH, 2012, Tidally Driven Export of Dissolved Organic Carbon, Total Mercury, and Methylmercury from a Mangrove-Dominated Estuary, *Environ. Sci. Technol.*, **46**, 1371-1378.

16 Bernhard G, Dahlback A, Fioletov V, Heikkila A, Johnsen B, Koskela T, Lakkala K, Svendby T, 2013, High levels of ultraviolet radiation observed by ground-based instruments below the 2011 Arctic ozone hole, *Atmos. Chem. Phys.*, **13**, 10573-10590.

17 Blei E, Heal MR, 2011, Methyl bromide and methyl chloride fluxes from temperate forest litter, *Atmos. Environ.*, **45**, 1543-1547.

18 Bodin J, Badeau V, Bruno E, Cluzeau C, Moisselin J-M, Walther G-R, Dupouey J-L, 2013, Shifts of forest species along an elevational gradient in Southeast France: climate change or stand maturation?, *J. Vegetati. Sci.*, **24**, 269-283.

19 Bond-Lamberty B, Thomson A, 2010, Temperature-associated increases in the global soil respiration record, *Nature*, **464**, 579-U132.

20 Borer P, Sulzberger B, Hug SJ, Kraemer SM, Kretzschmar R, 2009, Photoreductive Dissolution of Iron(III) (Hydr)oxides in the Absence and Presence of Organic ligands: Experimental Studies and Kinetic Modeling, *Environ. Sci. Technol.*, **43**, 1864-1870.

21 Boyce DG, Lewis MR, Worm B, 2010, Global phytoplankton decline over the past century, *Nature*, **466**, 591-596.

22 Boyle ES, Guerriero N, Thiallet A, Del Vecchio R, Blough NV, 2009, Optical properties of humic substances and CDOM: Relation to structure, *Environ. Sci. Technol.*, **43**, 2262-2268.

23 Bracchini L, Dattilo AM, Hull V, Loiselle SA, Nannicini L, Picchi MP, Ricci M, Santinelli C, Seritti A, Tognazzi A, Rossi C, 2010, Spatial and seasonal changes in optical properties of autochthonous and allochthonous chromophoric dissolved organic matter in a stratified mountain lake, *Photochem. Photobiol. Sci.*, **9**, 304-314.

24 Brandt LA, King JY, Hobbie SE, Milchunas DG, Sinsabaugh RL, 2010, The Role of Photodegradation in Surface Litter Decomposition Across a Grassland Ecosystem Precipitation Gradient, *Ecosystems*, **13**, 765-781.

25 Bret-Harte MS, Mack MC, Shaver GR, Huebner DC, Johnston M, Mojica CA, Pizano C, Reiskind JA, 2013, The response of Arctic vegetation and soils following an unusually severe tundra fire, *Philos. Trans. Roy. Soc. Lond. B.*, **368**.

26 Bricaud A, Ciotti AM, Gentili B, 2012, Spatial-temporal variations in phytoplankton size and colored detrital matter absorption at global and regional scales, as derived from twelve years of SeaWiFS data (1998-2009), *Glob. Biogeochem. Cycles*, **26**.

27 Brook BW, Ellis EC, Perring MP, Mackay AW, Blomqvist L, 2013, Does the terrestrial biosphere have planetary tipping points?, *Trends. Ecol. Evol.*, **28**, 396-401.
28 Brown JR, Blankinship JC, Niboyet A, van Groenigen KJ, Dijkstra P, Le Roux X, Leadley PW, Hungate BA, 2012, Effects of multiple global change treatments on soil N_2O fluxes, *Biogeochemistry*, **109**, 85-100.
29 Bruhn D, Albert KR, Mikkelsen TN, Ambus P, 2013, UV-induced carbon monoxide emission from living vegetation, *Biogeosci.*, **10**, 7877-7882.
30 Burke A, Robinson LF, 2012, The southern ocean's role in carbon exchange during the last deglaciation, *Science.*, **335**, 557-561.
31 Cai W, Lengaigne M, Borlace S, Collins M, Cowan T, McPhaden MJ, Timmermann A, Power S, Brown J, Menkes C, Ngari A, Vincent EM, Widlansky MJ, 2012, More extreme swings of the South Pacific convergence zone due to greenhouse warming, *Nature*, **488**, 365.
32 Cai WJ, Chen LQ, Chen BS, Gao ZY, Lee SH, Chen JF, Pierrot D, Sullivan K, Wang YC, Hu XP, Huang WJ, Zhang YH, Xu SQ, Murata A, Grebmeier JM, Jones EP, Zhang HS, 2010, Decrease in the CO_2 uptake capacity in an ice-free Arctic Ocean basin, *Science.*, **329**, 556-559.
33 Canadell JG, Le Quere C, Raupach MR, Field CB, Buitenhuis ET, Ciais P, Conway TJ, Gillett NP, Houghton RA, Marland G, 2007, Contributions to accelerating atmospheric CO_2 growth from economic activity, carbon intensity, and efficiency of natural sinks, *Proc. Nat. Acad. Sci. USA.*, **104**, 18866-18870.
34 Cantin NE, Cohen AL, Karnauskas KB, Tarrant AM, McCorkle DC, 2010, Ocean warming slows coral growth in the central Red Sea, *Science.*, **329**, 322-325.
35 Carlos L, Martire DO, Gonzalez MC, Gomis J, Bernabeu A, Amat AM, Arques A, 2012, Photochemical fate of a mixture of emerging pollutants in the presence of humic substances, *Water Res.*, **46**, 4732-4740.
36 Chen Y, Li H, Wang ZP, Li HJ, Tao T, Zuo YG, 2012, Photodegradation of selected beta-blockers in aqueous fulvic acid solutions: Kinetics, mechanism, and product analysis, *Water Res.*, **46**, 2965-2972.
37 Choat B, Jansen S, Brodribb TJ, Cochard H, Delzon S, Bhaskar R, Bucci SJ, Feild TS, Gleason SM, Hacke UG, Jacobsen AL, Lens F, Maherali H, Martinez-Vilalta J, Mayr S, Mencuccini M, Mitchell PJ, Nardini A, Pittermann J, Pratt RB, Sperry JS, Westoby M, Wright IJ, Zanne AE, 2012, Global convergence in the vulnerability of forests to drought, *Nature*, **491**, 752-755.
38 Clark GF, Stark JS, Johnston EL, Runcie JW, Goldsworthy PM, Raymond B, Riddle MJ, 2013, Light-driven tipping points in polar ecosystems, *Glob. Change Biol.*, **19**, 3749-3761.
39 Codispoti LA, 2010, Interesting times for marine N_2O, *Science.*, **327**, 1339-1340.
40 Corbitt ES, Jacob DJ, Holmes CD, Streets DG, Sunderland EM, 2011, Global source-receptor relationships for mercury deposition under present-day and 2050 emissions scenarios, *Environ. Sci. Technol.*, **45**, 10477-10484.
41 Cory RM, Kaplan LA, 2012, Biological lability of streamwater fluorescent dissolved organic matter, *Limnol. Oceanogr.*, **57**, 1347-1360.
42 Cory RM, Crump BC, Dobkowski JA, Kling GW, 2013, Surface exposure to sunlight stimulates CO_2 release from permafrost soil carbon in the Arctic, *Proc. Nat. Acad. Sci. USA.*, **110**, 3429-3434.
43 Coumou D, Rahmstorf S, 2012, A decade of weather extremes, *Nature Clim. Change*, **2**, 491-496.
44 Creamean JM, Suski KJ, Rosenfeld D, Cazorla A, DeMott PJ, Sullivan RC, White AB, Ralph FM, Minnis P, Comstock JM, Tomlinson JM, Prather KA, 2013, Dust and biological aerosols from the Sahara and Asia influence precipitation in the Western U.S., *Science.*, **339**, 1572-1578.
45 Davidson EA, de Araujo AC, Artaxo P, Balch JK, Brown IF, Bustamante MMC, Coe MT, DeFries RS, Keller M, Longo M, Munger JW, Schroeder W, Soares-Filho BS, Souza CM, Wofsy SC, 2012, The Amazon basin in transition (vol 481, pg 321, 2012), *Nature*, **483**, 232-232.
46 DeConto RM, Galeotti S, Pagani M, Tracy D, Schaefer K, Zhang T, Pollard D, Beerling DJ, 2012, Past extreme warming events linked to massive carbon release from thawing permafrost (vol 484, pg 87, 2012), *Nature*, **490**, 292-292.
47 Derendorp L, Quist JB, Holzinger R, Rockmann T, 2011, Emissions of H_2 and CO from leaf litter of *Sequoiadendron giganteum*, and their dependence on UV radiation and temperature, *Atmos. Environ.*, **45**, 7520-7524.
48 Dittmar T, de Rezende CE, Manecki M, Niggemann J, Ovalle ARC, Stubbins A, Bernardes MC, 2012, Continuous flux of dissolved black carbon from a vanished tropical forest biome, *Nature Geosci.*, **5**, 618-622.
49 Dlugokencky EJ, Nisbet EG, Fisher R, Lowry D, 2011, Global atmospheric methane: Budget, changes and dangers, *Philos. Trans. Roy. Soc. Lond. B.*, **369**, 2058-2072.
50 Falkowski P, 2012, Ocean Science: The power of plankton, *Nature*, **483**, S17-S20.
51 Feldstein SB, 2011, Subtropical rainfall and the Antarctic ozone hole, *Science.*, **332**, 925-926.

52 Fellman JB, Hood E, Spencer RGM, 2010, Fluorescence spectroscopy opens new windows into dissolved organic matter dynamics in freshwater ecosystems: A review, *Limnol. Oceanogr.*, **55**, 2452-2462.

53 Feng X, Hills KM, Simpson AJ, Whalen JK, Simpson MJ, 2011, The role of biodegradation and photo-oxidation in the transformation of terrigenous organic matter, *Org. Geochem.*, **42**, 262-274.

54 Fernanda Adame M, Wright SF, Grinham A, Lobb K, Reymond CE, Lovelock CE, 2012, Terrestrial-marine connectivity: Patterns of terrestrial soil carbon deposition in coastal sediments determined by analysis of glomalin related soil protein, *Limnol. Oceanogr.*, **57**, 1492-1502.

55 Fichot CG, Miller WL, 2010, An approach to quantify depth-resolved marine photochemical fluxes using remote sensing: Application to carbon monoxide (CO) photoproduction, *Rem. Sens. Environ.*, **114**, 1363-1377.

56 Fichot CG, Benner R, 2012, The spectral slope coefficient of chromophoric dissolved organic matter (S275-295) as a tracer of terrigenous dissolved organic carbon in river-influenced ocean margins, *Limnol. Oceanogr.*, **57**, 1453-1466.

57 Fichot CG, Kaiser K, Hooker SB, Amon RMW, Babin M, Belanger S, Walker SA, Benner R, 2013, Pan-Arctic distributions of continental runoff in the Arctic Ocean, *Sci. Rep.*, **3**.

58 Fisher MB, Love DC, Schuech R, Nelson KL, 2011, Simulated sunlight action spectra for inactivation of MS2 and PRD1 bacteriophages in clear water, *Environ. Sci. Technol.*, **45**, 9249-9255.

59 Foereid B, Bellarby J, Meier-Augenstein W, Kemp H, 2010, Does light exposure make plant litter more degradable?, *Plant and Soil*, **333**, 275-285.

60 Fountoulakis I, Bais AF, Tourpali K, Fragkos K, Misios S, 2014, Projected changes in solar UV radiation in the Arctic and sub-Arctic Oceans: Effects from changes in reflectivity, ice transmittance, clouds, and ozone *J. Geophys. Res. Atmos.*, **119**, 8073-8090.

61 Francis JA, Vavrus SJ, 2012, Evidence linking Arctic amplification to extreme weather in mid-latitudes, *Geophys. Res. Lett.*, **39**.

62 Francis JA, 2013, The where and when of wetter and drier: disappearing Arctic sea ice plays a role, *Environ. Res. Lett.*, **8**.

63 Frey K, Perovich D, Light B, 2011, The spatial distribution of solar radiation under a melting Arctic sea ice cover, *Geophys. Res. Lett.*, **38**, L22501.

64 Frouz J, Cajthaml T, Mudrak O, 2011, The effect of lignin photodegradation on decomposability of *Calamagrostis epigeios* grass litter, *Biodegradation*, **22**, 1247-1254.

65 Fujimori T, Yoneyama Y, Taniai G, Kurihara M, Tamegai H, Hashimoto S, 2012, Methyl halide production by cultures of marine proteobacteria *Erythrobacter* and *Pseudomonas* and isolated bacteria from brackish water, *Limnol. Oceanogr.*, **57**, 154-162.

66 Gangsto R, Joos F, Gehlen M, 2011, Sensitivity of pelagic calcification to ocean acidification, *Biogeosci.*, **8**, 433-458.

67 Gillett NP, Thompson DWJ, 2003, Simulation of recent Southern Hemisphere climate change, *Science.*, **302**, 273-275.

68 Gonsior M, Peake BM, Cooper WT, Podgorski DC, D'Andrilli J, Dittmar T, Cooper WJ, 2011, Characterization of dissolved organic matter across the Subtropical Convergence off the South Island, New Zealand, *Mar. Chem.*, **123**, 99-110.

69 Gonsior M, Schmitt-Kopplin P, Bastviken D, 2013, Depth-dependent molecular composition and photo-reactivity of dissolved organic matter in a boreal lake under winter and summer conditions, *Biogeosci.*, **10**, 6945-6956.

70 Gottfried M, Pauli H, Futschik A, Akhalkatsi M, Barancok P, Benito Alonso JL, Coldea G, Dick J, Erschbamer B, Fernandez Calzado MR, Kazakis G, Krajci J, Larsson P, Mallaun M, Michelsen O, Moiseev D, Moiseev P, Molau U, Merzouki A, Nagy L, Nakhutsrishvili G, Pedersen B, Pelino G, Puscas M, Rossi G, Stanisci A, Theurillat J-P, Tomaselli M, Villar L, Vittoz P, Vogiatzakis I, Grabherr G, 2012, Continent-wide response of mountain vegetation to climate change, *Nature Clim. Change*, **2**, 111-115.

71 Gouin T, Armitage JM, Cousins IT, Muir DCG, Ng CA, Reid L, Tao S, 2013, Influence of global climate change on chemical fate and bioaccumulation: The role of multimedia models, *Environ. Toxicol. Chem.*, **32**, 20-31.

72 Grannas AM, Bogdal C, Hageman KJ, Halsall C, Harner T, Hung H, Kallenborn R, Klan P, Klanova J, Macdonald RW, Meyer T, Wania F, 2013, The role of the global cryosphere in the fate of organic contaminants, *Atmos. Chem. Phys.*, **13**, 3271-3305.

73 Granskog MA, 2012, Changes in spectral slopes of colored dissolved organic matter absorption with mixing and removal in a terrestrially dominated marine system (Hudson Bay, Canada), *Mar. Chem.*, **134**, 10-17.

74 Granskog MA, Stedmon CA, Dodd PA, Amon RMW, Pavlov AK, de Steur L, Hansen E, 2012, Characteristics of colored dissolved organic matter (CDOM) in the Arctic outflow in the Fram Strait: Assessing the changes and fate of terrigenous CDOM in the Arctic Ocean, *J. Geophys. Res. Oceans*, **117**.

75 Gruber N, 2011, Warming up, turning sour, losing breath: ocean biogeochemistry under global change, *Philos. Trans. Roy. Soc. Lond. A.*, **369**, 1980-1996.

76 Guerard JJ, Chin YP, 2012, Photodegradation of ormetoprim in aquaculture and stream-derived dissolved organic matter, *J. Agric. Food. Chem.*, **60**, 9801-9806.

77 Haaland S, Hongve D, Laudon H, Riise G, Vogt RD, 2010, Quantifying the drivers of the increasing colored organic matter in boreal surface waters, *Environ. Sci. Technol.*, **44**, 2975-2980.

78 Häder D-P, Helbling EW, Williamson CE, Worrest RC, 2011, Effects on aquatic ecosystems and interactions with climate change, *Photochem. Photobiol. Sci.*, **8**, 242-260.

79 Haekkinen S, Rhines PB, Worthen DL, 2011, Atmospheric blocking and Atlantic multidecadal ocean variability, *Science.*, **334**, 655-659.

80 Halofsky JE, Hemstrom MA, Conklin DR, Halofsky JS, Kerns BK, Bachelet D, 2013, Assessing potential climate change effects on vegetation using a linked model approach, *Ecol. Model.*, **266**, 131-143.

81 Hardacre CJ, Heal MR, 2013, Characterization of methyl bromide and methyl chloride fluxes at temperate freshwater wetlands, *J. Geophys. Res. Atmos.*, **118**, 977-991.

82 Hatala JA, Detto M, Sonnentag O, Deverel SJ, Verfaillie J, Baldocchi DD, 2012, Greenhouse gas (CO_2, CH_4, H_2O) fluxes from drained and flooded agricultural peatlands in the Sacramento-San Joaquin Delta, *Agric. Ecosyst. Environ.*, **150**, 1-18.

83 Hauri C, Gruber N, McDonnell AMP, Vogt M, 2013, The intensity, duration, and severity of low aragonite saturation state events on the California continental shelf, *Geophys. Res. Lett.*, **40**, 3424-3428.

84 Heller MI, Croot PL, 2011, Superoxide decay as a probe for speciation changes during dust dissolution in Tropical Atlantic surface waters near Cape Verde, *Mar. Chem.*, **126**, 37-55.

85 Helms JR, Stubbins A, Perdue EM, Green NW, Chen H, Mopper K, 2013, Photochemical bleaching of oceanic dissolved organic matter and its effect on absorption spectral slope and fluorescence, *Mar. Chem.*, **155**, 81-91.

86 Henry HAL, Brizgys K, Field CB, 2008, Litter decomposition in a california annual grassland: Interactions between photodegradation and litter layer thickness, *Ecosystems*, **11**, 545-554.

87 Hickler T, Vohland K, Feehan J, Miller PA, Smith B, Costa L, Giesecke T, Fronzek S, Carter TR, Cramer W, Kuehn I, Sykes MT, 2012, Projecting the future distribution of European potential natural vegetation zones with a generalized, tree species-based dynamic vegetation model, *Glob. Ecol. Biogeog.*, **21**, 50-63.

88 Hofmann M, Schellnhuber H-J, 2009, Oceanic acidification affects marine carbon pump and triggers extended marine oxygen holes, *Proc. Nat. Acad. Sci. USA.*, **106**, 3017-3022.

89 Hofmann M, Schellnhuber HJ, 2010, Ocean acidification: a millennial challenge, *Energ. Environ. Sci.*, **3**, 1883-1896.

90 Holmes CD, Prather MJ, Sovde OA, Myhre G, 2013, Future methane, hydroxyl, and their uncertainties: key climate and emission parameters for future predictions, *Atmos. Chem. Phys.*, **13**, 285-302.

91 Hooper MJ, Ankley GT, Cristol DA, Maryoung LA, Noyes PD, Pinkerton KE, 2013, Interactions between chemical and climate stressors: A role for mechanistic toxicology in assessing climate change risks, *Environ. Toxicol. Chem.*, **32**, 32-48.

92 Hossaini R, Chipperfield MP, Dhomse S, Ordonez C, Saiz-Lopez A, Abraham NL, Archibald A, Braesicke P, Telford P, Warwick N, Yang X, Pyle J, 2012, Modelling future changes to the stratospheric source gas injection of biogenic bromocarbons, *Geophys. Res. Lett.*, **39**.

93 Hossaini R, Chipperfield MP, Feng W, Breider TJ, Atlas E, Montzka SA, Miller BR, Moore F, Elkins J, 2012, The contribution of natural and anthropogenic very short-lived species to stratospheric bromine, *Atmos. Chem. Phys.*, **12**, 371-380.

94 Hossaini R, Mantle H, Chipperfield MP, Montzka SA, Hamer P, Ziska E, Quack B, Krueger K, Tegtmeier S, Atlas E, Sala S, Engel A, Boenisch H, Keber T, Oram D, Mills G, Ordonez C, Saiz-Lopez A, Warwick N, Liang Q, Feng W, Moore E, Miller BR, Marecal V, Richards NAD, Dorf M, Pfeilsticker K, 2013, Evaluating global emission inventories of biogenic bromocarbons, *Atmos. Chem. Phys.*, **13**, 11819-11838.

95 Hou WC, Stuart B, Howes R, Zepp RG, 2013, Sunlight-driven reduction of silver ions by natural organic matter: formation and transformation of silver nanoparticles, *Environ. Sci. Technol.*, **47**, 7713-7721.

96 Houghton RA, 2007, Balancing the global carbon budget, *Annu. Rev. Earth Planet. Sci.*, **35**, 313-347.

97 Houweling S, Krol M, Bergamaschi P, Frankenberg C, Dlugokencky EJ, Morino I, Notholt J, Sherlock V, Wunch D, Beck V, Gerbig C, Chen H, Kort EA, Röckmann T, Aben I, 2013, A multi-year methane inversion using SCIAMACHY, accounting for systematic errors using TCCON measurements, *Atmos. Chem. Phys. Discuss.*, **13**, 28117-28171.

98 Hsu S-C, Huh C-A, Lin C-Y, Chen W-N, Mahowald NM, Liu S-C, Chou CCK, Liang M-C, Tsai C-J, Lin F-J, Chen J-P, Huang Y-T, 2012, Dust transport from non-East Asian sources to the North Pacific, *Geophys. Res. Lett.*, **39**.

99 Hu A, Meehl GA, Han W, Lu J, Strand WG, 2013, Energy balance in a warm world without the ocean conveyor belt and sea ice, *Geophys. Res. Lett.*, **40**, 6242-6246.

100 IPCC, 2013, Climate Change 2013 - The Physical Science Basis. Contribution of Working Group I to the fifth Assessment Report of the Interbovernamental Panel on Climate Change, Report No.

101 Ito T, Woloszyn M, Mazloff M, 2010, Anthropogenic carbon dioxide transport in the Southern Ocean driven by Ekman flow, *Nature*, **463**, 80-U85.

102 Jaffe R, Ding Y, Niggemann J, Vahatalo AV, Stubbins A, Spencer RGM, Campbell J, Dittmar T, 2013, Global charcoal mobilization from soils via dissolution and riverine transport to the oceans, *Science.*, **340**, 345-347.

103 Jin X, Gruber N, 2003, Offsetting the radiative benefit of ocean iron fertilization by enhancing N_2O emissions, *Geophys. Res. Lett.*, **30**.

104 Johnson KS, Riser SC, Karl DM, 2010, Nitrate supply from deep to near-surface waters of the North Pacific subtropical gyre, *Nature*, **465**, 1062-1065.

105 Jorgensen L, Stedmon CA, Kragh T, Markager S, Middelboe M, Sondergaard M, 2011, Global trends in the fluorescence characteristics and distribution of marine dissolved organic matter, *Mar. Chem.*, **126**, 139-148.

106 Joughin I, Alley RB, Holland DM, 2012, Ice-sheet response to oceanic forcing, *Science.*, **338**, 1172-1176.

107 Kanakidou M, Duce RA, Prospero JM, Baker AR, Benitez-Nelson C, Dentener FJ, Hunter KA, Liss PS, Mahowald N, Okin GS, Sarin M, Tsigaridis K, Uematsu M, Zamora LM, Zhu T, 2012, Atmospheric fluxes of organic N and P to the global ocean, *Glob. Biogeochem. Cycles*, **26**.

108 Kang SM, Polvani LM, Fyfe JC, Sigmond M, 2011, Impact of polar ozone depletion on subtropical precipitation, *Science.*, **332**, 951-954.

109 Kim K, Choi W, Hoffmann MR, Yoon H-I, Park B-K, 2010, Photoreductive dissolution of iron oxides trapped in ice and its environmental implications, *Environ. Sci. Technol.*, **44**, 4142-4148.

110 King AL, Barbeau KA, 2011, Dissolved iron and macronutrient distributions in the southern California Current System, *J. Geophys. Res. Oceans*, **116**.

111 King AL, Buck KN, Barbeau KA, 2012, Quasi-Lagrangian drifter studies of iron speciation and cycling off Point Conception, California, *Mar. Chem.*, **128**, 1-12.

112 King DA, Bachelet DM, Symstad AJ, 2013, Climate change and fire effects on a prairie-woodland ecotone: projecting species range shifts with a dynamic global vegetation model, *Ecol. Evolut.*, **3**, 5076-5097.

113 King JY, Brandt LA, Adair EC, 2012, Shedding light on plant litter decomposition: advances, implications and new directions in understanding the role of photodegradation, *Biogeochemistry*, **111**, 57-81.

114 Kingston C, Zepp R, Andrady A, Boverhof D, Fehir R, Hawkins D, Roberts J, Sayre P, Shelton B, Sultan Y, Vejins V, Wohlleben W, 2014, Release characteristics of selected carbon nanotube polymer composites, *Carbon*, **68**, 33-57.

115 Kitidis V, Upstill-Goddard RC, Anderson LG, 2010, Methane and nitrous oxide in surface water along the North-West Passage, Arctic Ocean, *Mar. Chem.*, **121**, 80-86.

116 Knorr W, 2009, Is the airborne fraction of anthropogenic CO_2 emissions increasing?, *Geophys. Res. Lett.*, **36**.

117 Kopparla P, Fischer EM, Hannay C, Knutti R, 2013, Improved simulation of extreme precipitation in a high-resolution atmosphere model, *Geophys. Res. Lett.*, **40**, 5803-5808.

118 Kort EA, Wofsy SC, Daube BC, Diao M, Elkins JW, Gao RS, Hintsa EJ, Hurst DF, Jimenez R, Moore FL, Spackman JR, Zondlo MA, 2012, Atmospheric observations of Arctic Ocean methane emissions up to 82^o north, *Nature Geosci.*, **5**, 318-321.

119 Krabbenhoft DP, Sunderland EM, 2013, Global change and mercury, *Science.*, **341**, 1457-1458.

120 Kulmala M, Nieminen T, Chellapermal R, Makkonen R, Bäck J, Veli-Matti K, 2013, Climate feedbacks linking the increasing atmospheric CO_2 concentration, BVOC emissions, aerosols and clouds in forest ecosystems, *Tree Physiol.*, **5**, 489-508.

121 Kurihara MK, Kimura M, Iwamoto Y, Narita Y, Ooki A, Eum YJ, Tsuda A, Suzuki K, Tani Y, Yokouchi Y, Uematsu M, Hashimoto S, 2010, Distributions of short-lived iodocarbons and biogenic trace gases in the open ocean and atmosphere in the western North Pacific, *Mar. Chem.*, **118**, 156-170.

122 Lambert F, Kug JS, Park RJ, Mahowald N, Winckler G, Abe-Ouchi A, O'Ishi R, Takemura T, Lee JH, 2013, The role of mineral-dust aerosols in polar temperature amplification, *Nature Clim. Change*, **3**, 487-491.

123 Laufkoetter C, Vogt M, Gruber N, 2013, Long-term trends in ocean plankton production and particle export between 1960-2006, *Biogeosci.*, **10**, 7373-7393.

124 Le Quere C, Takahashi T, Buitenhuis ET, Roedenbeck C, Sutherland SC, 2010, Impact of climate change and variability on the global oceanic sink of CO_2, *Glob. Biogeochem. Cycles*, **24**.

125 Lee H, Rahn T, Throop HL, 2012, An accounting of C-based trace gas release during abiotic plant litter degradation, *Glob. Change Biol.*, **18**, 1185-1195.

126 Lee S, Feldstein SB, 2013, Detecting ozone- and greenhouse gas-driven wind trends with observational data, *Science.*, **339**, 563-567.

127 Lelong A, Bucciarelli E, Hegaret H, Soudant P, 2013, Iron and copper limitations differently affect growth rates and photosynthetic and physiological parameters of the marine diatom *Pseudonitzschia delicatissima*, *Limnol. Oceanogr.*, **58**, 613-623.

128 Lenton A, Codron F, Bopp L, Metzl N, Cadule P, Tagliabue A, Le Sommer J, 2009, Stratospheric ozone depletion reduces ocean carbon uptake and enhances ocean acidification, *Geophys. Res. Lett.*, **36**.

129 Lenton TM, 2012, Arctic climate tipping points, *Ambio*, **41**, 10-22.

130 Letscher RT, Hansell DA, Kadko D, 2011, Rapid removal of terrigenous dissolved organic carbon over the Eurasian shelves of the Arctic Ocean, *Mar. Chem.*, **123**, 78-87.

131 Liang H, Chen ZM, Huang D, Zhao Y, Li ZY, 2013, Impacts of aerosols on the chemistry of atmospheric trace gases: a case study of peroxides and HO_2 radicals, *Atmos. Chem. Phys. Discuss.*, **13**, 16549-16595.

132 Lin CY, Manley SL, 2012, Bromoform production from seawater treated with bromoperoxidase, *Limnol. Oceanogr.*, **57**, 1857-1866.

133 Liu J, Curry JA, Wang H, Song M, Horton RM, 2012, Impact of declining Arctic sea ice on winter snowfall (vol 109, pg 4074, 2012), *Proc. Nat. Acad. Sci. USA.*, **109**, 6781-6783.

134 Lloret F, Escudero A, Maria Iriondo J, Martinez-Vilalta J, Valladares F, 2012, Extreme climatic events and vegetation: the role of stabilizing processes, *Glob. Change Biol.*, **18**, 797-805.

135 Ma S, Baldocchi DD, Hatala JA, Detto M, Curiel Yuste J, 2012, Are rain-induced ecosystem respiration pulses enhanced by legacies of antecedent photodegradation in semi-arid environments?, *Agric. Forest Meteorol.*, **154**, 203-213.

136 Mack MC, Bret-Harte MS, Hollingsworth TN, Jandt RR, Schuur EAG, Shaver GR, Verbyla DL, 2011, Carbon loss from an unprecedented Arctic tundra wildfire, *Nature*, **475**, 489-492.

137 Mahowald NM, 2012, Atmospheric Biogeochemistry, in *Encyclopedia of Sustainability Science and Technology*, Springer.

138 Manney GL, Santee ML, Rex M, Livesey NJ, Pitts MC, Veefkind P, Nash ER, Wohltmann I, Lehmann R, Froidevaux L, Poole LR, Schoeberl MR, Haffner DP, Davies J, Dorokhov V, Gernandt H, Johnson B, Kivi R, Kyro E, Larsen N, Levelt PF, Makshtas A, McElroy CT, Nakajima H, Parrondo MC, Tarasick DW, von der Gathen P, Walker KA, Zinoviev NS, 2011, Unprecedented Arctic ozone loss in 2011, *Nature*, **478**, 469-U65.

139 Mao J, Fan S, Jacob DJ, Travis KR, 2013, Radical loss in the atmosphere from Cu-Fe redox coupling in aerosols, *Atmos. Chem. Phys.*, **13**, 509-519.

140 Marshall GJ, 2003, Trends in the southern annular mode from observations and reanalyses, *J. Climate*, **16**, 4134-4143.

141 Marshall GJ, Di Battista S, Naik SS, Thamban M, 2011, Analysis of a regional change in the sign of the SAM-temperature relationship in Antarctica, *Clim. Dyn.*, **36**, 277-287.

142 Masiello CA, Louchouarn P, 2013, Fire in the ocean, *Science.*, **340**, 287-288.

143 Mayer LM, Thornton KR, Schick LL, Jastrow JD, Harden JW, 2012, Photodissolution of soil organic matter, *Geoderma*, **170**, 314-321.

144 McGuigan KG, Conroy RM, Mosler HJ, du Preez M, Ubomba-Jaswa E, Fernandez-Ibanez P, 2012, Solar water disinfection (SODIS): A review from bench-top to roof-top, *J. Haz. Matter.*, **235**, 29-46.

145 McKenzie RL, Aucamp PJ, Bais AF, Björn LO, Ilyas M, Madronich S, 2011, Ozone depletion and climate change: Impacts on UV radiation, *Photochem. Photobiol. Sci.*, **10**, 182-98.

146 McKinley GA, Fay AR, Takahashi T, Metzl N, 2011, Convergence of atmospheric and North Atlantic carbon dioxide trends on multidecadal timescales, *Nature Geosci.*, **4**, 606-610.

147 Min S-K, Zhang X, Zwiers FW, Hegerl GC, 2011, Human contribution to more-intense precipitation extremes, *Nature*, **470**, 376-379.
148 Ming Y, Ramaswamy V, Chen G, 2011, A model investigation of aerosol-induced changes in boreal winter extratropical circulation, *J. Climate*, **24**, 6077-6091.
149 Montzka SA, Dlugokencky EJ, Butler JH, 2011, Non-CO_2 greenhouse gases and climate change, *Nature*, **476**, 43-50.
150 Moore CM, Mills MM, Arrigo KR, Berman-Frank I, Bopp L, Boyd PW, Galbraith ED, Geider RJ, Guieu C, Jaccard SL, Jickells TD, La Roche J, Lenton TM, Mahowald NM, Maranon E, Marinov I, Moore JK, Nakatsuka T, Oschlies A, Saito MA, Thingstad TF, Tsuda A, Ulloa O, 2013, Processes and patterns of oceanic nutrient limitation, *Nature Geosci.*, **6**, 701-710.
151 Morel FMM, Kustka AB, Shaked Y, 2008, The role of unchelated Fe in the iron nutrition of phytoplankton, *Limnol. Oceanogr.*, **53**, 400-404.
152 Moreno CM, 2012, Hydrogen peroxide production driven by UV-B in planktonic microorganisms: a photocatalytic factor in sea warming and ice melting in regions with ozone depletion?, *Biogeochemistry*, **107**, 1-8.
153 Morin S, Erbland J, Savarino J, Domine F, Bock J, Friess U, Jacobi HW, Sihler H, Martins JMF, 2012, An isotopic view on the connection between photolytic emissions of NO_x from the Arctic snowpack and its oxidation by reactive halogens, *J. Geophys. Res. Atmos.*, **117**.
154 Morsky SK, Haapala JK, Rinnan R, Saarnio S, Suokanerva H, Latola K, Kyro E, Silvola J, Holopainen T, Martikainen PJ, 2012, Minor long-term effects of ultraviolet-B radiation on methane dynamics of a subarctic fen in Northern Finland, *Biogeochemistry*, **108**, 233-243.
155 Mundy CJ, Gosselin M, Starr M, Michel C, 2010, Riverine export and the effects of circulation on dissolved organic carbon in the Hudson Bay system, Canada, *Limnol. Oceanogr.*, **55**, 315-323.
156 Naik V, Voulgarakis A, Fiore AM, Horowitz LW, Lamarque JF, Lin M, Prather MJ, Young PJ, Bergmann D, Cameron-Smith PJ, Cionni I, Collins WJ, Dalsoren SB, Doherty R, Eyring V, Faluvegi G, Folberth GA, Josse B, Lee YH, MacKenzie IA, Nagashima T, van Noije TPC, Plummer DA, Righi M, Rumbold ST, Skeie R, Shindell DT, Stevenson DS, Strode S, Sudo K, Szopa S, Zeng G, 2013, Preindustrial to present-day changes in tropospheric hydroxyl radical and methane lifetime from the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP), *Atmos. Chem. Phys.*, **13**, 5277-5298.
157 Nelson NB, Siegel DA, Carlson CA, Swan CM, 2010, Tracing global biogeochemical cycles and meridional overturning circulation using chromophoric dissolved organic matter, *Geophys. Res. Lett.*, **37**.
158 Nelson NB, Siegel DA, 2013, The global distribution and dynamics of chromophoric dissolved organic matter, in *Annual Review of Marine Science,* **Vol. 5** eds.: Carlson CA, Giovannoni SJ, Annual Reviews, Palo Alto, pp. 447-476.
159 Olefeldt D, Devito KJ, Turetsky MR, 2013, Sources and fate of terrestrial dissolved organic carbon in lakes of a Boreal Plains region recently affected by wildfire, *Biogeosci.*, **10**, 6247-6265.
160 Oswald R, Behrendt T, Ermel M, Wu D, Su H, Cheng Y, Breuninger C, Moravek A, Mougin E, Delon C, Loubet B, Pommerening-Roeser A, Soergel M, Poeschl U, Hoffmann T, Andreae MO, Meixner FX, Trebs I, 2013, HONO emissions from soil bacteria as a major source of atmospheric reactive nitrogen, *Science.*, **341**, 1233-1235.
161 Paeth H, Pollinger F, 2010, Enhanced evidence in climate models for changes in extratropical atmospheric circulation, *Tellus Ser. A-Dynam. Meteorol. Oceanog.*, **62**, 647-660.
162 Pall P, Aina T, Stone DA, Stott PA, Nozawa T, Hilberts AGJ, Lohmann D, Allen MR, 2011, Anthropogenic greenhouse gas contribution to flood risk in England and Wales in autumn 2000, *Nature*, **470**, 380-384.
163 Pandolfi JM, Connolly SR, Marshall DJ, Cohen AL, 2011, Projecting coral reef futures under global warming and ocean acidification, *Science.*, **333**, 418-422.
164 Pautler BG, Woods GC, Dubnick A, Simpson AJ, Sharp MJ, Fitzsimons SJ, Simpson MJ, 2012, Molecular characterization of dissolved organic matter in glacial ice: Coupling natural abundance H-1 NMR and fluorescence spectroscopy, *Environ. Sci. Technol.*, **46**, 3753-3761.
165 Pearson RG, Phillips SJ, Loranty MM, Beck PSA, Damoulas T, Knight SJ, Goetz SJ, 2013, Shifts in Arctic vegetation and associated feedbacks under climate change, *Nature Clim. Change*, **3**, 673-677.
166 Pilegaard K, 2013, Processes regulating nitric oxide emissions from soils, *Philos. Trans. Roy. Soc. Lond. B.*, **368**.
167 Pithan F, Mauritsen T, 2014, Arctic amplification dominated by temperature feedbacks in contemporary climate models, *Nature Geosci.*, **7**, 181-184.

168 Pokrovsky OS, Shirokova LS, Kirpotin SN, Kulizhsky SP, Vorobiev SN, 2013a, Impact of western Siberia heat wave 2012 on greenhouse gases and trace metal concentration in thaw lakes of discontinuous permafrost zone, *Biogeosci.*, **10**, 5349-5365.
169 Polley HW, Jin VL, Fay PA, 2012, CO2-caused change in plant species composition rivals the shift in vegetation between mid-grass and tallgrass prairies, *Glob. Change Biol.*, **18**, 700-710.
170 Prather MJ, Hsu J, 2010, Coupling of nitrous oxide and methane by global atmospheric chemistry, *Science.*, **330**, 952-954.
171 Qureshi A, O'Driscoll NJ, MacLeod M, Neuhold Y-M, Hungerbuehler K, 2010, Photoreactions of mercury in surface ocean water: gross reaction kinetics and possible pathways, *Environ. Sci. Technol.*, **44**, 644-649.
172 Randall K, Scarratt M, Levasseur M, Michaud S, Xie H, Gosselin M, 2012, First measurements of nitrous oxide in Arctic sea ice, *J. Geophys. Res. Oceans*, **117**.
173 Reader HE, Miller WL, 2012, Variability of carbon monoxide and carbon dioxide apparent quantum yield spectra in three coastal estuaries of the South Atlantic Bight, *Biogeosciences Discuss.*, **9**, 6927-6985.
174 Regnier P, Friedlingstein P, Ciais P, Mackenzie FT, Gruber N, Janssens IA, Laruelle GG, Lauerwald R, Luyssaert S, Andersson AJ, Arndt S, Arnosti C, Borges AV, Dale AW, Gallego-Sala A, Godderis Y, Goossens N, Hartmann J, Heinze C, Ilyina T, Joos F, LaRowe DE, Leifeld J, Meysman FJR, Munhoven G, Raymond PA, Spahni R, Suntharalingam P, Thullner M, 2013, Anthropogenic perturbation of the carbon fluxes from land to ocean, *Nature Geosci.*, **6**, 597-607.
175 Ribas-Ribas M, Gomez-Parra A, Forja JM, 2011, Air-sea CO2 fluxes in the north-eastern shelf of the Gulf of Cadiz (southwest Iberian Peninsula), *Mar. Chem.*, **123**, 56-66.
176 Richards NK, Finlayson-Pitts BJ, 2012, Production of gas phase NO_2 and halogens from the photochemical oxidation of aqueous mixtures of sea salt and nitrate ions at room temperature, *Environ. Sci. Technol.*, **46**, 10447-10454.
177 Robinson SA, Erickson DJ, 2014, Not just about sunburn - the ozone hole's profound effect on climate has significant implications for Southern Hemisphere ecosystems, *Glob. Change Biol.*, **in press**.
178 Romera-Castillo C, Nieto-Cid M, Castro CG, Marrase C, Largier J, Barton ED, Alvarez-Salgado XA, 2011, Fluorescence: Absorption coefficient ratio - Tracing photochemical and microbial degradation processes affecting coloured dissolved organic matter in a coastal system, *Mar. Chem.*, **125**, 26-38.
179 Rontani JF, Zabeti N, Wakeham SG, 2011, Degradation of particulate organic matter in the equatorial Pacific Ocean: Biotic or abiotic?, *Limnol. Oceanogr.*, **56**, 333-349.
180 Rose KA, Sikes EL, Guilderson TP, Shane P, Hill TM, Zahn R, Spero HJ, 2010, Upper-ocean-to-atmosphere radiocarbon offsets imply fast deglacial carbon dioxide release, *Nature*, **466**, 1093-1097.
181 Ross AN, Wooster MJ, Boesch H, Parker R, 2013, First satellite measurements of carbon dioxide and methane emission ratios in wildfire plumes, *Geophys. Res. Lett.*, **40**, 4098-4102.
182 Rothenber D, Mahowald NM, Lindsay K, Scott D, Moore K, Thornton P, 2012, Volcano impacts on climate and biogeochemistry in a coupled carbon-climate model, *Earth System Dynamics*, **3**, 121-136.
183 Rowland GA, Bausch AR, Grannas AM, 2011, Photochemical processing of aldrin and dieldrin in frozen aqueous solutions under arctic field conditions, *Environ. Pollut.*, **159**, 1076-1084.
184 Rutledge S, Campbell D, Baldocchi D, Schipper L, 2010, Photodegradation leads to increased carbon dioxide losses from terrestrial organic matter, *Glob. Change Biol.*, **16**, 3065-3074.
185 Sabine CL, Tanhua T, 2010, Estimation of anthropogenic CO_2 inventories in the ocean, in *Annual Review of Marine Science,* **Vol. 2**, pp. 175-198.
186 Saiz-Lopez A, Lamarque JF, Kinnison DE, Tilmes S, Ordonez C, Orlando JJ, Conley AJ, Plane JMC, Mahajan AS, Santos GS, Atlas EL, Blake DR, Sander SP, Schauffler S, Thompson AM, Brasseur G, 2012, Estimating the climate significance of halogen-driven ozone loss in the tropical marine troposphere, *Atmos. Chem. Phys.*, **12**, 3939-3949.
187 Saiz-Lopez A, von Glasow R, 2012, Reactive halogen chemistry in the troposphere, *Chem. Soc. Rev.*, **41**, 6448-6472.
188 Santoro AE, Buchwald C, McIlvin MR, Casciotti KL, 2011, Isotopic signature of N_2O produced by marine ammonia-oxidizing Archaea, *Science.*, **333**, 1282-1285.
189 Schlosser C, De La Rocha CL, Streu P, Croot PL, 2012, Solubility of iron in the southern ocean, *Limnol. Oceanogr.*, **57**, 684-697.
190 Schmidt CE, Heikes BG, 2014, Aqueous carbon monoxide cycling in a fjord-like estuary, *Estuaries Coasts*, **37**, 751-762.
191 Schulz M, Prospero JM, Baker AR, Dentener F, Ickes L, Liss PS, Mahowald NM, Nickovic S, Garcia-Pando CP, Rodriguez S, Sarin M, Tegen I, Duce RA, 2012, Atmospheric transport and deposition of mineral dust to the ocean: Implications for research needs, *Environ. Sci. Technol.*, **46**, 10390-10404.

192 Schwalm CR, Williams CA, Schaefer K, Baldocchi D, Black TA, Goldstein AH, Law BE, Oechel WC, Kyaw Tha Paw U, Scott RL, 2012, Reduction in carbon uptake during turn of the century drought in western North America, *Nature Geosci.*, **5**, 551-556.
193 Screen JA, Simmonds I, 2010, The central role of diminishing sea ice in recent Arctic temperature amplification, *Nature*, **464**, 1334-1337.
194 Sedlacek J, Knutti R, Martius O, Beyerle U, 2012, Impact of reduced Arctic Sea ice cover on ocean and atmospheric properties, *J. Climate*, **25**, 307-319.
195 Shadwick EH, Thomas H, Azetsu-Scott K, Greenan BJW, Head E, Horne E, 2011, Seasonal variability of dissolved inorganic carbon and surface water pCO_2 in the Scotian Shelf region of the Northwestern Atlantic, *Mar. Chem.*, **124**, 23-37.
196 Shakhova N, Semiletov I, Salyuk A, Yusupov V, Kosmach D, Gustafsson O, 10, Extensive methane venting to the atmosphere from sediments of the East Siberian Arctic Shelf, *Science.*, **327**, 1246-1250.
197 Shank GC, Zepp RG, Vahatalo A, Lee R, Bartels E, 2010, Photobleaching kinetics of chromophoric dissolved organic matter derived from mangrove leaf litter and floating *Sargassum* colonies, *Mar. Chem.*, **119**, 162-171.
198 Shepherd A, 2012, A reconciled estimate of ice-sheet mass balance (vol 57, pg 88, 2010), *Science.*, **338**, 1539-1539.
199 Shi D, Xu Y, Hopkinson BM, Morel FMM, 2010, Effect of ocean acidification on iron availability to marine phytoplankton, *Science.*, **327**, 676-679.
200 Shi D, Kranz SA, Kim J-M, Morel FMM, 2012, Ocean acidification slows nitrogen fixation and growth in the dominant diazotroph *Trichodesmium* under low-iron conditions, *Proc. Nat. Acad. Sci. USA.*, **109**, E3094-E3100.
201 Shick JM, Iglic K, Wells ML, Trick CG, Doyle J, Dunlap WC, 2011, Responses to iron limitation in two colonies of *Stylophora pistillata* exposed to high temperature: Implications for coral bleaching, *Limnol. Oceanogr.*, **56**, 813-828.
202 Sigman DM, Hain MP, Haug GH, 2010, The polar ocean and glacial cycles in atmospheric CO_2 concentration, *Nature*, **466**, 47-55.
203 Silverman AI, Peterson BM, Boehm AB, McNeill K, Nelson KL, 2013, Sunlight inactivation of human viruses and bacteriophages in coastal waters containing natural photosensitizers, *Environ. Sci. Technol.*, **47**, 1870-1878.
204 Sinnhuber BM, Stiller G, Ruhnke R, von Clarmann T, Kellmann S, Aschmann J, 2011, Arctic winter 2010/2011 at the brink of an ozone hole, *Geophys. Res. Lett.*, **38**.
205 Sinutok S, Hill R, Doblin MA, Wuhrer R, Ralph PJ, 2011, Warmer more acidic conditions cause decreased productivity and calcification in subtropical coral reef sediment-dwelling calcifiers, *Limnol. Oceanogr.*, **56**, 1200-1212.
206 Smith WK, Gao W, Steltzer H, Wallenstein MD, Tree R, 2010, Moisture availability influences the effect of ultraviolet-B radiation on leaf litter decomposition, *Glob. Change Biol.*, **16**, 484-495.
207 Song G, Xie H, Belanger S, Leymarie E, Babin M, 2013, Spectrally resolved efficiencies of carbon monoxide (CO) photoproduction in the western Canadian Arctic: Particles versus solutes, *Biogeosci.*, **10**, 3731-3748.
208 Spencer RGM, Aiken GR, Dornblaser MM, Butler KD, Holmes RM, Fiske G, Mann PJ, Stubbins A, 2013, Chromophoric dissolved organic matter export from U.S. rivers, *Geophys. Res. Lett.*, **40**, 1575-1579.
209 Spielhagen RF, Werner K, Sorensen SA, Zamelczyk K, Kandiano E, Budeus G, Husum K, Marchitto TM, Hald M, 2011, Enhanced modern heat transfer to the arctic by warm Atlantic water, *Science.*, **331**, 450-453.
210 Stedmon CA, Amon RMW, Rinehart AJ, Walker SA, 2011, The supply and characteristics of colored dissolved organic matter (CDOM) in the Arctic Ocean: Pan Arctic trends and differences, *Mar. Chem.*, **124**, 108-118.
211 Stubbins A, Spencer RGM, Chen H, Hatcher PG, Mopper K, Hernes PJ, Mwamba VL, Mangangu AM, Wabakanghanzi JN, Six J, 2010, Illuminated darkness: Molecular signatures of Congo River dissolved organic matter and its photochemical alteration as revealed by ultrahigh precision mass spectrometry, *Limnol. Oceanogr.*, **55**, 1467-1477.
212 Stubbins A, Law CS, Uher G, Upstill-Goddard RC, 2011, Carbon monoxide apparent quantum yields and photoproduction in the Tyne estuary, *Biogeosci.*, **8**, 703-713.
213 Stubbins A, Niggemann J, Dittmar T, 2012, Photo-lability of deep ocean dissolved black carbon, *Biogeosci.*, **9**, 1661-1670.
214 Su H, Cheng Y, Oswald R, Behrendt T, Trebs I, Meixner FX, Andreae MO, Cheng P, Zhang Y, Poeschl U, 2011, Soil nitrite as a source of atmospheric HONO and OH radicals, *Science.*, **333**, 1616-1618.

215 Sulzberger B, Durisch-Kaiser E, 2009, Chemical characterization of dissolved organic matter (DOM): A prerequisite for understanding UV-induced changes of DOM absorption properties and bioavailability, *Aquat. Sci.*, **71**, 104-126.

216 Swan CM, Nelson NB, Siegel DA, Kostadinov TS, 2012, The effect of surface irradiance on the absorption spectrum of chromophoric dissolved organic matter in the global ocean, *Deep Sea Res. Part I: Oceanog. Res. Pap.*, **63**, 52-64.

217 Swann ALS, Fung IY, Chiang JCH, 2012, Mid-latitude afforestation shifts general circulation and tropical precipitation, *Proc. Nat. Acad. Sci. USA.*, **109**, 712-716.

218 Tang Q, Zhang X, Yang X, Francis JA, 2013, Cold winter extremes in northern continents linked to Arctic sea ice loss, *Environ. Res. Lett.*, **8**.

219 Tranvik L, 2014, Carbon cycling in the Arctic, *Science.*, **345**, 8070.

220 Tschumi T, Joos F, Gehlen M, Heinze C, 2011, Deep ocean ventilation, carbon isotopes, marine sedimentation and the deglacial CO_2 rise, *Climate of the Past*, **7**, 771-800.

221 UNEP, 2011, Climate change and POPs: Predicting the impacts. Report of the UNEP/AMAP Expert Group, (Ed.: Secretariat of the Stockholm Convention), United Nations Environment Programme/Arctic Monitoring and Assessment program, Geneva, Switzerland.

222 Valiela I, Camilli L, Stone T, Giblin A, Crusius J, Fox S, Barth-Jensen C, Monteiro RO, Tucker J, Martinetto P, Harris C, 2012, Increased rainfall remarkably freshens estuarine and coastal waters on the Pacific coast of Panama: Magnitude and likely effects on upwelling and nutrient supply, *Glob. Planet. Change*, **92-93**, 130-137.

223 van Groenigen KJ, Osenberg CW, Hungate BA, 2011, Increased soil emissions of potent greenhouse gases under increased atmospheric CO_2, *Nature*, **475**, 214-U121.

224 Vasileva A, Moiseenko K, 2013, Methane emissions from 2000 to 2011 wildfires in Northeast Eurasia estimated with MODIS burned area data, *Atmos. Environ.*, **71**, 115-121.

225 Venables HJ, Clarke A, Meredith MP, 2013, Wintertime controls on summer stratification and productivity at the western Antarctic Peninsula, *Limnol. Oceanogr.*, **58**, 1035-1047.

226 Villafane VE, Banaszak AT, Guendulain-Garcia SD, Strauch SM, Halac SR, Helbling EW, 2013, Influence of seasonal variables associated with climate change on photochemical diurnal cycles of marine phytoplankton from Patagonia (Argentina), *Limnol. Oceanogr.*, **58**, 203-214.

227 Voss M, Bange HW, Dippner JW, Middelburg JJ, Montoya JP, Ward B, 2013, The marine nitrogen cycle: recent discoveries, uncertainties and the potential relevance of climate change, *Philos. Trans. Roy. Soc. Lond. B.*, **368**.

228 Walker JT, Stow CA, Geron C, 2010, Nitrous oxide emissions from the Gulf of Mexico hypoxic zone, *Environ. Sci. Technol.*, **44**, 1617-1623.

229 Walsh JE, 2013, Melting ice what is happening to Arctic Sea Ice, and what does it mean for us?, *Oceanography*, **26**, 171-181.

230 Ward DS, Kloster S, Mahowald NM, Rogers BM, Randerson JT, Hess PG, 2012, The changing radiative forcing of fires: global model estimates for past, present and future, *Atmos. Chem. Phys.*, **12**, 10857-10886.

231 Wargent JJ, Jordan BR, 2013, From ozone depletion to agriculture: understanding the role of UV radiation in sustainable crop production, *New. Phytol.*, **197**, 1058-1076.

232 Waugh DW, Primeau F, DeVries T, Holzer M, 2013, Recent changes in the ventilation of the southern oceans, *Science.*, **339**, 568-570.

233 White EM, Kieber DJ, Sherrard J, Miller WL, Mopper K, 2010, Carbon dioxide and carbon monoxide photoproduction quantum yields in the Delaware Estuary, *Mar. Chem.*, **118**, 11-21.

234 Williamson CE, Zepp RG, Lucas RM, Madronich S, Austin AT, Ballare CL, Norval M, Sulzberger B, Bais AF, McKenzie RL, Robinson SA, Hader DP, Paul ND, Bornman JF, 2014, Solar UV radiation in a changing climate, *Nature Clim. Change*, **4**, 434-441.

235 Worden J, Jiang Z, Jones DBA, Alvarado M, Bowman K, Frankenberg C, Kort EA, Kulawik SS, Lee M, Liu J, Payne V, Wecht K, Worden H, 2013, El Nino, the 2006 Indonesian peat fires, and the distribution of atmospheric methane, *Geophys. Res. Lett.*, **40**, 4938-4943.

236 Wu Y, Polvani LM, Seager R, 2013, The importance of the Montreal Protocol in protecting Earth's hydroclimate, *J. Climate*, **26**, 4049-4068.

237 Xie H, Belanger S, Song G, Benner R, Taalba A, Blais M, Tremblay JE, Babin M, 2012, Photoproduction of ammonium in the southeastern Beaufort Sea and its biogeochemical implications, *Biogeosci.*, **9**, 3047-3061.

238 Xu Y, Shi D, Aristilde L, Morel FMM, 2012, The effect of pH on the uptake of zinc and cadmium in marine phytoplankton: Possible role of weak complexes, *Limnol. Oceanogr.*, **57**, 293-304.

239 Yamashita Y, Nosaka Y, Suzuki K, Ogawa H, Takahashi K, Saito H, 2013, Photobleaching as a factor controlling spectral characteristics of chromophoric dissolved organic matter in open ocean, *Biogeosci.*, **10**, 7207-7217.

240 Yang GP, Ren CY, Lu XL, Liu CY, Ding HB, 2011, Distribution, flux, and photoproduction of carbon monoxide in the East China Sea and Yellow Sea in spring, *J. Geophys. Res. Oceans*, **116**.

241 Young IR, Zieger S, Babanin AV, 2011, Global trends in wind speed and wave height, *Science.*, **332**, 451-455.

242 Zepp RG, Erickson DJ, III, Paul ND, Sulzberger B, 2011, Effects of solar UV radiation and climate change on biogeochemical cycling: interactions and feedbacks, *Photochem. Photobiol. Sci.*, **10**, 261-79.

243 Zhang J, Hudson J, Neal R, Sereda J, Clair T, Turner M, Jeffries D, Dillon P, Molot L, Somers K, Hesslein R, 2010, Long-term patterns of dissolved organic carbon in lakes across eastern Canada: Evidence of a pronounced climate effect, *Limnol. Oceanogr.*, **55**, 30-42.

244 Zhang Y, Xie HX, 2012, The sources and sinks of carbon monoxide in the St. Lawrence estuarine system, *Deep Sea Res. Part II: Top. Stud. Oceanog.*, **81-84**, 114-123.

245 Zhang Y, Chu D, Li Y, Wang L, Wu Y, 2013, Effect of elevated UV-B radiation on CH_4 emissions from the stands of *Spartina alterniflora* and *Phragmites australis* in a coastal salt marsh, *Aquat. Bot.*, **111**, 150-156.

246 Zhao MS, Running SW, 2010, Drought-Induced reduction in global terrestrial net primary rroduction from 2000 through 2009, *Science.*, **329**, 940-943.

Chapter 6. Changes in air quality and tropospheric composition due to depletion of stratospheric ozone and interactions with changing climate: Implications for human and environmental health

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Summary

UV radiation is an essential driver for the formation of photochemical smog, which includes ground-level ozone and particulate matter (PM). Recent analyses support earlier work showing that poor outdoor air quality is a major environmental hazard as well as quantifying health effects on regional and global scales more accurately. Greater exposures to these pollutants have been linked to increased risks of cardiovascular and respiratory diseases in humans and are associated globally with several million premature deaths per year. Ozone also has adverse effects on yields of crops, leading to loss of billions of US dollars each year. These detrimental effects also may alter biological diversity and affect the function of natural ecosystems.

Future air quality will depend mostly on changes in emission of pollutants and their precursors, but changes in UV radiation and climate will contribute as well. Significant reductions in emissions, mainly from the energy and transportation sectors, have already led to improved air quality in many locations. Air quality will continue to improve in those cities/states that can afford controls, and worsen where the regulatory infrastructure is not available. Future changes in UV radiation and climate will alter the rates of formation of ground-level ozone and photochemically-generated particulate matter and must be considered in predictions of air quality. The decrease in UV radiation associated with recovery of stratospheric ozone will, according to recent global atmospheric model simulations, lead to increases in ground-level ozone at most locations. If correct, this will add significantly to future ground-level ozone trends. However, the spatial resolution of these global models is insufficient to inform policy at this time, especially for urban areas.

UV radiation affects the atmospheric concentration of hydroxyl radicals, •OH, which are responsible for the self-cleaning of the atmosphere. Recent measurements confirm that, on a local scale, •OH radicals respond rapidly to changes in UV radiation. However, on large (global) scales, models differ in their predictions by nearly a factor of two, with consequent uncertainties for estimating the atmospheric lifetime and concentrations of key greenhouse gases and air pollutants. Projections of future climate need to consider these uncertainties.

No new negative environmental effects of the substitutes for the ozone depleting substances or their breakdown-products have been identified. However, some substitutes for the ozone depleting

substances will continue to contribute to global climate change if concentrations rise above current levels.

Introduction

The degradation of air quality is one of the major environmental hazards facing modern society. Human activities result in the emission of many chemicals to the atmosphere, which are either toxic themselves, or produce noxious compounds when exposed to ambient ultraviolet (UV) radiation. UV radiation is an essential driver for the generation of ground-level ozone (O_3) and some particulate matter (PM, frequently called aerosol) including sulfate, nitrate, and organic aerosols. These pollutants have major health implications for humans and the environment. Future changes in tropospheric UV radiation, whether from stratospheric ozone changes or other factors such as clouds, are likely to contribute to trends in air quality and associated health effects.

UV radiation makes hydroxyl (•OH) radicals, the so-called cleaning agents of the troposphere. These radicals limit the atmospheric lifetime of many gases that are important to both tropospheric and stratospheric chemistry as well as climate change, including methane (CH_4), hydrogen-containing halocarbons (e.g., hydrofluorocarbons, hydrochlorofluorocarbons and hydrobromocarbons), and the oxides of sulfur and nitrogen (SO_2 and NOx).

This paper provides an assessment of how UV radiation affects air quality, particularly ground-level O_3 and PM, in the context of the growing body of knowledge on their health impacts, geographic distributions, and long-term trends. It should be recognised that many factors drive these trends, including changes in both natural and anthropogenic emissions, as well as climate variability through changes in temperature, moisture, and atmospheric circulation patterns. Tropospheric UV radiation is one of these factors, and its effects can be approximately superimposed onto the effects of the other factors, but complex non-linear interactions must be considered to obtain reliable estimates.

Since the previous assessment of the interactions between ozone depletion, climate change, and air-quality in the troposphere,[135, 139] significant advances are noted in: (i) Understanding and quantifying the important consequences of poor air quality for human health, separating the effects of O_3 and PM. (ii) Understanding changes in air pollution on urban and regional scales, in terms of changes in anthropogenic emissions (increases or decreases, depending on location) as well as long-range transport. (iii) Understanding long-term changes of key tropospheric oxidants (O_3 and •OH) on continental and global scales, as anthropogenic emissions continue in an environment where both stratospheric ozone and climate are also changing.

An equally important advance is a better understanding of uncertainties inherent in numerical models used to predict the future chemical composition of the atmosphere. These computer models endeavor to represent and integrate the many chemical, physical, and biological processes that control air quality as well as climate. Recent inter-comparisons among the models (see below) highlight important differences that cast some doubt on the reliability of future projections, while also indicating the path to model improvements.

Ozone-depleting substances could also affect air quality. While the long-lived chlorofluorocarbons (CFCs) break down almost exclusively in the stratosphere, the halogenated replacements break down in the troposphere. The cycling of the halogenated species in the troposphere needs to be assessed to ensure that there are no other significant short- and long-term effects that will result from the replacements for the halocarbons. Health effects could result from exposures to these substances, and are therefore included in this assessment (previously this was included in the health assessment which now focuses on UV-mediated effects).

This paper provides summaries of the state of knowledge on ground-level O_3, PM, and •OH radicals, and addresses some of the more complex but still largely unquantified interactions between air quality, climate change, and human activities. An important additional interaction between air quality and stratospheric ozone depletion is the introduction of substitute compounds for ozone-depleting substances (ODS) pursuant to international agreements. The last part of this paper provides an update on selected substitutes whose potential environmental and health impacts should be considered.

In summary, our assessment updates and reinforces several key conclusions. Air pollution is increasingly recognised as a major environmental hazard and a risk to human health, globally leading to several million premature deaths per year. Air pollution also damages vegetation and reduces agricultural yields, with associated economic losses estimated as $10-20 billion annually. UV radiation is an essential ingredient for the formation of ground-level O_3 and some PM, and of •OH radicals that control the global self-cleaning capacity of the troposphere. Future trends in UV radiation will modulate future trends in air quality. Air quality is sensitive to other changes in the environment including atmospheric circulation, hydrological cycles, and temperatures, all of which are likely to change due to the combined effects of changing stratospheric ozone and climate. No new negative environmental effects of the substitutes for the ODSs have been identified.

Ground-level ozone

Health effects

Tropospheric O_3 has significant effects on human morbidity and mortality. Premature mortality has been estimated in recent studies summarised in Table 1. Ozone and particulate matter (PM) often co-occur in the troposphere and therefore their effects on human health are difficult to separate. However, there appears to be no interaction between these in terms of premature mortality. Earlier epidemiological studies (reviewed in [7]) have supported this conclusion and further studies by the same authors[5, 6] on the individual components of PM have shown that there is no interaction between these and ozone. Thus for the purposes of protecting human health, PM and O_3 can be treated separately. Premature mortality associated with exposure to ground-level ozone, while lower than that from PM, is still substantial with several hundred thousand people affected globally each year (Table 1). Recent studies are broadly consistent on effects of ozone on mortality in humans from cardiovascular and respiratory diseases in Oporto, Portugal,[30] Taipei,[54] and Prague.[55, 78]

Table 1 Premature mortality from ground-level ozone (O_3) and particulate matter (PM)

			Premature mortality, millions per year	
Source	**Year**	**Area**	**From O_3**	**From PM**
OECD[99]	2010	Global	0.35	1.4
	2050	Global	0.75	3.6
Lim et al.[78]	2010	Global	0.05-0.27	2.8-3.6
Fang et al.[35]	2000	Global	0.38	1.5
Fann et al.[36]	2005	US only	0.005	0.05-0.2

Ozone-related morbidities manifested as acute and chronic bronchitis, asthma and/or atopic dermatitis,[71] appendicitis,[64] venous thromboembolic disease, and pulmonary embolisms[29] have been reported. Ozone may also interact synergistically with viral infections. A study in Hong Kong reported interactive effects between viral infections and concentration of O_3 that resulted in increased risks for hospitalisation for respiratory disease.[151] The mechanism for this apparent synergism was not reported.

A number of studies have extrapolated the effects of exposure to O_3 into the future. Based on the OECD[99] study, premature deaths from ground-level ozone will increase to about 0.75 million per year worldwide by 2050. The greatest increases are predicted in India (130 premature deaths per million per decade by 2050) but those in OECD countries will be almost as large (95 premature deaths per million per decade by 2050), mostly as a result of greater sensitivity in an ageing population.[99] Modelling of the interactions between concentrations of tropospheric ozone, precursors of ozone in the atmosphere, and climate change suggests that, by 2050, concentrations of O_3 will increase in developing countries and decrease in developed countries,[72] due to regional differences in future emissions.

Effects on plants

For plants, the most important air-pollutant is O_3[118, 148]; particulates have not been observed to have substantial direct effects on plants. In our previous assessment,[135] we noted that damage to crops by air-pollutants is likely to become more severe in the future. Since the last assessment, further studies have reinforced this conclusion. Based on a scenario of a world population of 9.1 billion, concentration of CO_2 of 550 ppm[1], a concentration of ozone of 60 ppb (about 10 ppb above current), and the climate warmer by ca. 2°C by 2050, Jaggard et al.[59] postulated that yields of major crops (e.g., wheat, rice, soy, and maize) may be reduced by about 5% because of O_3. However, this would be compensated by an increase in yield for most crops by about 13% because of the increased concentrations of CO_2, depending on water availability.

In a review of studies on the effects of O_3 on plants, it was concluded that reductions in the yields of 18 to 27% result from exposures to O_3 at concentrations of 70 to 100 ppb, at the upper end of typical regional concentrations.[74] Not all crops are equally sensitive to ozone. In a sensitive crop, such as soybean, yields in several cultivars were shown to decrease by as much as a factor of 2 with long-term exposure to 20-30 ppb (24 hour mean) of added ozone.[10] Reductions in photosynthesis upon exposure to O_3 were estimated in three different forest types and found to be statistically significant for an orange orchard, and observable for ponderosa pine.[37] The potential for damage from O_3 in crop plants was assessed in relation to the IPCC (pessimistic) A2 scenario[56] for 2100.[2] Changes in gross plant productivity resulting from changes in tropospheric O_3 were projected to range from -40 to +15%, depending on location (Fig. 1). In another example, the ranges of global crop losses for wheat and soybean in 2030 as estimated from the IPCC A2 scenario were 5.4-26% and 15-19%, respectively.[8] In this same study, yield reductions in the B1 (optimistic) scenario were 4.0-17% for wheat and 9.5-15% for soybean, with monetised annual losses estimated to range from $12-21 billion (year 2000 dollar equivalents).

Although most of the research on the effects of O_3 in ecosystems has been directed toward plants, effects on soil microorganisms have also been reported.[38] The abundance and diversity of methanogenic bacteria in soils of rice paddies were found to be reduced after exposure to elevated concentrations of O_3 (60 ppb) in ground-level air.

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[1] A ppm of X, parts per million, is a mixing ratio of 1 molecule of X per million molecules of air. Similarly, ppb is parts per billion.

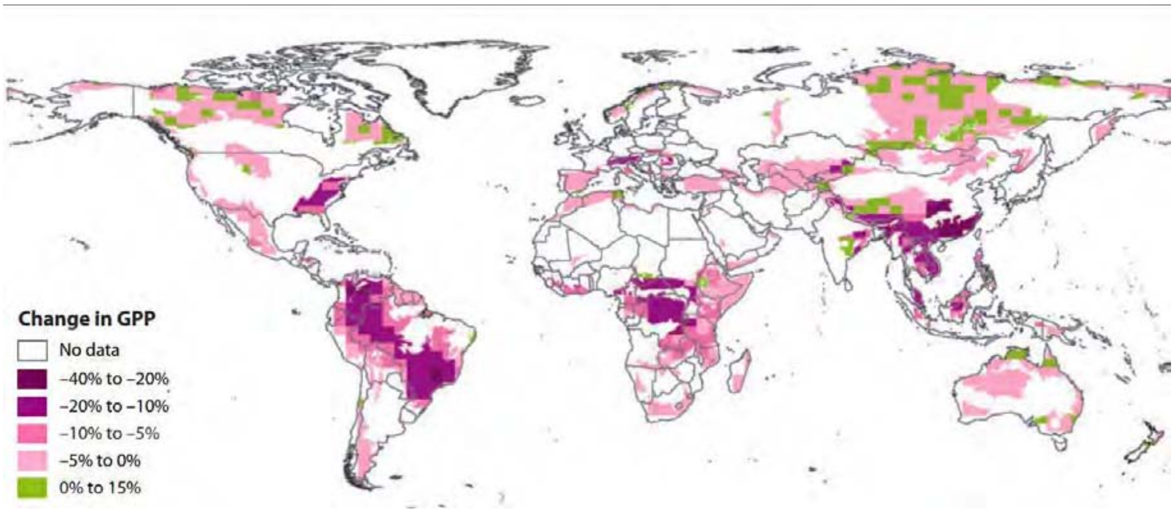

Fig. 1 Global assessment of the projected percentage changes in gross primary productivity (GPP) due to O_3 under the Intergovernmental Panel on Climate Change A2 scenario in 2100 within the World Wildlife Foundation Global 200 priority conservation areas. From Ainsworth et al.[2]. Reproduced with permission of the Royal Society.

Overall, productivity and yields of crops will likely be reduced as a result of increases in concentrations of tropospheric O_3. There is some hope that genetic selection of plants tolerant to O_3 will mitigate these adverse effects on production of food and fibre but other plants in the ecosystem are likely to suffer greater adverse effects. These are expected to impact diversity and functions of natural ecosystems. Other effects of climate change, e.g., mediated by temperature and precipitation, will also affect yields of crops.

Photochemical processes

Atmospheric ozone (O_3) is generated primarily in the atmosphere by photochemical reactions involving UV radiation. In the stratosphere, it is made directly by the photo-dissociation of molecular oxygen (O_2) into two oxygen atoms (2O), followed by the association of each of these atoms with remaining O_2 (see Table 2) to make two O_3 molecules. In the troposphere, this direct formation is not possible because photons of sufficient energy to dissociate O_2 (λ <240 nm) are nearly completely absorbed by stratospheric O_2, and so are not available in the troposphere. Descent of stratospheric ozone to the troposphere does occur (e.g., during stratospheric intrusions common during springtime at mid-latitudes) but accounts for only about 1/10th of the tropospheric production in global models,[155] and is only a minor source of ozone found near the surface in polluted regions.

Formation of O_3 in polluted urban atmospheres has been recognised since the 1950s [44], and occurs when mixtures of volatile organic compounds (VOCs) and nitrogen oxides ($NOx = NO + NO_2$) are exposed to the UV radiation available in the troposphere. The chemistry leading to tropospheric O_3 formation is generally complex because it (*i*) requires the absorption of multiple photons, (*ii*) is augmented by several catalytic cycles, and (*iii*) can be fueled by many different VOCs, including those of anthropogenic and biogenic origin. Table 2 provides a highly simplified schematic of the major chemical pathways. The production of tropospheric O_3 is autocatalytic because photolysis of an initial amount of O_3 (Table 2, reactions 3 and 4) results in two •OH radicals, each of which can then continue through the reaction sequence to regenerate more O_3. Note that two photons are required for this process (Table 2, reactions 3 and 7) with their combined minimum energy being more than sufficient to break O_2 directly.

Table 2 Atmospheric photochemical reactions

Stratospheric Ozone Formation:	**Reaction**
O_2 + hν (λ **<240 nm**) → O + O	(1)
O + O_2 → O_3	(2)
Tropospheric Ozone and •OH Formation:	
O_3 + hν (λ **< 330 nm**) → O* + O_2	(3)
O* + H_2O → •OH + •OH	(4)
•OH + VOC + O_2 → HO_2 (or organic analog RO_2) + other products	(5)
HO_2 + NO → NO_2 + •OH	(6)
NO_2 + hν (λ **<420 nm**) → NO + O	(7)
O + O_2 → O_3	(2)
Secondary Tropospheric Radical Sources:	
CH_2O + hν (λ **<340 nm**) + 2 O_2 → HO_2 + HO_2 + CO	(8)
H_2O_2 + hν (λ **<350 nm**) → •OH + •OH	(9)
HONO + hν (λ **<395 nm**) → •OH + NO	(10)

Reaction 3 in Table 2, the photolysis of ozone to yield excited oxygen atoms O*, is the primary source of radicals (•OH, HO_2, and RO_2) involved in production of O_3. It is also very sensitive to the overhead ozone column (see Table 1 of McKenzie et al.[90]). Other sources of radicals include the photolysis of formaldehyde (CH_2O), hydrogen peroxide (H_2O_2), and nitrous acid (HONO). These latter compounds are typically the products of previous chemical reactions initiated by O_3 and •OH and so they are sensitive to the production of primary radicals (Table 2, reaction 3) and therefore to UV-B radiation as affected by changes in stratospheric ozone.

Distributions and trends

Tropospheric ozone has increased since preindustrial times, mostly because of increasing anthropogenic emissions of the precursor gases, VOCs and NOx. Relative to that, the effects of changing the UV radiation environment, e.g., from mid-latitude stratospheric ozone depletion, have been smaller but remain important due to the very large number of people living in areas with poor air quality.

Urban ozone trends differ in different cities. Considerable progress has been made in reducing urban O_3 in Europe, the United States, and some other locations.[22, 103, 149, 160] Fig. 2 shows the reductions in ground level ozone achieved in Los Angeles and Mexico City over the past several decades. In Beijing, from 2005 to 2011, ground-based measurements give daytime average O_3 increasing at 2.6 ppb (5%) per year.[159] In comparison, increases of 3% per year over 2002-2010 have been reported for the tropospheric O_3 column above Beijing.[146] Other Asian cities showing increases include Hong Kong (0.55 ppb per year over 1994-2007), Seoul (about 5 ppb over 1991-2007), and

Tokyo with a doubling of days with O_3 exceedances (incidences where air quality standards are exceeded).[160]

Regional ozone (ozone averaged over large areas extending well beyond cities) is increasing at some locations, particularly in densely populated areas, for example 6-7% per decade in the Indo-Gangetic Plains.[70] Regional production of ozone was also shown to be a factor limiting air quality improvements from local emission reductions during the Beijing Olympics.[145] Background ozone continues to increase at many locations, such as central and northwestern Europe, but is decreasing in eastern and southwestern Europe.[22, 149] Increases of 0.25 ppb/year have been reported for ground-level ozone at Mace Head, Ireland.[32] In the western U.S., mid-tropospheric (3-10 km) ozone has increased by 0.6 ppb/year in the springtime over 1995-2008, and may be indicative of long range transport.[24] Changes in the seasonal cycle observed at various mid-latitude locations in the Northern Hemisphere are consistent with increasing emissions of precursors.[104] On the other hand, a review of measurements made with balloon-borne instruments (ozone sondes) and surface observations at remote locations showed that most of the increases in both hemispheres occurred in the early part of the 20-40 year record, with more recent changes characterised by little or no increase.[100]

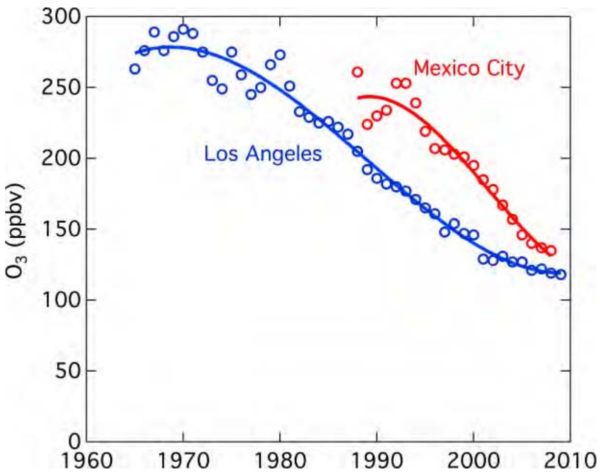

Fig. 2 Improvements in air quality in Los Angeles and Mexico City. Plotted is the 3-year average of the 4th highest maximum ozone 8-hour average (from Parrish et. al[103]).

Changes in atmospheric circulation are also likely to have affected trends of tropospheric ozone. Some increases may have been due to changes in the rate of stratosphere-troposphere air exchange.[48] Trends at Mauna Loa, Hawaii, were influenced by changes in circulation due to El Niño, transporting air masses from different regions of Asia to Hawaii.[79]

Prediction of tropospheric concentrations of O_3 via numerical models remains problematic, with large differences at regional[22] and global scales.[131, 155] This is illustrated in Fig. 3, where several global models, represented by different lines, are seen to differ by as much as 25% for current conditions, and future predictions show a wider range depending on the choice of future scenario as well as model. However, it should be noted that future photochemical ozone formation will in any case depend to a large extent on details of future emissions, particularly those associated with different fuel choices (e.g., diesel, gasoline, or biofuels).

The specific response of tropospheric O_3 to future changes in stratospheric O_3 was modeled by Zeng et al.[157] and Zhang et al.[158], with both studies showing large-scale increases in tropospheric O_3, as a net result of slowing both production and loss in response to declining UV levels. However the low resolution of their models (several degrees latitude x longitude) is insufficient to discern urban effects where higher levels of NOx are expected to maintain an opposite (positive) relationship between UV radiation and ground-level ozone[80, 136] that would indicate improvement in air quality in response to recovery of stratospheric ozone. Global models also do not agree well with measurements of the background atmosphere, (e.g.,[105]) indicating that there is still significant work to be done in understanding this chemistry. These uncertainties make it difficult to identify precisely which geographic regions will experience decreases in tropospheric ozone as stratospheric ozone recovers, and which ones will suffer increases. Nevertheless, all models agree that over large regions tropospheric ozone will increase.

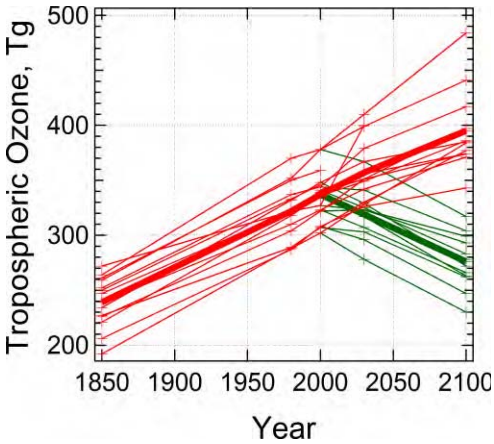

Fig. 3 Global tropospheric ozone burden simulated by different models. Drawn from data in Table 1 of Young et al.[155]. Thin lines are for individual model results, thick lines are multi-model averages, for two scenarios of future emissions, RCP2.6 (green) and RCP8.5 (red), as defined by the Intergovernmental Panel on Climate Change.[57]

Nitrogen dioxide

The near-term outlook for tropospheric oxidants can also be surmised from satellite measurements of NO_2 (see Fig. 4) a precursor of tropospheric ozone and an important pollutant in its own right. The geographic distribution agrees with the general understanding of major emission sources, particularly over the U.S., Europe, and East Asia. Trends, also derived from satellite-based observations, are shown in the lower panel for specific regions. Notably, decreases in NO_2 are seen to have occurred over the U.S. and Europe, in accordance with NOx emission reduction policies, and consistent with the reductions in urban ozone reported for these regions. However, positive trends are noted for east-central China, the Middle East, and north-central India. It seems likely that such recent trends will also continue into the near-term future, with the associated expectation that ground-level ozone (and other photochemical pollutants) may increase in some areas and decrease in others.

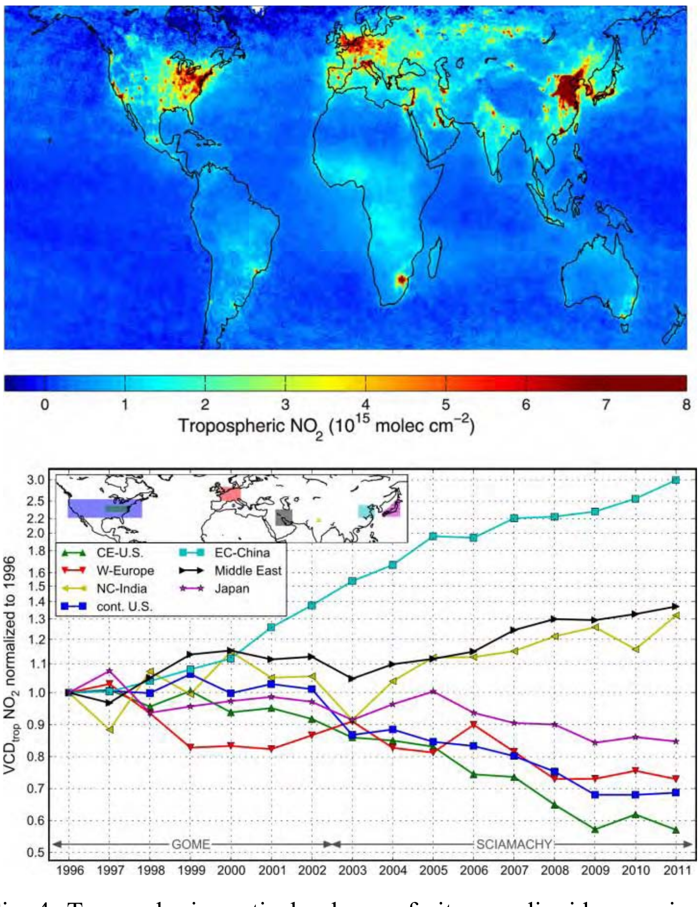

Fig. 4 Tropospheric vertical column of nitrogen dioxide, a major air pollutant and precursor of tropospheric ozone. Top panel: global distribution averaged from May 2004 to April 2005 [87]; Bottom panel: region-specific trends.[49]

Particulate matter

Particulate matter (PM) in the atmosphere consists of small solid or liquid particles suspended in air, also called *aerosols*. The size of PM is recognised as important for health effects, with PM smaller than 2.5 µm (termed PM2.5) being inhaled deeper into lungs than larger particles, typically measured as all particles below 10 µm (PM10).

Health effects

Particulate matter in the troposphere causes significant adverse health effects. A large body of literature spanning decades of research has been reviewed and assessed confirming this causal relationship (e.g.,[142]). Table 1 shows recent estimates of premature deaths from particulate matter. Recent studies have reported PM health effects from different locations. In the time-series analysis of hospitalisations for venous thromboembolic disease in Chile between 2000 and 2007 discussed for ozone above, an increase in concentration of PM2.5 of 20 μg m^{-3} resulted in a relative risk (RR) of 1.05 (95% CI 1.03-1.06) for all hospitalisations.[29] A similar RR was observed for pulmonary embolism. In a study of 90 cities in China over 1981-2000, those north of the river Huai had total suspended particulates (PM of all sizes) higher by 100 μg m^{-3} (95% CI = 61-307) than those south of the river, and were associated with a decrease in life-expectancy of 3 years (95% CI 0.4-5.6).[21] Much of PM2.5 is due to particles generated in the atmosphere by UV-dependent photochemistry (e.g., sulfate, nitrate, and organics, see below), although other PM sources can be extremely important, e.g., biomass burning plumes reaching densely populated urban areas (e.g., van Donkelaar et al.[143]).

Where control of emissions into the troposphere has resulted in decreases in PM2.5, fewer health effects have been observed. In a study of life expectancy in 545 U.S. counties, reductions in PM2.5 of 10 μg m^{-3} from 2000 to 2007 were associated with an increase in mean life expectancy of 0.35 years (SD = 0.16 years).[25]

Overall, the global relevance of particulates to human health is very large, and substantial changes are expected to occur in response to changes in climate.[129] Future predictions are uncertain due to limitations of atmospheric models and their assumptions[110] and specifically for human health effects, the difficulty to clearly separate effects of O_3 and PM2.5.[111]. Future changes in aerosols are uncertain but may be substantial regionally. A multi-model analysis of past and future trends in aerosol, described in Fig. 8 in Chapter 1, indicates large changes in industrialised regions, particularly in China.

Effects on plants

Direct effects of PM on plants appear to be minor, for example by direct deposition of PM on foliage.[142] However, two important indirect effects should be recognised. The first is an increase in diffuse visible radiation from the scattering of solar photons by aerosol particles, altering photosynthetic efficiency within partly shaded canopies. The second is the surface deposition of some aerosol chemicals, for example, the heavy metals Cu, Ni, and Zn, with potential effects on soil chemistry, microbial communities, and nutrient cycling.[142]

Atmospheric processes

Particles in the atmosphere include those emitted directly, such as wind-blown dust and soil, combustion-generated soot (black carbon), and salt from sea-spray, as well as those formed *in-situ* by condensation of vapours, such as sulfates, nitrates, and many organics. The latter, secondary, aerosols depend on UV-initiated reactions of •OH radicals (see section on Global •OH models), and thus are likely to be affected by changes in stratospheric ozone. However, we note the absence of specific studies addressing how changes in UV associated with stratospheric O_3 would affect the formation and removal of tropospheric particles.

The formation of sulfate and nitrate aerosols is well understood, in terms of the •OH oxidation of SO_2 and NO_2 giving sulfuric and nitric acids, respectively. While the majority of this production occurs in the gas phase, the sulfate and nitrate condense rapidly to form particles, particularly if ammonia is present. Chemical reactions in cloud and rain water can also contribute.[122]

Considerable progress has been made recently in understanding secondary organic aerosols (SOA), which previous observations had shown to be seriously underestimated by models. While many details remain poorly understood, numerous studies support the basic conceptual model that hydrocarbons are oxidised (by •OH and NO_3 radicals, and O_3) into a myriad of heavier more functionalised molecules as well as smaller fragments.[12] Molecules with multiple functional groups (e.g., alcohols, ketones, aldehydes, organic acids, nitrates and peroxides) typically have lower vapour pressures and therefore are likely to condense onto particles. However, quantification remains a problem due to the large number of chemical species contributing to particle mass. Significant advances in modelling have been made by classifying these multifunctional compounds according to relevant properties, such as vapour pressure,[33, 61] solubility,[50] oxidation state,[68] atomic ratios (O, C, H, etc.),[18, 46] and carbon number and polarity.[102] In practice, for ambient aerosols many of these properties are not known and therefore cannot be used to constrain predictions. However, these modelling frameworks now allow exploratory sensitivity analyses to help identify the most important processes for more accurate parameterisation.

Removal of aerosols from the atmosphere is poorly understood. Ultimately removal from the atmosphere occurs by wet or dry deposition. Incorporation of aerosol particles into raindrops (wet deposition) leads to lifetimes estimated to range from 0.5 to 2 weeks.[26, 27, 67] Dry deposition of particles is generally slower.[122, 156]

Distributions and trends

The global distribution of aerosols is shown in Fig. 5. Satellite observations and models agree on broad features, including the dust belt extending from N. Africa to S. Asia, biomass burning evident over tropical S. America, and high values over E. Asia. These optical depth values represent the entire aerosol vertical column and not necessarily those at ground level. Surface network data are available in many countries and have been used to show detailed geographical and seasonal distributions of major chemical constituents of collected particles (e.g., [45] for the U.S.).

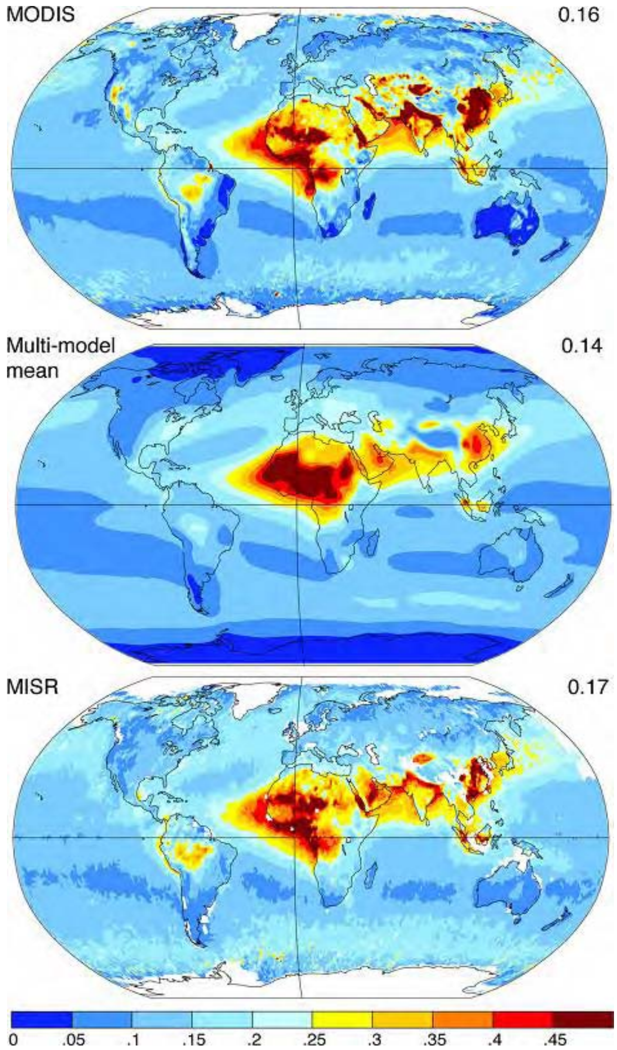

Fig. 5 Annual average aerosol optical depth at 550 nm from the MODIS and MISR satellite instruments (top and bottom, for the years 2004-2006) and models (middle, for the year 2000). From Schindell et al.[123]

Heavily populated urban locations are of special interest, and some recently reported measurements in megacities are summarised in Table 3. World Health Organization (WHO) guidelines are frequently exceeded by all cities listed. Reductions in PM concentrations are occurring in many cities, in some cases well-documented by long-term urban monitoring networks, and evidently related to emissions-lowering technologies for both fixed and mobile sources. However, measurements at many polluted locations are still sparse, making an assessment of trend difficult.

Future concentrations of aerosols are subject to similar scenario assumptions as other pollutants.[3, 123, 126] Organic and black carbon are expected to continue to increase over the next few decades globally, but then decrease, with timing and magnitude depending on the specific scenario. Organic and black carbon are expected to continue to increase over the next few decades globally, but then decrease with the timing and magnitude, depending on the scenario.

On smaller geographic scales, aerosol concentrations are sensitive to local and regional emissions, and may improve or worsen depending on regulatory strategies. For example, a multi-model analysis of past and future trends in aerosols, described in Fig. 8 Chapter 1, shows strong regional reductions of aerosol concentrations by 2090, particularly in China.

Table 3 Concentrations of particulate matter in megacities

City	PM10 µg m^{-3}	PM2.5 µg m^{-3}	Measurement period
WHO guidelines	*20*	*10*	*Annual mean*
	50	*25*	*24-hour mean*
Cairo	90-260	30-220	1999-2002
Dakar		30-60	2008-2009
Bangkok	40-90 (-)		1995-2008
Beijing	150-180 (-)	95-155	1999-2008
Delhi	50-300	50-250	2004-2009
Dhaka	>100 (+)	>30 (+)	2002-2006
Hong Kong	40-50 (-)	20-40	1998-2008
Jakarta	60-100 (-)		2001-2007
Manila	40-50	20-30 (-)	2001-2008
Seoul	60-80 (-)		1995-2007
Shanghai	90-110 (-)		2002-2007
Tokyo		15-30 (-)	2001-2008
Tehran	65-370		2003
Santiago	50-100 (-)	20-30 (-)	2000-2008
Sao Paulo	40-70 (-)		1996-2006
Los Angeles		40-80 (-)	1998-2008
Houston		30-40 (-)	1998-2008
New York City		30-70 (-)	1998-2008
Mexico City	50-180 (-)	20-25 (-)	1990-2010
London	20-35		1994-2004
Moscow	35-50 (+)		2006-2008
Milan	35-60 (-)		2000-2009
Istanbul	45	20	2002-2003

Positive (+) and negative (-) trends are indicated. Values shown are ranges observed over the measurement period. Compiled from data reported by Zhu et al.[160]; see original for details of the sampling intervals.

Hydroxyl radicals

Tropospheric self-cleaning capacity

An important role of UV radiation in the troposphere is the production of •OH radicals by photolysis of tropospheric ozone (Reaction 3 in Table 2) followed by reaction with H_2O (Reaction 4, Table 2). The •OH radicals react with many of the gases emitted at the Earth's surface, including carbon monoxide (CO), methane (CH_4) and other volatile organic compounds (VOCs), oxides of nitrogen and sulfur (NO_2 and SO_2), and hydrohalocarbons (HFCs and HCFCs). The reactions with •OH determine the atmospheric residence time of these gases, as well as their amount in the atmosphere since this is directly proportional to the product of emission rates and lifetime.

Understanding •OH is fundamental to understanding the chemistry of ozone and secondary aerosols, as well. Cycling between •OH and HO_2 (Reactions 5 and 6, Table 2) is essential for tropospheric ozone formation. Notably, •OH itself has a lifetime of only seconds, but it affects O_3 on the time scale of hours to days, CO over months, and methane over a decade. For this reason, direct detection of •OH has focused on local short-term measurements, while longer-term impacts, for example, on methane lifetimes, have been estimated from global models.

Local measurements of •OH

Direct measurements of •OH are difficult because of its high chemical reactivity. Within seconds of being produced, •OH reacts with various gases (see previous paragraph) limiting its concentration to low values (about 10^6 - 10^7 molec cm^{-3} during daytime, smaller at night) that are exceedingly difficult to detect and quantify. The high reactivity also implies that •OH has high spatial and temporal fluctuations, being sensitive to variations in production (e.g., to variations in UV radiation, O_3, and H_2O) as well as loss (e.g., via reactions with CO, NOx, or VOCs). For this reason, it is important to note that locally measured •OH concentrations cannot be easily integrated spatially or temporally to estimate, for example, an annually averaged global •OH concentration. The main objective of direct local measurements is to evaluate whether the variations in •OH follow the expected variations in simultaneously measured meteorological (UV radiation, humidity) and chemical variables (O_3, NOx, VOCs, etc.).

Several techniques have been developed over the past few decades to detect and measure concentrations of •OH. Measurements have been reviewed by Heard and Pilling[47] and more recently by Stone et al.[133]. Most of the recent measurements are consistent with model calculations within a factor of approximately two, (e.g., urban locations including New York City,[115] Tokyo,[63] Mexico City,[34, 76] and Houston[20]). Studies in forested locations, specifically West Africa[132] and northern Michigan[43] also show reasonable agreement with models.

Measured •OH is much greater, by as much as an order of magnitude, than predicted by models in environments containing high concentrations of biogenic hydrocarbons (e.g., isoprene, methyl butenol, and terpenes) and low concentrations of NOx, including over the tropical forest of Suriname,[69, 75, 88] Borneo,[112, 147] the Pearl River Delta (PRD),[51, 82] and suburban Beijing during low-NOx episodes.[83] This apparent underestimation of •OH by models has led to a re-examination of the chemistry of isoprene at low NOx, and to the suggestion that at least part of the •OH initially lost by reaction with isoprene is later regenerated by secondary reactions.[107, 108] Simulations using an environmental smog chamber also indicate the need for some recycling of •OH by isoprene chemistry under very low NOx conditions, although not to an extent that would explain the large discrepancies between observations and models found over tropical Suriname.[41]

Several intercomparisons between different •OH instruments show good agreement in some circumstances but also disagreement in others.[40, 116, 120, 133] The largest discrepancies appear to occur in environments dominated by biogenic hydrocarbons. For example, Mao et al. [85] found a factor of two difference between laser-induced fluorescence and a chemical analysis methods at Blodget Forest, California.

Instruments have been developed recently to measure the total •OH reactivity, i.e. the rate at which •OH molecules are removed by reaction with the many constituents of sampled air (e.g., CO, VOCs, and NOx). The reactivity of •OH provides an important constraint on the budget of •OH since it must essentially balance the rate of production. Measurements show that this reactivity is larger than predicted from the simple sum of typically known constituents, indicating the presence of substantial but unmeasured amounts of other reactive compounds, by values ranging from 25-35% in Tokyo,[154] about 30% in a terpene-rich mid-latitude forest,[95] a factor of 2 in the Pearl River Delta[81] and 60-90% in a boreal forest.[97, 125] The missing compounds are presumed to be a multitude of partly oxygenated organic compounds (aldehydes, ketones, etc.) formed during the •OH-initiated photo-degradation of VOCs.

Despite unresolved differences among various •OH instruments and models, some fundamental aspects of the photo-chemistry have been clearly demonstrated. Important in the present context is the theoretical expectation that, for relatively clean conditions, concentrations of •OH should scale more or less linearly with the photolysis of O_3 to generate O* (Reaction 3, Table 2), $j(O_3)$, which in turn is dependent on the amount of UV radiation. This linear correlation has now been re-confirmed by direct measurements of •OH and $j(O_3)$ over a year at Mace Head, Ireland[9] and is in agreement with earlier observations in the tropical Atlantic[14] and in the European Alps.[117] Because tropospheric $j(O_3)$ values are sensitive to the overhead ozone column, with a ~1.5% increase in $j(O_3)$ for each 1% decrease in the O_3 column (see Table 1 of McKenzie et al., [90]), these studies reaffirm the importance of stratospheric ozone to tropospheric •OH and to the photochemistry of the lower atmosphere.

Global •OH models

Estimates of long-term changes in global •OH are uncertain and variable. Empirical estimates, based on the measured concentrations of trace gases, such as methyl chloroform, whose emissions and •OH kinetics are well known, are difficult due to large changes in emissions of suitable gases. An analysis of the decline in concentrations of methyl chloroform by Montzka et al.[92] concluded that globally averaged •OH varied by less than ±5% during 1997-2007. On the other hand, Monteil et al.[91] interpreted measurements of methane isotopes (^{13}C) to infer that the slowing of CH_4 trends in the early 2000s was due to increasing concentrations of •OH, at about 5% per decade, due to global increases in NOx emissions. Thus, the direction and magnitude of recent trends in global •OH remains unclear.

Estimates over longer time scales are largely based on models, which differ significantly. This was demonstrated by the recent intercomparison of 16 global chemistry-transport models for predictions of the methane lifetime, which is limited by reaction with •OH.[94, 144]. The modelled mean lifetime of methane was 8.6 ± 1.2 years (range 6.4-11.6 years) for the year 2000. Pre-industrial (1850) to present day (2000) changes in •OH were either positive or negative (see Fig. 6), depending largely on how each model specified relative changes in emissions of CO and NOx. Pike and Young[109] showed that global concentrations of •OH (and therefore the lifetime of CH_4) were sensitive to how models represent •OH recycling by isoprene, which remains uncertain as discussed above. If such buffering of •OH by biogenic VOCs is pervasive, it casts doubt on the strong sensitivities to anthropogenic emissions of CO and NOx shown in Fig. 6 for current models.

An alternate approach to estimating changes in •OH based on sulfate isotopic studies suggested a 10% decrease in global •OH since the pre-industrial times,[127] broadly in line with some of the models reported by Naik et al.[94] However, the accuracy of this method remains untested.

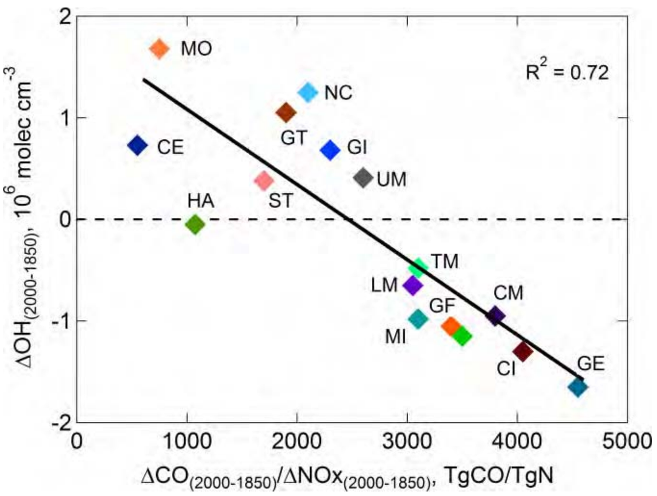

Fig. 6 Changes in globally averaged hydroxyl radicals (•OH) between pre-industrial times (1850) and present day (2000) calculated by 16 different models (model-mean for the year 2000 •OH ~1.1x10^6 molec cm^{-3}) for relative changes in emissions of carbon monoxide (ΔCO) and nitrogen oxides (ΔNOx) specified within each model (From Naik et al.[94]).

The multi-model mean changes in predicted •OH concentrations at the surface, for the year 2100 and two different emission scenarios, RCP2.6 and RCP8.5 have been calculated[144] and are shown in Fig. 7. Substantial reductions in •OH are expected throughout much of the southern hemisphere due to large increases in methane (CH_4) in the RCP 8.5 scenario, while regional increases and decreases occur in both scenarios due to changes in shorter-lived precursors NOx and CO. Another model study focused on the recovery of stratospheric O_3 to 1980 levels (holding all other factors constant) predicted that global concentrations of •OH will decrease by 1.7% due to the lower tropospheric UV radiation levels.[158]

Global models are also sensitive to climate change, including changes in temperature, humidity, stratospheric ozone, and uncertain NOx emissions from natural sources such as biomass burning and lightning.[52, 62, 93] Thus, multi-model averages such as those shown in Fig. 7 do not truly reflect the model variability or actual uncertainties. However, in clean marine atmospheres, concentrations of •OH are well predicted by models,[11, 128] but other unidentified oxidants appear to be important.[11] These other oxidants could be halogens.

Climate-mediated changes in air quality

Air pollution is a complex, multifaceted problem that can only be correctly considered when integrated within the whole Earth system. Direct emissions from human activities are well recognized, but emissions that would otherwise be considered natural can also change due to, for example, deforestation, biomass burning, and even feedbacks between air quality, climate change (especially the hydrological cycle), and ecosystem health. Atmospheric transport of pollutants and their precursors is subject to circulation patterns that are likely to change under a changing climate. In particular, changes in the frequency of stagnation episodes that limit the dispersion of pollutants may have large impacts on air quality in affected areas. Chemical transformations, e.g., those making ground-level O_3 from the photo-oxidation of hydrocarbons and nitrogen oxides, are sensitive to climate variables including temperature and moisture, as well as UV radiation. Removal of pollutants occurs mainly via contact with the Earth's surfaces (dry deposition) or scavenging by precipitation (wet deposition). Both could change significantly in the future, e.g., changes in land-use altering rates of dry deposition, and changes in precipitation patterns modifying wet deposition rates.

Several potentially major interactions are discussed here. Many other feedbacks are possible and may be plausible but are not fully understood and cannot yet be quantified reliably. These are, by and large, outside the scope of the present assessment, except to the extent that we recognise their existence and therefore provide a cautionary note that the general aspects of our assessment need to be evaluated carefully for any given location with full consideration of these additional factors.

Ozone

Concentrations of ozone in urban environments are determined by a number of key factors. Firstly, the amount of ozone in the air entering the urban environment may be important. Then, within the urban airshed, reactions involving a range of emitted chemicals, most notably VOCs and NOx, produce ozone as a result of UV-driven photochemistry. These chemicals arise from both anthropogenic and biogenic sources, the latter often being outside normal air quality management. Finally, a number of processes such as dry deposition (loss at the surface) might remove ozone from the atmosphere.

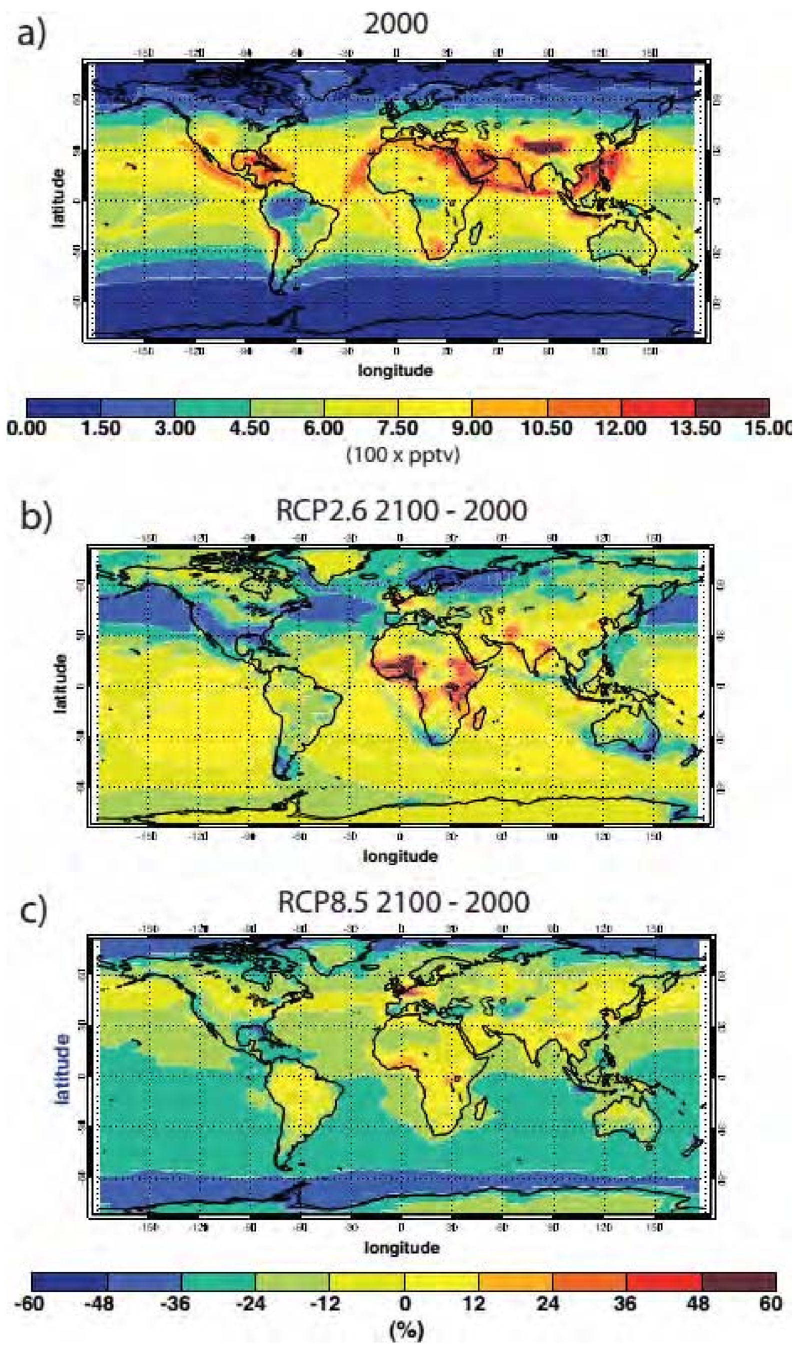

Fig. 7 (a) Annual average surface •OH concentration, mean of 14 models, for the year 2000. (b) Model-mean % change in surface •OH concentrations in 2100 relative to 2000, for the IPCC RCP 2.6 emission scenario; (c) same for RCP 8.5 scenarios (From Voulgarakis et al.[144]).

Background ozone concentrations can be influenced by long-range air transport, and this is likely to be an important factor into the future, transporting air between continents.[73] The background ozone concentrations can also be altered by changes in stratosphere/troposphere exchange and by the changes in global atmospheric composition, notably some greenhouse gases.[93] By analysing the natural variability of stratospheric transport, it has been estimated that changes in stratospheric circulation due to climate change will lead to around a 2% increase in tropospheric ozone in the northern mid-latitudes by the end of this century.[96] Although small, the significant geographic extent implies that this might be an additional factor affecting air quality.

Increased temperatures at ground level are expected to increase biogenic emissions of reactive organics (e.g., refs[60, 65]). However, emissions may well depend on other factors as well, such as water stress on the plants.[37] Indeed, changes in the climate, coupled to decreases in air quality, can substantially alter biogenic activity in ways that are difficult to predict.

Models suggest that other critical processes are also likely to be altered by climate change. Variations in cloudiness can alter the rate of photochemical production of ozone. Increased surface heating can result in changes in atmospheric movement (wind speed, both horizontal and vertical). Cloudiness can also be altered by human activity, with evidence that controls on air pollution have increased solar radiation at some locations.[42] Finally changes in rainfall patterns and cloudiness can alter the rate of removal of both reactive precursors and ozone itself.[72] Estimates predict increasing ozone concentrations at ground level throughout the 21st century, driven by all of these meteorological factors, which are regionally dependent. This can be offset by changes in emissions from human activity, which may either augment or reverse the overall trend, depending on the levels of controls implemented.[23, 72] Significant regional air quality changes may result, even if only episodically.[31]

Particles

The impact of climate change on aerosols remains highly uncertain. As mentioned above, increasing temperatures will increase biogenic gas emissions. The oxidation of these compounds will produce aerosols. Additional wild fires could become more important as a source of particulate matter.[58] These aerosols can scatter radiation and reduce warming (a negative feedback), and also impact upon cloud properties.[101] Changes in clouds in turn can alter the transformation (growth, chemistry) of aerosols in the atmosphere. In polluted environments the changes induced by climate will be overwhelmed by anthropogenic emissions, but in locations where anthropogenic emissions are small these changes could be significant. However, the net effect of climate change on aerosols remains unclear.[23, 58] While there has been a lot of work in this area (e.g., on climate/aerosol feedback models,[19]) the level of scientific understanding remains very low.

Biological interactions between air-pollutants and climate change

Increased ambient temperatures may interact directly or indirectly to exacerbate the effects of pollutants such as O_3 in humans. A study of cardiovascular and respiratory mortality in 2002 to 2006 in Buenos Aires showed a relative risk of 1.0184 (95% Confidence interval (CI) = 1.0139-1.0229) on the same day for each 1°C increase in temperature.[1] Another study in several large cities in the UK reported that temperature increased mortality from cardiovascular and respiratory diseases and other non-accidental causes.[106] These authors also reported that the mean mortality rate ratio for O_3 was 1.003 (95% CI = 1.001-1.005) per 10 μg m^{-3} increase in concentration. On hot days (greater than the whole-year 95th centile) this increased to 1.006 (95% CI = 1.002-1.009) but was only statistically significant for London. A study in older men in 2000 to 2008 in Boston showed that greater ambient temperature was associated with decreases in heart rate variability via dysfunction of the autonomic nervous system.[114] These warm-season associations were significantly greater when ambient ozone concentrations were above the median but were not affected by particulates (PM2.5). These studies are consistent with earlier analyses of the 2003 European heat wave episode[39, 130] which attributed a significant fraction (20-60%) of excess mortality to the effects of elevated levels of O_3 and PM.

Change in climate also may affect human health indirectly. A study on allergic respiratory diseases and bronchial asthma showed that while exacerbation is related to air-pollutants, amounts of allergen in the air are also important.[28] The presence of allergenic pollens in the atmosphere might be prolonged by climate change and increase frequency and severity of these diseases.

Halogenated organic and other substitutes in the troposphere

Toxicity and risks of replacements for ozone depleting chemicals to humans and the environment

The United States Environmental Protection Agency (USEPA) has a regulatory process for evaluating alternatives for Ozone Depleting Substances (ODS) prior to their wide-spread use in the U.S. Anyone planning to market or produce a new substitute must provide 90-days advance notice to the Significant New Alternatives Policy (SNAP) program at USEPA of their intent as well as providing health and safety information before introducing it into interstate commerce in the U.S. Normally the health and safety information will include information on chemical and physical properties, flammability and basic toxicological information, and more recently, global warming potential. The SNAP program reviews the information in the context of the proposed use, and issues one of 4 decisions: acceptable; acceptable subject to use conditions; acceptable subject to narrowed use limits; and unacceptable. This information on a particular compound is continually updated so that compounds may be proposed for additional uses or additional information may be added to the portfolio for a particular use that could change the initial decision.

Updates on selected halocarbons

Brominated substances. Natural bromo-carbons bromoform and dibromomethane are emitted from the oceans, and their emission strengths and role in the atmosphere are becoming better understood. These compounds release bromine upon oxidation in the atmosphere that is generally observed as bromine monoxide (BrO). The presence of bromine can lead to depletion of ground level ozone.[113] However, observations in other marine locations do not find such events occurring.[86] In the tropics, where sources are believed to be the biggest and vertical motion is enhanced, it has been estimated that these compounds have a lifetime in the atmosphere of 1 to 3 weeks. However, even with this relatively short lifetime, over 90% of the bromine that is transported to the stratosphere comes from these species.[53]

Bromine monoxide (BrO) is also calculated to be a significant oxidant for dimethylsulfide (20%) in the clean marine environment of the southern hemisphere.[15] This oxidation is a significant source of aerosol in this environment (nearly 20% of the total) and so has direct impacts upon cloud formation and light scattering, and hence climate. A large fraction of this BrO is derived from sea salt, and thus is an important part of the natural bromine background to which anthropogenic brominated organics are added. The overall significance of changes due to climate, as noted above, is not yet known.

N-Propyl bromide (C_3H_7Br), or 1-bromopropane, was introduced in the early to mid-1990s as an intermediate in a variety of closed commercial manufacturing processes for products such as pesticides, pharmaceuticals, and quaternary ammonium compounds. From the mid-1990s, it began to be used as a less toxic substitute for methylene chloride in open air uses such as vapour and immersion degreasing and cleaning of electronics and metals.[98] In 2003, it was first proposed by the SNAP program as an acceptable alternative for CFC-113 and methyl chloroform in a limited number of specific applications where emissions could be tightly controlled for both environmental and exposure concerns. Specifically, these included use as a solvent in industrial equipment for metals, electronics, and precision cleaning and in aerosol solvents and adhesive end-uses. However, the final rule issued in 2007[140] allowed use only as a solvent for industrial equipment; other uses such as aerosol solvents and adhesives are listed as unacceptable by the Agency.

The SNAP program decisions were based on health data related to reproductive and neurological end-points for which they considered a work place standard of an 8-hour time-weight acceptable exposure limit (AEL) of 25 ppm to be acceptable.[141] Subsequent to that information, reports have indicated that additional adverse effects have been added to the toxicological dossier for n-propyl bromide including immunotoxicity (significant decreases in a specific antibody) in rodents following 10 week inhalation exposures at levels of 125-500 ppm (mice) or 1,000 ppm (rat)[4] and multi-site carcinogenicity following two-year chronic inhalation exposures at 250 or 500 ppm in rats and mice.[98]

Chlorinated substances. Chloroform ($CHCl_3$) has a number of poorly known natural sources as well as anthropogenic sources.[152] Peat bogs may be a large unrecognized natural source of chloroform (10% of the total).[66, 124] Sources such as these are likely to be sensitive to both climate and land use change, and so represent an uncertainty in future predictions.

Production and consumption of carbon tetrachloride (CCl_4) are regulated under the Montreal Protocol. Observations show that atmospheric CCl_4 mixing ratios are decreasing at a rate slower than expected from assumed phase-out schedules.[77, 153] The sources and sinks of CCl_4, and their uncertainties, are beyond the scope of this paper, but it is probable that the slower decline is due to yet unidentified emissions. If such sources involve personal exposure, e.g., in solvent use, potential health effects may be anticipated.[84]

Chlorofluorinated Substances. Historically the first compounds developed as replacements for refrigerants, the largest sector where CFCs were used, were saturated hydrochlorofluorocarbons (HCFCs) and then saturated hydrofluorocarbons (HFCs), both classes of compounds which because of their hydrogen content, were susceptible to attack from hydroxyl radials in the atmosphere resulting in shorter atmospheric lifetimes than CFCs. Readers are referred to earlier reports for a review about the human and environmental risks for many of these replacements.

There is one compound in this category, trans-1-chloro,3,3,3- trifluoropropene (HCFO 1233zd(E)), which is just now being developed as a foam blowing agent, refrigerant, and solvent. A recent toxicology study[138] reported that HCFO 1233zd(E) was not acutely toxic and was not associated with any genetic toxicity in a battery of tests. The compound had an acute 4-hour 50% lethal concentration value (LC_{50}) of 120,000 ppm in rats, and a no observed effect level (NOEL) in canine cardiac sensitization studies of 25,000 ppm. The heart was identified as the apparent target organ on the basis of histopathological observations from a 2 week range finding study in male and female rats exposed levels of 0, 2,000, 5,700 and 20,000 ppm 6 hours/day for 5 days/week, Males at the mid and high doses and females at the high dose developed multifocal mononuclear infiltrates of cardiac tissue. In a 12-week study at 4,000, 10,000 and 15,000 ppm, 6 hours/day for 5 days/week, a NOEL/lowest observed adverse effect level for multifocal mononuclear infiltrates of the heart was 4,000 ppm. In a full inhalation developmental toxicity study at concentrations of 0, 4,000, 10,000 and 150,000 ppm, HCFO 1233zd(E) was not associated with any effects on uterine, placental or fetal weights, nor were there any fetal abnormalities observed so that the study resulted in a NOEL for developmental toxicity of 15,000 ppm.

Fluorinated substances. Sulfuryl fluoride (SO_2F_2) is a substitute for the ozone-depleting fumigant methyl bromide used on crops and soils. Several reports on its use in agriculture have been published recently[13, 16, 17, 134] and it will likely become more widely used in the future. As previously stated,[135] its atmospheric oxidation lifetime is estimated to be large (>300 years). However, SO_2F_2 is relatively soluble in water and is expected to partition into cloud water and ultimately rain out of the atmosphere with a half-life of about 2 weeks. The major sink is the oceans where the ultimate breakdown products are inorganic sulfate and fluoride. These breakdown products are not of concern for environment or health. However, SO_2F_2 has a large global warming potential (GWP) and its use is likely to increase in the future, so that monitoring of concentrations in the atmosphere should continue.

Hydrochlorofluorocarbons and hydrofluorocarbons (HCFCs and HFCs): As has been discussed previously,[135, 150] several of the hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) used as substitutes for ozone-depleting CFCs and a new fluorinated olefin (**HFO**) can break down into **trifluoroacetic acid (TFA)**. TFA is stable in the environment but is water soluble and accumulates in playas, land-locked lakes, and the oceans where it combines with cations such as sodium, potassium, calcium, and magnesium (Na^+, K^+, Ca^{++}, and Mg^{++}). More than 95% of the salts of TFA found in the oceans are naturally produced. These salts are inert and not of toxicological or environmental concern in the small concentrations (≈ 200 ng L^{-1}) that are present in the oceans.

Perfluoro-n-butyl iodide (PFBI) is a compound being investigated as a substitute for CFCs. Its use is being explored as a replacement in aircraft maintenance operations as an alternative cleaner for liquid and gaseous oxygen aerospace systems and as a wipe cleaner solvent. A recent publication[89] summarised earlier preliminary toxicity testing results in which an acute inhalation of no observed adverse effect level (NOAEL) of 3,900 ppm for cardiac sensitisation was established. Based on the results of a preliminary 4-week inhalation toxicity test, a 13-week inhalation study was conducted in which 15 male and 10 female rats per group were exposed by inhalation via nose-only exposure for 6 hours/day and 5 days/week to nominal concentrations of 500, 1,500, and 5,000 ppm PFBI. The 13-week inhalation exposure at 1,500 ppm was associated with increases in concentrations of thyroid hormones and thyroid stimulating hormone in serum of male and female rats. These concentrations returned to control values following the 4-week recovery period without exposure in males (the only animals given a recovery period). The authors noted that, based on published information, they assumed that the return to normal following the recovery period indicated that the hormonal changes were only transient and not adverse and that the changes in female rats would also return to normal. Thus the NOAEL was selected to be 1,500 ppm. The 3,900 ppm from the earlier work served as an occupational acute exposure limit for PFBI, while the 1,500 ppm NOAEL was converted to an occupational exposure limit (OEL) by adjusting it to an 8-hour/day time-weighted average exposure and applying uncertainty factors for animal to human, inter-human variability and subchronic to chronic extrapolation to arrive at a final value of 40 ppm.

Modelling of susceptibility of the analogous compound (perfluoro-n-propyl iodide) to photolysis suggested a half-life of a few hours in sunlight. Based on rapid degradation, PFBI has zero GWP and is not an ODS. Its atmospheric degradation is likely to produce trifluoro acetic acid (TFA), analogously to many other fluorinated organics, e.g., some HCFCs and HFCs (see above).

Hydrofluoroolefins (HFOs). Among the other new compounds being used as substitutes are those belonging to the class known as hydrofluoroolefins (HFOs). Two examples currently being developed for use in the refrigeration, foam-blowing and/or aerosol sectors, 1,3,3,3 tetrafluoropropene (HFO 1234ze) and 2,3,3,3 tetrafluoropropene (HFO-1234yf) have recently been characterised toxicologically.[119, 121, 137] In the case of HFO 1234ze, the compound was not acutely toxic at levels as high as 207,000 ppm following 4 hours of exposure and showed no activity in a battery of genetic toxicity tests. In addition, the compound did not induce cardiac sensitization at levels as high as 120,000. Following a 2 week range finding study at 5,000, 20,000 and 50,000 ppm 6 hours/day, 5 days/week, the liver and heart were identified as the target organs; however, in a subsequent 4 week study at 1000, 5,000, 10,000, and 15,000, and a 90 day study at 1,500, 5,000, and 15,000, only the heart was identified as the target organ. The associated finding was multifocal mononuclear cell infiltrates with no evidence of fibrosis and no evidence of increase severity with increased duration of exposure.

No new papers on the relevance of TFA to human health and the environment have been published in the literature since the date of the previous assessment (2010). Thus, projected future increased loadings of TFA to playas, land-locked lakes, and the oceans due to continued use of HCFCs, HFCs, and replacement products are still judged to present negligible risks for aquatic organisms and humans.

Gaps in knowledge

A key air quality constituent is ozone, and any future changes in ozone have significant outcomes for both human and environmental health. However, the direction and the magnitude of change in tropospheric ozone due to recovery of stratospheric ozone are still under debate, may depend on location, and need to be better quantified. Modulation by UV radiation will modify the impacts of climate change and regulation of local emissions. This represents a significant gap in our understanding. Computer modelling now has the potential to address this issue, but still requires the development and refinement of parameterisations for physical and chemical processes, as well as future scenarios under different socio-economic assumptions.

Particulate matter (aerosol) plays a significant role in climate change and also in air quality. While the role of UV radiation in PM formation is known, the sensitivity of PM properties to changes in UV radiation has not been sufficiently quantified.

The oxidation capacity of the atmosphere remains poorly characterised in a number of environmentally sensitive regions, with an order of magnitude difference between measurements and models. Both measurements and our understanding of the key chemical processes have large uncertainties. One example of this lack of understanding is the uncertainty in future methane concentrations, with models predicting •OH driven lifetimes that differ by a factor of 2.

References

1 Abrutzky R, 2012, Health effects of climate and air pollution in Buenos Aires: A first time series analysis, *J. Environ. Protect.*, **03**, 262-271.

2 Ainsworth EA, Yendrek CR, Sitch S, Collins WJ, Emberson LD, 2012, The effects of tropospheric ozone on net primary productivity and implications for climate change, *Annu. Rev. Plant Biol.*, **63**, 637-61.

3 Amann M, Klimont Z, Wagner F, 2013, Regional and Global Emissions of Air Pollutants: Recent Trends and Future Scenarios, *Ann. Rev Environ. Resources*, **38**, 31-55.

4 Anderson SE, Munson AE, Butterworth LF, Germolec D, Morgan DL, Roycroft JA, Dill J, Meade BJ, 2010, Whole-body inhalation exposure to 1-bromopropane suppresses the IgM response to sheep red blood cells in female B6C3F1 mice and Fisher 344/N rats, *Inhal Toxicol*, **22**, 125-132.

5 Anenberg SC, Horowitz LW, Tong DQ, West JJ, 2010, An estimate of the global burden of anthropogenic ozone and fine particulate matter on premature human mortality using atmospheric modeling, *Environ. Health Perspect.*, **118**, 1189-95.

6 Anenberg SC, West JJ, Horowitz LW, Tong DQ, 2011, The global burden of air pollution on mortality: Anenberg et al. respond, *Environ. Health Perspect.*, **119**, A158-159.

7 Anenberg SC, Schwartz J, Shindell D, Amann M, Faluvegi G, Klimont Z, Janssens-Maenhout G, Pozzoli L, Van Dingenen R, Vignati E, Emberson L, Muller NZ, West JJ, Williams M, Demkine V, Hicks WK, Kuylenstierna J, Raes F, Ramanathan V, 2012, Global air quality and health co-benefits of mitigating near-term climate change through methane and black carbon emission controls, *Environ. Health Perspect.*, **120**, 831-9.

8 Avnery S, Mauzerall DL, Liu J, Horowitz LW, 2011, Global crop yield reductions due to surface ozone exposure: 2. Year 2030 potential crop production losses and economic damage under two scenarios of O_3 pollution, *Atmos. Environ.*, **45**, 2297-2309.

9 Berresheim H, McGrath J, Adam M, Mauldin RL, Bohn B, Rohrer F, 2013, Seasonal measurements of OH, NOx, and J(O1D) at Mace Head, Ireland, *Geophys. Res. Lett.*, **40**, 1659-1663.

10 Betzelberger AM, Yendrek CR, Sun J, Leisner CP, Nelson RL, Ort DR, Ainsworth EA, 2012, Ozone exposure response for U.S. soybean cultivars: linear reductions in photosynthetic potential, biomass, and yield, *Plant Physiol.*, **160**, 1827-39.

11 Beygi ZH, Fischer H, Harder HD, Martinez M, Sander R, Williams J, Brookes DM, Monks PS, Lelieveld J, Ca VPN, 2011, Oxidation photochemistry in the Southern Atlantic boundary layer: unexpected deviations of photochemical steady state, *Atmos. Chem. Phys. Disc.*, **11**, 8497-8513.

12 Bi X, Simoneit BR, Sheng G, Ma S, Fu J, 2008, Composition and major sources of organic compounds in urban aerosols, *Atmos. Res.*, **88**, 256-265.

13 Bonifacio LF, Sousa E, Naves P, Inacio ML, Henriques J, Mota M, Barbosa P, Drinkall MJ, Buckley S, 2014, Efficacy of sulfuryl fluoride against the pinewood nematode, *Bursaphelenchus xylophilus* (Nematoda: Aphelenchidae), in *Pinus pinaster* boards, *Pest Manag. Sci.*, **70**, 6-13.

14 Brauers T, Hausmann M, Bister A, Kraus A, Dorn H-P, 2001, OH radicals in the boundary layer of the Atlantic Ocean: 1. Measurements by long-path laser absorption spectroscopy, *J. Geophys. Res.*, **106**, 7399.

15 Breider TJ, Chipperfield MP, Richards NAD, Carslaw KS, Mann GW, Spracklen DV, 2010, Impact of BrO on dimethylsulfide in the remote marine boundary layer, *Geophys. Res. Lett.*, **37**.

16 Buckman KA, Campbell JF, Subramanyam B, 2013, *Tribolium castaneum* (Coleoptera: Tenebrionidae) associated with tice mills: Fumigation efficacy and population rebound, *J. Econ. Entomol.*, **106**, 499-512.

17 Cao A, Guo M, Yan D, Mao L, Wang Q, Li Y, Duan X, Wang P, 2014, Evaluation of sulfuryl fluoride as a soil fumigant in China, *Pest Manag. Sci.*, **70**, 219-27.

18 Cappa CD, Wilson KR, 2012, Multi-generation gas-phase oxidation, equilibrium partitioning, and the formation and evolution of secondary organic aerosol, *Atmos. Chem. Phys.*, **12**, 9505-9528.

19 Carslaw KS, Boucher O, Spracklen DV, Mann GW, Rae JGL, Woodward S, Kulmala M, 2010, A review of natural aerosol interactions and feedbacks within the Earth system1737, *Atmos. Chem. Phys.*, **10**, 1701-1737.

20 Chen S, Ren X, Mao J, Chen Z, Brune WH, Lefer B, Rappenglück B, Flynn J, Olson J, Crawford JH, 2010, A comparison of chemical mechanisms based on TRAMP-2006 field data, *Atmos. Environ.*, **44**, 4116-4125.

21 Chen Y, Ebenstein A, Greenstone M, Li H, 2013, Evidence on the impact of sustained exposure to air pollution on life expectancy from China's Huai River policy, *Proc. Natl. Acad. Sci.*, **110**, 12936-12941.

22 Colette A, Granier C, Hodnebrog Ø, Jakobs H, Maurizi A, Nyiri A, Bessagnet B, D'Angiola A, D'Isidoro M, Gauss M, Meleux F, Memmesheimer M, Mieville A, Rouïl L, Russo F, Solberg S, Stordal F, Tampieri F, 2011, Air quality trends in Europe over the past decade: a first multi-model assessment, *Atmos. Chem. Phys.*, **11**, 11657-11678.

23 Colette A, Bessagnet B, Vautard R, Szopa S, Rao S, Schucht S, Klimont Z, Menut L, Clain G, Meleux F, Curci G, Rouil L, 2013, European atmosphere in 2050, a regional air quality and climate perspective under CMIP5 scenarios, *Atmos. Chem. Phys.*, **13**, 7451-7471.

24 Cooper OR, Parrish DD, Stohl A, Trainer M, Nedelec P, Thouret V, Cammas JP, Oltmans SJ, Johnson BJ, Tarasick D, Leblanc T, McDermid IS, Jaffe D, Gao R, Stith J, Ryerson T, Aikin K, Campos T, Weinheimer A, Avery MA, 2010, Increasing springtime ozone mixing ratios in the free troposphere over western North America, *Nature*, **463**, 344-8.

25 Correia AW, Pope CA, 3rd, Dockery DW, Wang Y, Ezzati M, Dominici F, 2013, Effect of air pollution control on life expectancy in the United States: an analysis of 545 U.S. counties for the period from 2000 to 2007, *Epidemiol.*, **24**, 23-31.

26 Croft B, Pierce JR, Martin RV, Hoose C, Lohmann U, 2012, Uncertainty associated with convective wet removal of entrained aerosols in a global climate model, *Atmos. Chem. Phys.*, **12**, 10725-10748.

27 Croft B, Pierce JR, Martin RV, 2014, Interpreting aerosol lifetimes using the GEOS-Chem model and constraints from radionuclide measurements, *Atmos. Chem. Phys.*, **14**, 4313-4325.

28 D'Amato G, Cecchi L, D'Amato M, Liccardi G, 2010, Urban air pollution and climate change as environmental risk factors of respiratory allergy: an update, *J Investig Allergol Clin Immunol*, **20**, 95-102.

29 Dales RE, Cakmak S, Vidal CB, 2010, Air pollution and hospitalization for venous thromboembolic disease in Chile, *J. Thromb. Haemost.*, **8**, 669-74.

30 de Almeida SP, Casimiro E, Calheiros J, 2011, Short-term association between exposure to ozone and mortality in Oporto, Portugal, *Environ. Res.*, **111**, 406-10.

31 Demuzere M, van Lipzig NPM, 2010, A new method to estimate air-quality levels using a synoptic-regression approach. Part II: Future O3 concentrations, *Atmos. Environ.*, **44**, 1356-1366.

32 Derwent RG, Manning AJ, Simmonds PG, Spain TG, O'Doherty S, 2013, Analysis and interpretation of 25 years of ozone observations at the Mace Head Atmospheric Research Station on the Atlantic Ocean coast of Ireland from 1987 to 2012, *Atmos. Environ.*, **80**, 361-368.
33 Donahue NM, Henry KM, Mentel TF, Kiendler-Scharr A, Spindler C, Bohn B, Brauers T, Dorn HP, Fuchs H, Tillmann R, Wahner A, Saathoff H, Naumann K-H, Möhler O, Leisner T, Müller L, Reinnig M-C, Hoffmann T, Salo K, Hallquist M, Frosch M, Bilde M, Tritscher T, Barmet P, Praplan AP, DeCarlo PF, Dommen J, Prévôt ASH, Baltensperger U, 2012, Aging of biogenic secondary organic aerosol via gas-phase OH radical reactions, *Proc. Natl. Acad. Sci.*, **109**, 13503–13508.
34 Dusanter S, Vimal D, Stevens PS, Volkamer R, Molina LT, Baker A, Meinardi S, Blake D, Sheehy P, Merten A, Zhang R, Zheng J, Fortner EC, Junkermann W, Dubey M, Rahn T, Eichinger B, Lewandowski P, Prueger J, Holder H, 2009, Measurements of OH and HO_2 concentrations during the MCMA-2006 field campaign – Part 2: Model comparison and radical budget, *Atmos. Chem. Phys.*, **9**, 6655-6675.
35 Fang Y, Naik V, Horowitz LW, Mauzerall DL, 2013, Air pollution and associated human mortality: the role of air pollutant emissions, climate change and methane concentration increases from the preindustrial period to present, *Atmos. Chem. Phys. Disc.*, **13**, 1377–1394.
36 Fann N, Lamson AD, Anenberg SC, Wesson K, Risley D, Hubbell BJ, 2012, Estimating the national public health burden associated with exposure to ambient PM2.5 and ozone, *Risk Anal.*, **32**, 81-95.
37 Fares S, Vargas R, Detto M, Goldstein AH, Karlik J, Paoletti E, Vitale M, 2013, Tropospheric ozone reduces carbon assimilation in trees: estimates from analysis of continuous flux measurements, *Glob. Change Biol.*, **19**, 2427-43.
38 Feng Y, Lin X, Yu Y, Zhang H, Chu H, Zhu J, 2013, Elevated ground-level O_3 negatively influences paddy methanogenic archaeal community, *Sci. Rep.*, **3**, 3193.
39 Fischer PH, Brunekreef B, Lebret E, 2004, Air pollution related deaths during the 2003 heat wave in the Netherlands, *Atmos. Environ.*, **38**, 1083-1085.
40 Fuchs H, Dorn HP, Bachner M, Bohn B, Brauers T, Gomm S, Hofzumahaus A, Holland F, Nehr S, Rohrer F, Tillmann R, Wahner A, 2012, Comparison of OH concentration measurements by DOAS and LIF during SAPHIR chamber experiments at high OH reactivity and low NO concentration, *Atmos. Measure. Tech. Disc.*, **5**, 2077-2110.
41 Fuchs H, Hofzumahaus A, Rohrer F, Bohn B, Brauers T, Dorn HP, Haseler R, Holland F, Kaminski M, Li X, Lu K, Nehr S, Tillmann R, Wegener R, Wahner A, 2013, Experimental evidence for efficient hydroxyl radical regeneration in isoprene oxidation, *Nature Geosci*, **6**, 1023-1026.
42 Gan CM, Pleim J, Mathur R, Hogrefe C, Long CN, Xing J, Roselle S, Wei C, 2014, Assessment of the effect of air pollution controls on trends in shortwave radiation over the United States from 1995 through 2010 from multiple observation networks, *Atmos. Chem. Phys.*, **14**, 1701-1715.
43 Griffith SM, Hansen RF, Dusanter S, Stevens PS, Alaghmand M, Bertman SB, Carroll MA, Erickson M, Galloway M, Grossberg N, Hottle J, Hou J, Jobson BT, Kammrath A, Keutsch FN, Lefer BL, Mielke LH, O'Brien A, Shepson PB, Thurlow M, Wallace W, Zhang N, Zhou XL, 2013, OH and HO_2 radical chemistry during PROPHET 2008 and CABINEX 2009 -- Part 1: Measurements and model comparison, *Atmos. Chem. Phys.*, **13**, 5403-5423.
44 Haagen-Smit AJ, Bradley CE, Fox MM, 1953, Ozone formation in photochemical oxidation of organic substances, *Indust. Eng. Chem. Res.*, **45**, 2086-2089.
45 Hand JL, Schichtel BA, Pitchford M, Malm WC, Frank NH, 2012, Seasonal composition of remote and urban fine particulate matter in the United States, *Journal of Geophysical Research: Atmospheres*, **117**, D05209.
46 Heald CL, Kroll JH, Jimenez JL, Docherty KS, DeCarlo PF, Aiken AC, Chen Q, Martin ST, Farmer DK, Artaxo P, 2010, A simplified description of the evolution of organic aerosol composition in the atmosphere, *Geophys. Res. Lett.*, **37**, L08803.
47 Heard DE, Pilling MJ, 2003, Measurement of OH and HO_2 in the troposphere, *Chem. Rev.*, **103**, 5163-98.
48 Hess PG, Zbinden R, 2013, Stratospheric impact on tropospheric ozone variability and trends: 1990-2009, *Atmospheric Chemistry & Physics*, **13**, 649-674.
49 Hilboll A, Richter A, Burrows JP, 2013, Long-term changes of tropospheric NO_2 over megacities derived from multiple satellite instruments, *Atmos. Chem. Phys.*, **13**, 4145-4169.
50 Hodzic A, Madronich S, Aumont B, Lee-Taylor J, Karl T, Camredon M, Mouchel-Vallon C, 2013, Limited influence of dry deposition of semivolatile organic vapors on secondary organic aerosol formation in the urban plume, *Geophys. Res. Lett.*, **40**, 3302-3307.
51 Hofzumahaus A, Rohrer F, Lu K, Bohn B, Brauers T, Chang CC, Fuchs H, Holland F, Kita K, Kondo Y, Li X, Lou S, Shao M, Zeng L, Wahner A, Zhang Y, 2009, Amplified trace gas removal in the troposphere, *Science.*, **324**, 1702-4.

52 Holmes CD, Prather MJ, Søvde OA, Myhre G, 2013, Future methane, hydroxyl, and their uncertainties: key climate and emission parameters for future predictions, *Atmos. Chem. Phys.*, **13**, 285-302.

53 Hossaini R, Hossaini R, Chipperfield MP, Monge-Sanz BM, Richards NAD, Atlas E, Blake DR, 2010, Bromoform and dibromomethane in the tropics: a 3-D model study of chemistry and transport, *Atmos. Chem. Phys.*, **10**, 719-735.

54 Hsieh YL, Yang YH, Wu TN, Yang CY, 2010, Air pollution and hospital admissions for myocardial infarction in a subtropical city: Taipei, Taiwan, *J. Toxicol. Environ. Hlth. A.*, **73**, 757-65.

55 Hůnová I, Malý M, Řezáčová J, Braniš.Martin, 2012, Association between ambient ozone and health outcomes in Prague, *Int. Arch. Occup. Environ. Hlth.*, **86**, 89-97.

56 IPCC, 2000, Special Report on Emissions Scenarios: A Special Report of Working Group III of the Intergovernmental Panel on Climate Change, Intergovernmental Panel on Climate Change Report No., Geneva

57 IPCC, 2014, Climate Change 2014: Mitigation of Climate Change. Contribution of Working Group III to the Fifth Assessment Report, Intergovernmental Panel on Climate Change Report No., Geneva

58 Jacob DJ, Winner DA, 2009, Effect of climate change on air quality, *Atmos. Environ.*, **43**, 51-63.

59 Jaggard KW, Qi A, Ober ES, 2010, Possible changes to arable crop yields by 2050, *Philos. Trans. Roy. Soc. Lond. B.*, **365**, 2835-51.

60 Jimenez-Guerrero P, Gomez-Navarro JJ, Baro R, Lorente R, Ratola N, Montavez JP, 2013, Is there a common pattern of future gas-phase air pollution in Europe under diverse climate change scenarios?, *Clim.Change*, **121**, 661-671.

61 Jimenez JL, Canagaratna MR, Donahue NM, Prevot ASH, Zhang Q, Kroll JH, DeCarlo PF, Allan JD, Coe H, Ng NL, Aiken AC, Docherty KS, Ulbrich IM, Grieshop AP, Robinson AL, Duplissy J, Smith JD, Wilson KR, Lanz VA, Hueglin C, Sun YL, Tian J, Laaksonen A, Raatikainen T, Rautiainen J, Vaattovaara P, Ehn M, Kulmala M, Tomlinson JM, Collins DR, Cubison MJE, Dunlea J, Huffman JA, Onasch TB, Alfarra MR, Williams PI, Bower K, Kondo Y, Schneider J, Drewnick F, Borrmann S, Weimer S, Demerjian K, Salcedo D, Cottrell L, Griffin R, Takami A, Miyoshi T, Hatakeyama S, Shimono A, Sun JY, Zhang YM, Dzepina K, Kimmel JR, Sueper D, Jayne JT, Herndon SC, Trimborn AM, Williams LR, Wood EC, Middlebrook AM, Kolb CE, Baltensperger U, Worsnop DR, 2009, Evolution of organic aerosols in the atmosphere, *Science.*, **326**, 1525-1529.

62 John JG, Fiore AM, Naik V, Horowitz LW, Dunne JP, 2012, Climate versus emission drivers of methane lifetime against loss by tropospheric OH from 1860–2100, *Atmos. Chem. Phys.*, **12**, 12021-12036.

63 Kanaya Y, Cao R, Akimoto H, Fukuda M, Komazaki Y, Yokouchi Y, Koike M, Tanimoto H, Takegawa N, Kondo Y, 2007, Urban photochemistry in central Tokyo: 1. Observed and modeled OH and HO2radical concentrations during the winter and summer of 2004, *J. Geophys. Res.*, **112**, 10.1029/2007JD008670.

64 Kaplan GG, Tanyingoh D, Dixon E, Johnson M, Wheeler AJ, Myers RP, Bertazzon S, Saini V, Madsen K, Ghosh S, Villeneuve PJ, 2013, Ambient ozone concentrations and the risk of perforated and nonperforated appendicitis: a multicity case-crossover study, *Environ. Health Perspect.*, **121**, 939-43.

65 Katragkou E, Zanis P, Kioutsioukis I, Tegoulias I, Melas D, Krüger BC, Coppola E, 2011, Future climate change impacts on summer surface ozone from regional climate-air quality simulations over Europe, *J. Geophys. Res.*, **116**.

66 Khan MAH, Whelan ME, Rhew RC, 2012, Effects of temperature and soil moisture on methyl halide and chloroform fluxes from drained peatland pasture soils, *J. Environ. Monit.*, **14**, 241-249.

67 Kristiansen NI, Stohl A, Wotawa G, 2012, Atmospheric removal times of the aerosol-bound radionuclides ^{137}Cs and ^{131}I measured after the Fukushima Dai-ichi nuclear accident -- a constraint for air quality and climate models, *Atmos. Chem. Phys.*, **12**, 10759-10769.

68 Kroll JH, Donahue NM, Jimenez JL, Kessler SH, Canagaratna MR, Wilson KR, Altieri KE, Mazzoleni LR, Wozniak AS, Bluhm H, Mysak ER, Smith JD, Kolb CE, Worsnop DR, 2011, Carbon oxidation state as a metric for describing the chemistry of atmospheric organic aerosol, *Nature Chem.*, **3**, 133-139.

69 Kubistin D, Harder H, Martinez M, Rudolf M, Sander R, Bozem H, Eerdekens G, Fischer H, Gurk C, Klüpfel T, Königstedt R, Parchatka U, Schiller CL, Stickler A, Taraborrelli D, Williams J, Lelieveld J, 2010, Hydroxyl radicals in the tropical troposphere over the Suriname rainforest: comparison of measurements with the box model MECCA, *Atmos. Chem. Phys.*, **10**, 9705-9728.

70 Lal DM, Ghude SD, Patil SD, Kulkarni SH, Jena C, Tiwari S, Srivastava MK, 2012, Tropospheric ozone and aerosol long-term trends over the Indo-Gangetic Plain (IGP), India, *Atmos. Res.*, **116**, 82-92.

71 Lee JT, Cho YS, Son JY, 2010, Relationship between ambient ozone concentrations and daily hospital admissions for childhood asthma/atopic dermatitis in two cities of Korea during 2004-2005, *Int. J. Environ. Hlth. Res.*, **20**, 1-11.

72 Lei H, Wuebbles DJ, Liang X-Z, 2012, Projected risk of high ozone episodes in 2050, *Atmos. Environ.*, **59**, 567-577.

73 Lei H, Wuebbles DJ, Liang X-Z, Olsen S, 2013, Domestic versus international contributions on 2050 ozone air quality: How much is convertible by regional control?, *Atmos. Environ.*, **68**, 315-325.

74 Leisner CP, Ainsworth EA, 2011, Quantifying the effects of ozone on plant reproductive growth and development, *Glob. Change Biol.*, **18**, 606-616.

75 Lelieveld J, Butler TM, Crowley JN, Dillon TJ, Fischer H, Ganzeveld L, Harder H, Lawrence MG, Martinez M, Taraborrelli D, Williams J, 2008, Atmospheric oxidation capacity sustained by a tropical forest, *Nature*, **452**, 737-40.

76 Li G, Lei W, Zavala M, Volkamer R, Dusanter S, Stevens P, Molina LT, 2010, Impacts of HONO sources on the photochemistry in Mexico City during the MCMA-2006/MILAGO Campaign, *Atmos. Chem. Phys.*, **10**, 6551-6567.

77 Liang Q, Newman PA, Daniel JS, Reimann S, Hall BD, Dutton G, Kuijpers LJM, 2014, Constraining the carbon tetrachloride (CCl_4) budget using its global trend and inter-hemispheric gradient, *Geophys. Res. Lett.*, **41**, 2014GL060754.

78 Lim SS, Vos T, Flaxman AD, Danaei G, Shibuya K, Adair-Rohani H, AlMazroa MA, Amann M, Anderson HR, Andrews KG, Aryee M, Atkinson C, Bacchus LJ, Bahalim AN, Balakrishnan K, Balmes J, Barker-Collo S, Baxter A, Bell ML, Blore JD, Blyth F, Bonner C, Borges G, Bourne R, Boussinesq M, Brauer M, Brooks P, Bruce NG, Brunekreef B, Bryan-Hancock C, Bucello C, Buchbinder R, Bull F, Burnett RT, Byers TE, Calabria B, Carapetis J, Carnahan E, Chafe Z, Charlson F, Chen H, Chen JS, Cheng AT-A, Child JC, Cohen A, Colson KE, Cowie BC, Darby S, Darling S, Davis A, Degenhardt L, Dentener F, Des Jarlais DC, Devries K, Dherani M, Ding EL, Dorsey ER, Driscoll T, Edmond K, Ali SE, Engell RE, Erwin PJ, Fahimi S, Falder G, Farzadfar F, Ferrari A, Finucane MM, Flaxman S, Fowkes FGR, Freedman G, Freeman MK, Gakidou E, Ghosh S, Giovannucci E, Gmel G, Graham K, Grainger R, Grant B, Gunnell D, Gutierrez HR, Hall W, Hoek HW, Hogan A, Hosgood Iii HD, Hoy D, Hu H, Hubbell BJ, Hutchings SJ, Ibeanusi SE, Jacklyn GL, Jasrasaria R, Jonas JB, Kan H, Kanis JA, Kassebaum N, Kawakami N, Khang Y-H, Khatibzadeh S, Khoo J-P, Kok C, et al., 2012, A comparative risk assessment of burden of disease and injury attributable to 67 risk factors and risk factor clusters in 21 regions, 1990–2010: a systematic analysis for the Global Burden of Disease Study 2010, *The Lancet*, **380**, 2224-2260.

79 Lin M, Horowitz LW, Oltmans SJ, Fiore AM, Fan S, 2014, Tropospheric ozone trends at Mauna Loa Observatory tied to decadal climate variability, *Nature Geosci.*, **7**, 136-143.

80 Liu SC, Trainer M, 1988, Responses of the tropospheric ozone and odd hydrogen radicals to column ozone change, *J. Atmos. Chem.*, **6**, 221-233.

81 Lou S, Holland F, Rohrer F, Lu K, Bohn B, Brauers T, Chang CC, Fuchs H, Häseler R, Kita K, Kondo Y, Li X, Shao M, Zeng L, Wahner A, Zhang Y, Wang W, Hofzumahaus A, 2010, Atmospheric OH reactivities in the Pearl River Delta – China in summer 2006: measurement and model results, *Atmos. Chem. Phys.*, **10**, 11243-11260.

82 Lu KD, Rohrer F, Holland F, Fuchs H, Bohn B, Brauers T, Chang CC, Häseler R, Hu M, Kita K, Kondo Y, Li X, Lou SR, Nehr S, Shao M, Zeng LM, Wahner A, Zhang YH, Hofzumahaus A, 2012, Observation and modelling of OH and HO_2 concentrations in the Pearl River Delta 2006: a missing OH source in a VOC rich atmosphere, *Atmos. Chem. Phys.*, **12**, 1541-1569.

83 Lu KD, Hofzumahaus A, Holland F, Bohn B, Brauers T, Fuchs H, Hu M, Häseler R, Kita K, Kondo Y, Li X, Lou SR, Oebel A, Shao M, Zeng LM, Wahner A, Zhu T, Zhang YH, Rohrer F, 2013, Missing OH source in a suburban environment near Beijing: observed and modelled OH and HO_2 concentrations in summer 2006, *Atmos. Chem. Phys.*, **13**, 1057-1080.

84 Malaguarnera G, Cataudella E, Giordano M, Nunnari G, Chisari G, Malaguarnera M, 2012, Toxic hepatitis in occupational exposure to solvents, *World J. Gastroenterol.*, **18**, 2756-2766.

85 Mao J, Ren X, Zhang L, Van Duin DM, Cohen RC, Park JH, Goldstein AH, Paulot F, Beaver MR, Crounse JD, Wennberg PO, DiGangi JP, Henry SB, Keutsch FN, Park C, Schade GW, Wolfe GM, Thornton JA, Brune WH, 2012, Insights into hydroxyl measurements and atmospheric oxidation in a California forest, *Atmos. Chem. Phys.*, **12**, 8009-8020.

86 Martin JCG, Mahajan AS, Hay TD, Prados-Roman C, Ordonez C, MacDonald SM, Plane JMC, Sorribas M, Gil M, Mora JFP, Reyes MVA, Oram DE, Leedham E, Saiz-Lopez A, 2013, Iodine chemistry in the eastern Pacific marine boundary layer, *J. Geophys. Res. Atmos.*, **118**, 887-904.

87 Martin RV, Sioris CE, Chance K, Ryerson TB, Bertram TH, Wooldridge PJ, Cohen RC, Neuman JA, Swanson A, Flocke FM, 2006, Evaluation of space-based constraints on global nitrogen oxide

emissions with regional aircraft measurements over and downwind of eastern North America, *J. Geophys. Res. Atmos.*, **111**, D15308.
88 Martinez M, Harder H, Kubistin D, Rudolf M, Bozem H, Eerdekens G, Fischer H, Klüpfel T, Gurk C, Königstedt R, Parchatka U, Schiller CL, Stickler A, Williams J, Lelieveld J, 2010, Hydroxyl radicals in the tropical troposphere over the Suriname rainforest: airborne measurements, *Atmos. Chem. Phys.*, **10**, 3759-3773.
89 Mattie DR, Hoffman GM, Narayanan L, Sterner TR, Wagner MJ, Dodd DE, 2010, A 13-week nose-only inhalation toxicity study for perfluoro-n-butyl iodide (PFBI) in rats with recommended occupational exposure levels, *Inhal Toxicol*, **22**, 847-60.
90 McKenzie RL, Aucamp PJ, Bais AF, Björn LO, Ilyas M, Madronich S, 2011, Ozone depletion and climate change: Impacts on UV radiation, *Photochem. Photobiol. Sci.*, **10**, 182-198.
91 Monteil G, Houweling S, Dlugockenky EJ, Maenhout G, Vaughn BH, White JWC, Rockmann T, 2011, Interpreting methane variations in the past two decades using measurements of CH_4 mixing ratio and isotopic composition, *Atmos. Chem. Phys.*, **11**, 9141-9153.
92 Montzka SA, Dlugokencky EJ, Butler JH, 2011, Non-CO_2 greenhouse gases and climate change, *Nature*, **476**, 43-50.
93 Morgenstern O, Zeng G, Luke Abraham N, Telford PJ, Braesicke P, Pyle JA, Hardiman SC, O'Connor FM, Johnson CE, 2013, Impacts of climate change, ozone recovery, and increasing methane on surface ozone and the tropospheric oxidizing capacity, *J. Geophys. Res. Atmos.*, **118**, 1028-1041.
94 Naik V, Voulgarakis A, Fiore AM, Horowitz LW, Lamarque JF, Lin M, Prather MJ, Young PJ, Bergmann D, Cameron-Smith PJ, Cionni I, Collins WJ, Dalsøren SB, Doherty R, Eyring V, Faluvegi G, Folberth GA, Josse B, Lee YH, MacKenzie IA, Nagashima T, van Noije TPC, Plummer DA, Righi M, Rumbold ST, Skeie R, Shindell DT, Stevenson DS, Strode S, Sudo K, Szopa S, Zeng G, 2013, Preindustrial to present day changes in tropospheric hydroxyl radical and methane lifetime from the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP), *Atmos. Chem. Phys.*, **13**, 5277–5298.
95 Nakashima Y, Kato S, Greenberg J, Harley P, Karl T, Turnipseed A, Apel E, Guenther A, Smith J, Kajii Y, 2014, Total OH reactivity measurements in ambient air in a southern Rocky mountain ponderosa pine forest during BEACHON-SRM08 summer campaign, *Atmos. Environ.*, **85**, 1-8.
96 Neu JL, Flury T, Manney GL, Santee ML, Livesey NJ, Worden J, 2014, Tropospheric ozone variations governed by changes in stratospheric circulation, *Nature Geosci*, **7**, 340-344.
97 Nölscher AC, Williams J, Sinha V, Custer T, Song W, Johnson AM, Axinte R, Bozem H, Fischer H, Pouvesle N, Phillips G, Crowley JN, Rantala P, Rinne J, Kulmala M, Gonzales D, Valverde-Canossa J, Vogel A, Hoffmann T, Ouwersloot HG, Vilà-Guerau de Arellano J, Lelieveld J, 2012, Summertime total OH reactivity measurements from boreal forest during HUMPPA-COPEC 2010, *Atmos. Chem. Phys. Disc.*, **12**, 7419-7452.
98 NTP, 2011, Toxicology and Carcinogenesis Studies of 1-Bromopropane (CAS No. 106-94-5) in F344/N Rats and B6C3F1 Mice (Inhalation Studies), National Toxicology Program Report No. NTP TR 564, Research Triangle Park, NC, August 2011, p. 195
99 OECD, 2012, OECD Environmental Outlook to 2050: The Consequences of Inaction: Key Findings on Health and Environment, Organization for Economic Cooperation and Development Report No., Paris. http://www.oecd.org/environment/outlookto2050
100 Oltmans SJ, Lefohn AS, Shadwick D, Harris JM, Scheel HE, Galbally I, Tarasick DW, Johnson BJ, Brunke EG, Claude H, Zeng G, Nichol S, Schmidlin F, Davies J, Cuevas E, Redondas A, Naoe H, Nakano T, Kawasato T, 2013, Recent tropospheric ozone changes – A pattern dominated by slow or no growth, *Atmos. Environ.*, **67**, 331-351.
101 Paasonen P, Asmi A, Petäjä T, Kajos MK, Äijälä M, Junninen H, Holst T, Abbatt JPD, Arneth A, Birmili W, van der Gon HD, Hamed A, Hoffer A, Laakso L, Laaksonen A, Richard Leaitch W, Plass-Dülmer C, Pryor SC, Räisänen P, Swietlicki E, Wiedensohler A, Worsnop DR, Kerminen V-M, Kulmala M, 2013, Warming-induced increase in aerosol number concentration likely to moderate climate change, *Nature Geosci.*, **6**, 438-442.
102 Pankow JF, Barsanti KC, 2009, The carbon number-polarity grid: A means to manage the complexity of the mix of organic compounds when modeling atmospheric organic particulate matter, *Atmos. Environ.*, **43**, 2829-2835.
103 Parrish DD, Singh HB, Molina L, Madronich S, 2011, Air quality progress in North American megacities: A review, *Atmos. Environ.*, **45**, 7015-7025.
104 Parrish DD, Law KS, Staehelin J, Derwent R, Cooper OR, Tanimoto H, Volz-Thomas A, Gilge S, Scheel HE, Steinbacher M, Chan E, 2013, Lower tropospheric ozone at northern midlatitudes: Changing seasonal cycle, *Geophys. Res. Lett.*, **40**, 1631-1636.

105 Parrish DD, Lamarque JF, Naik V, Horowitz L, Shindell DT, Staehelin J, Derwent R, Cooper OR, Tanimoto H, Volz-Thomas A, Gilge S, Scheel HE, Steinbacher M, Fröhlich M, 2014, Long-term changes in lower tropospheric baseline ozone concentrations: Comparing chemistry-climate models and observations at northern mid-latitudes, *J. Geophys. Res. Atmos.*, 2013JD021435.

106 Pattenden S, Armstrong B, Milojevic A, Heal MR, Chalabi Z, Doherty R, Barratt B, Kovats RS, Wilkinson P, 2010, Ozone, heat and mortality: Acute effects in 15 British conurbations, *Occ. Environ. Med.*, **67**, 699-707.

107 Paulot F, Crounse JD, Kjaergaard HG, Kroll JH, Seinfeld JH, Wennberg PO, 2009, Isoprene photooxidation: new insights into the production of acids and organic nitrates, *Atmos. Chem. Phys.*, **9**, 1479-1501.

108 Peeters J, Muller JF, 2010, HO(x) radical regeneration in isoprene oxidation via peroxy radical isomerisations. II: experimental evidence and global impact, *Phys Chem Chem Phys*, **12**, 14227-35.

109 Pike RC, Young PJ, 2009, How plants can influence tropospheric chemistry: The role of isoprene emissions from the biosphere, *Weather*, **64**, 332-336.

110 Post ES, Grambsch A, Weaver C, Morefield P, Huang J, Leung LY, Nolte CG, Adams P, Liang XZ, Zhu JH, Mahoney H, 2012, Variation in estimated ozone-related health Impacts of climate change due to modeling choices and assumptions, *Environ. Health Perspect.*, **120**, 1559-1564.

111 Prueitt RL, Goodman RL, 2011, The global burden of ozone on respiratory mortality: No clear evidence for association, *Environ. Health Perspect.*, **119**, A158.

112 Pugh TAM, MacKenzie AR, Hewitt CN, Langford B, Edwards PM, Furneaux KL, Heard DE, Hopkins JR, Jones CE, Karunaharan A, Lee J, Mills G, Misztal P, Moller S, Monks PS, Whalley LK, 2010, Simulating atmospheric composition over a South-East Asian tropical rainforest: performance of a chemistry box model, *Atmos. Chem. Phys.*, **10**, 279-298.

113 Read KA, Mahajan AS, Carpenter LJ, Evans MJ, Faria BVE, Heard DE, Hopkins JR, Lee JD, Moller SJ, Lewis AC, Mendes L, McQuaid JB, Oetjen H, Saiz-Lopez A, Pilling MJ, Plane JMC, 2008, Extensive halogen-mediated ozone destruction over the tropical Atlantic Ocean, *Nature*, **453**, 1232-1235.

114 Ren C, O'Neill MS, Park SK, Sparrow D, Vokonas P, Schwartz J, 2011, Ambient temperature, air pollution, and heart rate variability in an aging population, *Am. J. Epid.*, **173**, 1013-21.

115 Ren X, Brune WH, Mao J, Mitchell MJ, Lesher RL, Simpas JB, Metcalf AR, Schwab JJ, Cai C, Li Y, 2006, Behavior of OH and HO2 in the winter atmosphere in New York City, *Atmos. Environ.*, **40**, 252-263.

116 Ren X, Mao J, Brune WH, Cantrell CA, Mauldin Iii RL, Hornbrook RS, Kosciuch E, Olson JR, Crawford JH, Chen G, Singh HB, 2012, Airborne intercomparison of HO_x measurements using laser-induced fluorescence and chemical ionization mass spectrometry during ARCTAS, *Atmos. Measure. Tech. Disc.*, **5**, 2529-2565.

117 Rohrer F, Berresheim H, 2006, Strong correlation between levels of tropospheric hydroxyl radicals and solar ultraviolet radiation, *Nature*, **442**, 184-7.

118 Royal Society, 2008, Ground-level ozone in the 21st century: future trends, impacts and policy implications, The Royal Society Report No. RS Policy document 15/08, London, UK, October 2008, p. 148. http://royalsociety.org/policy/publications/2008/ground-level-ozone/

119 Rusch GM, Tveit A, Muijser H, Tegelenbosch-Schouten MM, Hoffman GM, 2013, The acute, genetic, developmental and inhalation toxicology of trans-1,3,3,3-tetrafluoropropene (HFO-1234ze), *Drug Chem. Toxicol.*, **36**, 170-80.

120 Schlosser E, Brauers T, Dorn HP, Fuchs H, Häseler R, Hofzumahaus A, Holland F, Wahner A, Kanaya Y, Kajii Y, Miyamoto K, Nishida S, Watanabe K, Yoshino A, Kubistin D, Martinez M, Rudolf M, Harder H, Berresheim H, Elste T, Plass-Dülmer C, Stange G, Schurath U, 2009, Technical Note: Formal blind intercomparison of OH measurements: results from the international campaign HOxComp, *Atmos. Chem. Phys.*, **9**, 7923-7948.

121 Schmidt T, Bertermann R, Rusch GM, Hoffman GM, Dekant W, 2012, Biotransformation of 2,3,3,3-tetrafluoropropene (HFO-1234yf) in male, pregnant and non-pregnant female rabbits after single high dose inhalation exposure, *Toxicol. Appl. Pharmacol.*, **263**, 32-8.

122 Seinfeld JH, Pandis SN, 2006, *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, John Wiley & Sons, Hoboken, NJ, USA.

123 Shindell DT, Lamarque JF, Schulz M, Flanner M, Jiao C, Chin M, Young PJ, Lee YH, Rotstayn L, Mahowald N, Milly G, Faluvegi G, Balkanski Y, Collins WJ, Conley AJ, Dalsoren S, Easter R, Ghan S, Horowitz L, Liu X, Myhre G, Nagashima T, Naik V, Rumbold ST, Skeie R, Sudo K, Szopa S, Takemura T, Voulgarakis A, Yoon JH, Lo F, 2013, Radiative forcing in the ACCMIP historical and future climate simulations, *Atmos. Chem. Phys.*, **13**, 2939-2974.

124 Simmonds PG, Derwent RG, Manning AJ, O'Doherty S, Spain G, 2010, Natural chloroform emissions from the blanket peat bogs in the vicinity of Mace Head, Ireland over a 14-year period, *Atmos. Environ.*, **44**, 1284-1291.

125 Sinha V, Williams J, Lelieveld J, Ruuskanen TM, Kajos MK, Patokoski J, Hellen H, Hakola H, Mogensen D, Boy M, Rinne J, Kulmala M, 2010, OH reactivity neasurements within a boreal forest: Evidence for unknown reactive emissions, *Environ. Sci. Technol.*, **44**, 6614-6620.

126 Smith SJ, Bond TC, 2013, Two hundred fifty years of aerosols and climate: the end of the age of aerosols, *Atmos. Chem. Phys. Discuss.*, **13**, 6419-6453.

127 Sofen ED, Alexander B, Kunasek SA, 2011, The impact of anthropogenic emissions on atmospheric sulfate production pathways, oxidants, and ice core $\Delta^{17}O(SO_4^{2-})$, *Atmos. Chem. Phys.*, **11**, 3565-3578.

128 Sommariva R, Haggerstone AL, Carpenter LJ, Carslaw N, Creasey DJ, Heard DE, Lee JD, Lewis AC, Pilling MJ, Zádor J, 2004, OH and HO2 chemistry in clean marine air during SOAPEX-2, *Atmos. Chem. Phys.*, **4**, 839-856.

129 Spickett JT, Brown HL, Rumchev K, 2011, Climate change and air quality: the potential impact on health, *Asia Pac J Public Health*, **23**, 37S-45.

130 Stedman JR, 2004, The predicted number of air pollution related deaths in the UK during the August 2003 heatwave, *Atmos. Environ.*, **38**, 1087-1090.

131 Stevenson DS, Young PJ, Naik V, Lamarque JF, Shindell DT, Voulgarakis A, Skeie RB, Dalsoren SB, Myhre G, Berntsen TK, Folberth GA, Rumbold ST, Collins WJ, MacKenzie IA, Doherty RM, Zeng G, van Noije TPC, Strunk A, Bergmann D, Cameron-Smith P, Plummer DA, Strode SA, Horowitz L, Lee YH, Szopa S, Sudo K, Nagashima T, Josse B, Cionni I, Righi M, Eyring V, Conley A, Bowman KW, Wild O, Archibald A, 2013, Tropospheric ozone changes, radiative forcing and attribution to emissions in the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP), *Atmos. Chem. Phys.*, **13**, 3063-3085.

132 Stone D, Evans MJ, Commane R, Ingham T, Floquet CFA, McQuaid JB, Brookes DM, Monks PS, Purvis R, Hamilton JF, Hopkins J, Lee J, Lewis AC, Stewart D, Murphy JG, Mills G, Oram D, Reeves CE, Heard DE, 2010, HO_x observations over West Africa during AMMA: impact of isoprene and NO_x, *Atmos. Chem. Phys.*, **10**, 9415-9429.

133 Stone D, Whalley LK, Heard DE, 2012, Tropospheric OH and HO_2 radicals: field measurements and model comparisons, *Chem. Soc. Rev.*, **41**, 6348-404.

134 Susaya J, Kim KH, Shon ZH, Brown RJ, 2013, Demonstration of long-term increases in tropospheric O_3 levels: causes and potential impacts, *Chemosphere*, **92**, 1520-8.

135 Tang X, Wilson SR, Solomon KR, Shao M, Madronich S, 2011, Changes in tropospheric composition and air quality due to stratospheric ozone depletion and interactions with changes in climate, *Photochem. Photobiol. Sci.*, **10**, 280–291.

136 Thompson AM, Stewart RW, Owens MA, Herwehe JA, 1989, Sensitivity of tropospheric oxidants to global chemical and climate change, *Atmos. Environ.*, **23**, 519-532.

137 Tveit A, Rusch GM, Muijser H, Tegelenbosch-Schouten MM, 2013, The acute, developmental, genetic and inhalation toxicology of 2,3,3,3-tetrafluoropropene (HFO-1234yf), *Drug Chem. Toxicol.*, **36**, 412-20.

138 Tveit A, Rusch GM, Muijser H, van den Hoven MJ, Hoffman GM, 2014, The acute, genetic, developmental and inhalation toxicology of trans-1-chloro,3,3,3-trifluoropropene (HCFO-1233zd(E)), *Drug Chem. Toxicol.*, **37**, 83-92.

139 UNEP, 2010, Environmental effects of ozone depletion and its interactions with climate change: Progress Report 2009, *Photochem. Photobiol. Sci.*, **9**, 275-294.

140 USEPA, 2007, Protection of stratospheric ozone: Listing of substitutes for ozone-depleting substances-n-propyl bromide in solvent cleaning, *Fed. Reg.*, **72**, 30142-30167.

141 USEPA, 2007, Q and A: 2007 Final and Proposed Regulations for n-Propyl Bromide (nPB), United States Environmental Protection Agency http://www.epa.gov/ozone/snap/solvents/2007nPBRegsQA.html, accessed March 03, 2014.

142 USEPA, 2010, Integrated Science Assessment for Particulate Matter, U.S. Environmental Protection Agency, Office of Research and Development Report No. EPA/600/R-08/139F, Research Triangle Park, NC, p. 2228

143 van Donkelaar A, Martin R, Levy RC, da Silva AM, Krzyzanowski M, Chubarova NE, Semutnikova E, Cohen AJ, 2011, Satellite-based estimates of ground-level fine particulate matter during extreme events: A case study of the Moscow fires, *Atmos. Environ.*, **45**, 6225-6232.

144 Voulgarakis A, Naik V, Lamarque JF, Shindell DT, Young PJ, Prather MJ, Wild O, Field RD, Bergmann D, Cameron-Smith P, Cionni I, Collins WJ, Dalsøren SB, Doherty RM, Eyring V, Faluvegi G, Folberth GA, Horowitz LW, Josse B, MacKenzie IA, Nagashima T, Plummer DA, Righi M,

Rumbold ST, Stevenson DS, Strode SA, Sudo K, Szopa S, Zeng G, 2013, Analysis of present day and future OH and methane lifetime in the ACCMIP simulations, *Atmos. Chem. Phys.*, **13**, 2563-2587.
145 Wang T, Nie W, Gao J, Xue LK, Gao XM, Wang XF, Qiu J, Poon CN, Meinardi S, Blake D, Wang SL, Ding AJ, Chai FH, Zhang QZ, Wang WX, 2010, Air quality during the 2008 Beijing Olympics: secondary pollutants and regional impact, *Atmos. Chem. Phys.*, **10**, 7603-7615.
146 Wang Y, Konopka P, Liu Y, Chen H, Müller R, Plöger F, Riese M, Cai Z, Lü D, 2012, Tropospheric ozone trend over Beijing from 2002–2010: ozonesonde measurements and modeling analysis, *Atmos. Chem. Phys.*, **12**, 8389-8399.
147 Whalley LK, Edwards PM, Furneaux KL, Goddard A, Ingham T, Evans MJ, Stone D, Hopkins JR, Jones CE, Karunaharan A, Lee JD, Lewis AC, Monks PS, Moller SJ, Heard DE, 2011, Quantifying the magnitude of a missing hydroxyl radical source in a tropical rainforest, *Atmos. Chem. Phys.*, **11**, 7223-7233.
148 Wilkinson S, Mills G, Illidge R, Davies WJ, 2012, How is ozone pollution reducing our food supply?, *J. Exp. Bot.*, **63**, 527-36.
149 Wilson RC, Fleming ZL, Monks PS, Clain G, Henne S, Konovalov IB, Szopa S, Menut L, 2012, Have primary emission reduction measures reduced ozone across Europe? An analysis of European rural background ozone trends 1996–2005, *Atmos. Chem. Phys.*, **12**, 437-454.
150 Wilson SR, Solomon KR, Tang X, 2007, Changes in tropospheric composition and air quality due to stratospheric ozone depletion and climate change, *Photochem. Photobiol. Sci.*, **6**, 301-310.
151 Wong CM, Thach TQ, Chau PY, Chan EK, Chung RY, Ou CQ, Yang L, Peiris JS, Thomas GN, Lam TH, Wong TW, Hedley AJ, 2010, Part 4. Interaction between air pollution and respiratory viruses: time-series study of daily mortality and hospital admissions in Hong Kong, *Research Report*, 283-362.
152 Worton DR, Sturges WT, Schwander J, Mulvaney R, Barnola JM, Chappellaz J, 2006, 20th century trends and budget implications of chloroform and related tri-and dihalomethanes inferred from firn air, *Atmos. Chem. Phys.*, **6**, 2847-2863.
153 Xiao X, Prinn RG, Fraser PJ, Weiss RF, Simmonds PG, O'Doherty S, Miller BR, Salameh PK, Harth CM, Krummel PB, Golombek A, Porter LW, Butler JH, Elkins JW, Dutton GS, Hall BD, Steele LP, Wang RHJ, Cunnold DM, 2010, Atmospheric three-dimensional inverse modeling of regional industrial emissions and global oceanic uptake of carbon tetrachloride, *Atmos. Chem. Phys.*, **10**, 10421-10434.
154 Yoshino A, Nakashima Y, Miyazaki K, Kato S, Suthawaree J, Shimo N, Matsunaga S, Chatani S, Apel E, Greenberg J, Guenther A, Ueno H, Sasaki H, Hoshi J-y, Yokota H, Ishii K, Kajii Y, 2012, Air quality diagnosis from comprehensive observations of total OH reactivity and reactive trace species in urban central Tokyo, *Atmos. Environ.*, **49**, 51-59.
155 Young PJ, Archibald AT, Bowman KW, Lamarque JF, Naik V, Stevenson DS, Tilmes S, Voulgarakis A, Wild O, Bergmann D, Cameron-Smith P, Cionni I, Collins WJ, Dalsøren SB, Doherty RM, Eyring V, Faluvegi G, Horowitz LW, Josse B, Lee YH, MacKenzie IA, Nagashima T, Plummer DA, Righi M, Rumbold ST, Skeie RB, Shindell DT, Strode SA, Sudo K, Szopa S, Zeng G, 2013, Pre-industrial to end 21st century projections of tropospheric ozone from the Atmospheric Chemistry and Climate Model Intercomparison Project (ACCMIP), *Atmos. Chem. Phys.*, **13**, 2063-2090.
156 Zalakeviciute R, Alexander ML, Allwine E, Jimenez JL, Jobson BT, Molina LT, Nemitz E, Pressley SN, VanReken TM, Ulbrich IM, Velasco E, Lamb BK, 2012, Chemically-resolved aerosol eddy covariance flux measurements in urban Mexico City during MILAGRO 2006, *Atmos. Chem. Phys.*, **12**, 7809-7823.
157 Zeng G, Morgenstern O, Braesicke P, Pyle JA, 2010, Impact of stratospheric ozone recovery on tropospheric ozone and its budget, *Geophys. Res. Lett.*, **37**.
158 Zhang H, Wu S, Huang Y, Wang Y, 2014, Effects of stratospheric ozone recovery on photochemistry and ozone air quality in the troposphere, *Atmos. Chem. Phys.*, **14**, 4079-4089.
159 Zhang Q, Yuan B, Shao M, Wang X, Lu S, Lu K, Wang M, Chen L, Chang CC, Liu SC, 2014, Variations of ground-level O_3 and its precursors in Beijing in summertime between 2005 and 2011, *Atmos. Chem. Phys.*, **14**, 6089-6101.
160 Zhu T, Melamed M, Parrish D, Gauss M, Gallardo L, Lawrence M, Knare A, Liousse C, 2013, WMO/IGAC Impacts of Megacities on Air Pollution and Climate, World Meteorological Organization Report No. World Meteorological Organization (WMO) Global Atmosphere Watch (GAW) Report No. 205, Geneva, January 2013. http://www.wmo.int/pages/prog/arep/gaw/gaw-reports.html

Chapter 7. Consequences of Stratospheric Ozone Depletion and Climate Change on the Use of Materials.

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Summary
Materials used in exteriors of buildings and in construction are routinely exposed to solar UV radiation. Especially in the case of wood and plastic building materials, the service life is determined by their weather-induced deterioration. Any further increase in ground-level solar UV radiation, UV-B radiation in particular, will therefore reduce the outdoor service life of these products. Any increase in ambient temperature due to climate change will also have the same effect. However, the existing light-stabilizer technologies are likely to be able to mitigate the additional damaging effects due to increased solar UV radiation and maintain the outdoor lifetimes of these materials at the present levels. These mitigation choices invariably increase the lifetime cost of these products. A reliable estimate of what this additional cost might be for different products is not available at the present time. Personal exposure to UV radiation is reduced both by clothing fabrics and glass windows used in buildings and automobiles. This assessment describes how the recent technical advances in degradation and stabilization techniques impact the lifetimes of plastics and wood products routinely exposed to solar UV radiation and the protection to humans offered by materials against solar UV radiation.

Introduction
Wood and plastics are used extensively as construction materials. Of the 280 million tons of plastics produced globally [2011 data], about 23% is used in building construction, the second largest market for plastics after packaging applications.[120] Rigid poly(vinyl chloride) [rPVC] is the dominant plastic used in building applications. Polymers are also used extensively in architectural and industrial coatings. Wood is used widely in building construction, often as the principal structural element. Annually, ≈1.8 billion m^3 of industrial roundwood [all industrial wood in the rough] is harvested worldwide. Materials for construction used in exterior applications require long-term durability that is delivered by stabilized plastics and coated or treated wood.

Some of the materials used in agricultural and transportation applications are also regularly exposed to solar radiation, rain, and pollution but are expected to have service lives that span several decades. Those used as coatings on automobiles or on aircraft exteriors in particular are exposed to high heat and UV radiation fluxes on a routine basis. Their outer clear-coat layers responsible for finish and gloss is often compromised by exposure to UV radiation. Fig. 1 shows the main uses of plastics in outdoor applications.

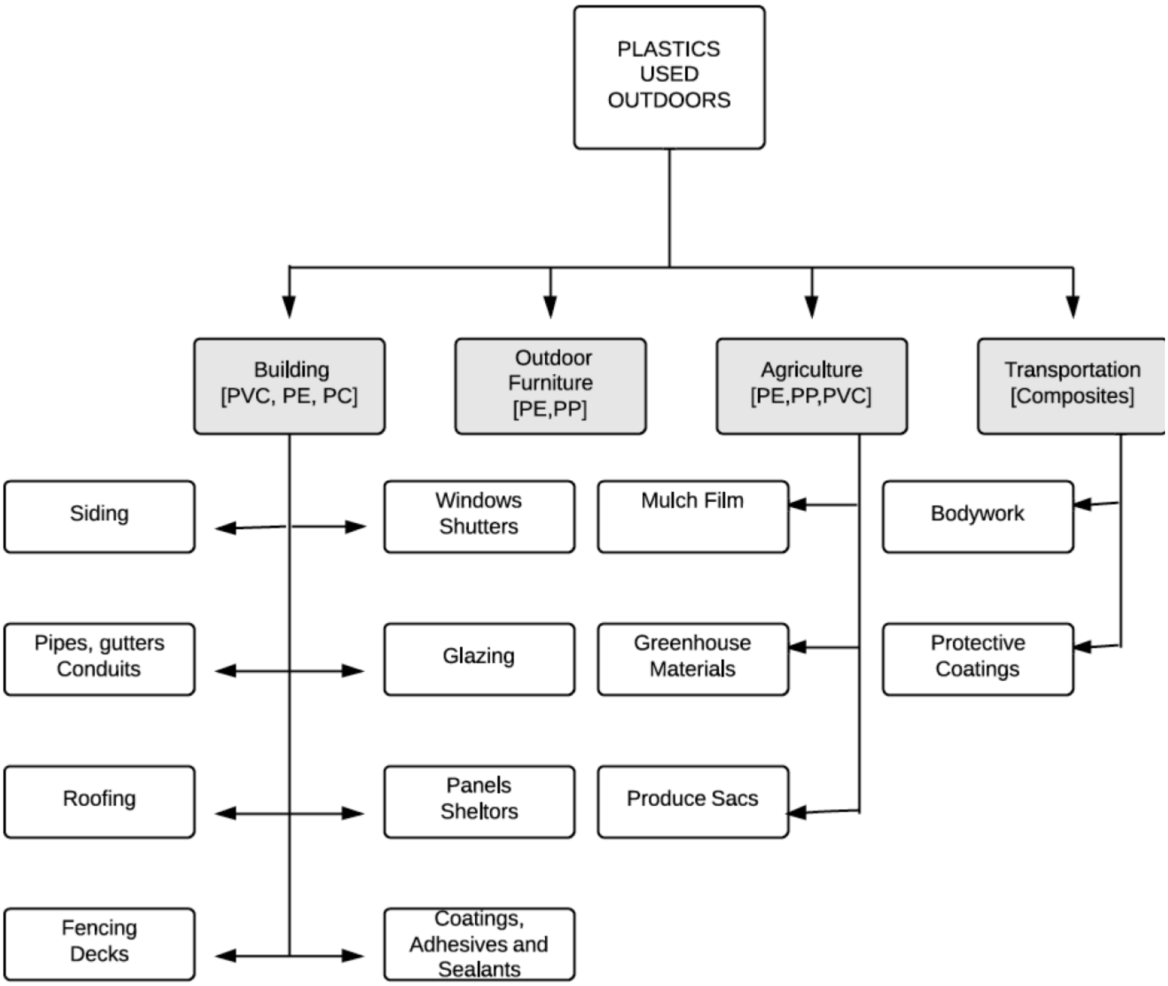

Fig. 1 Uses of plastic materials in outdoor applications. PE = Polyethylene; PP = Polypropylene; PVC = Poly(vinyl chloride); PC = Polycarbonate

Plastics and wood absorb solar UV radiation and are inherently susceptible to damage, especially at high ambient temperatures. The primary cause of weathering damage to wood and plastics is from solar UV-B radiation that is efficiently absorbed by chromophores generally present in these materials. High humidity, temperature, and pollutants in air often accelerate light-induced degradation. With plastics, the damage ranges from uneven discoloration or surface changes to cracking and loss of material strength.[112] With wood products, weathering degradation also renders the surface hydrophilic, facilitating subsequent moisture absorption and surface biodegradation. [131]

Depletion of the stratospheric ozone layer to any extent increases the fraction of UV-B (290–315 nm) in the solar radiation reaching the Earth's surface. Potential latitude-dependent increases in UV-B radiation can significantly shorten the service life of wood and plastics used outdoors, especially at locations where the ambient temperatures are relatively high. Levels of UV radiation are expected to decrease globally in the decades ahead (see Chapter 1), but there is still concern about its impact on materials due to the interactive effects with climate change. Climate change is widely expected to result in an increase in the average global temperature by 1.1–6.4°C by the end of the century and there is an international effort to keep the increase under 2°C.[75] Any increase in ambient temperatures exacerbates the damage as weathering reactions in both wood and plastics proceed at faster rates at the higher temperatures.[28] Intrinsic factors such as additives or impurities of trace metals (including pro-oxidant additives to make the plastic photodegradable)[115] also tend to accelerate the rate of light-induced photo-damage to both classes of materials.

The use of efficient UV stabilizers in compounding of plastics and effective surface coatings or treatments of wood, allows them to be successfully used in long-term outdoor applications such as in cladding, panels, fencing, or decking. Even at concentrations as low as <0.1 % by wt., light stabilizers, such as the Hindered–Amine Light Stabilizers [HALS] can control light-induced damage in plastics to yield service lives of several decades. Existing stabilizer and coating technologies are likely able to mitigate additional damaging effects from small potential increases in UV-B radiation in the solar spectrum reaching the Earth. [75] Either greater concentrations of stabilizers in plastics or the use of more efficient surface treatments for wood will have to be employed to mitigate these effects. Intensive industrial research effort is focused on discovering better and lower-cost light stabilizers for specific classes of plastics used in building[7] and improved surface coatings for preserving wood against weathering. New materials, additives or new variants of existing plastics that are more weather-resistant emerge in the marketplace regularly.

Polymeric materials are also used to protect humans against exposure to solar UV radiation. These include clothing made of synthetic fibers and plastic glazing used in buildings (and vehicles) filter out the UV radiation. The effective use of these limits exposure and therefore the adverse health impacts of UV radiation on humans. This paper assesses the relevant literature published since the last report in 2010.

Plastics use in building

Unlike with biota, that may show a limited capacity to adapt to increased UV-B radiation levels and where evolution of new traits is relatively slow, man-made materials can be designed to withstand new, harsher, solar UV radiation environments. Plastics, for instance, can be formulated with either greater levels of conventional stabilizers or more efficient novel stabilizers, to ensure a minimal loss in their service life. A substitution of materials with different, more UV-resistant classes of plastic or non-plastic material is a second strategy. Surface coatings and modifications of wood can also be designed for better resistance to solar UV radiation. However, invariably, it is the economics of their use that will dictate the specific mitigation strategy adopted. Regardless of the technology choice, it will inevitably add to the lifetime cost of using either class of materials.

Durability of materials outdoors is determined primarily by the dose of solar UV radiation, especially the proportion of UV-B radiation the material will be exposed to. As the dose of UV-B is latitude and altitude dependent, the durability of a given material will vary widely with the geographic location. The certified lifetime for a plastic material assessed at one location cannot be assumed to be the same for another with a different UV environment. Global UV-A and UV-B radiation maps (for Nov. 1, 1978 to June 30, 2000) estimated from TOMS data, corrected for the effect of cloud,[92] (Fig. 2) illustrates the wide range of UV-B radiation environments encountered at different locations around the World. However, these must be viewed with caution. Firstly, they are generally based on data from a single satellite overpass each day, and amounts of cloud at that time may not be representative of a true average. Secondly, satellite estimations of UV tend to be too high under polluted conditions[16].

The main uses of plastics in building construction include plastic pipes, siding, windows, soffit, fascia, rainwater goods and decorative panels and a majority of these are made of rigid PVC (rPVC). In fact, 76% of the PVC produced globally is used in the construction of buildings. The most popular cladding in residential housing in North America is rPVC siding produced by a profile extrusion process. In this application, the useful lifetime of the product is generally determined by uneven discoloration and loss of impact strength from photodamage by solar UV radiation.

Polycarbonate [PC] glazing used in architectural window panels as well as continuous windows and domes is similar to or better in performance than the conventional glazing in several characteristics.[104] One important advantage of these is their lower thermal conductivity, k, relative to glass. The value of k for PC glazing panels are as low as 1.2–1.9 W/m^2 (25-mm thickness), but new technology such as PC/aerogel composites[25] can bring this value down to 0.5 W/m^2 (25-mm section). In these products as well, discoloration induced by solar radiation, determines their useful lifetime.

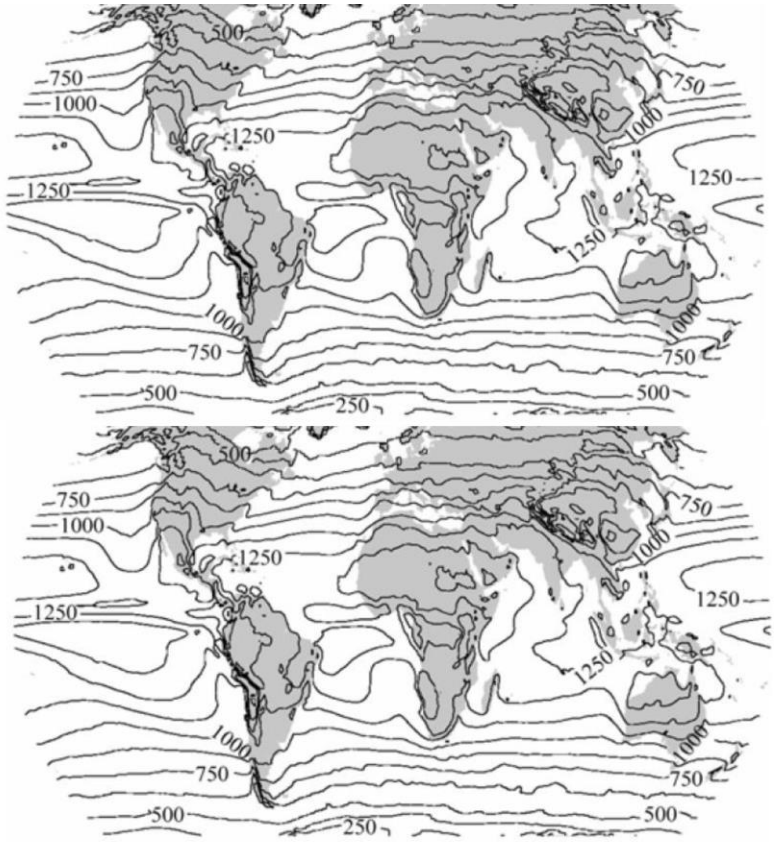

Fig. 2 A global map of the annual un-weighted mean dose of UVA (above) and UVB (below) in units of kJ m^{-2} day^{-1}. Reproduced with permission from Lee-Taylor.[92]

The present push towards sustainable materials in construction has led to some reassessment of the use of PVC materials in buildings. [89] Despite its dominance in the building sector and excellent performance in construction, PVC is perhaps the worst choice of a plastic in terms of environmental merit.[5] Not only does the production of PVC result in potential emission of toxic monomers and precursors to air but it is also compounded into soft products with phthalate plasticizers that are potent endocrine disruptors. Nevertheless, no imminent move away from its use in buildings is apparent. Alternative plastics that can replace PVC in construction such as polyolefins are available, but at a greater lifetime cost. The susceptibility of these alternatives to solar UV radiation will also influence their lifetime costs.

PVC in building and construction

Improvements in rigid PVC technology aimed at making it more environmentally acceptable, better performing, and with lower lifetime costs, are being made on a continuing basis. In the face of competition from alternative materials, PVC technology has advanced considerably. The lighter micro-foamed PVC siding[50] and the emerging (polystyrene) foam-backed PVC siding with greater insulation efficiency are examples of such improvements.

Most of the PVC products are processed as extruded profiles. Recent introduction to the market of a new processing aid[14] as well as an acrylic impact modifier[13] for PVC extrusion products (in profile, window, and siding applications) is a significant improvement in the technology. The new additives allow PVC to be extruded at a lower temperature with reduced risk of degradation and atmospheric emissions. On heating, PVC breaks down emitting hazardous corrosive HCl gas making it difficult to process. Typically, either tin-based or lead-based heat stabilizers are used to allow the thermal processing of rPVC. A new thermal stabilizer[4] with a lower tin content (19%) was recently commercialized for use in the same types of PVC products used in building. Improved processibility and superior thermal stabilization of PVC are afforded by the use of new stabilizers, which also are claimed to impart superior weatherability to the plastic material. Lower thermal degradation during processing improves the service lifetimes of rPVC products as it reduces the buildup of UV-absorbing functionalities in the polymer. No long-term UV-stability data for PVC compounds that incorporate these newer additives are as yet available. However newer tin-maleate stabilizers effectively control yellowing due to weathering of the material. Other manufacturers[76] have also introduced their own novel PVC additives for the same set of building products.

The solar UV-B-induced degradation of rPVC is catalyzed by ZnO used as a filler in the plastic. [132] The findings have implications only in the management of plastic waste as outdoor PVC products are generally formulated to be resistant to UV radiation. The wavelength sensitivity and activation spectra for typical injection molded rPVC formulations are known. Similar data for solvent-cast sheets of PVC, manufactured for graphic arts applications, were recently published and the merit of the material as a UV dosimeter discussed.[8] The data on wavelength sensitivity as well as activation spectra determined for solvent-cast plastic generally agreed with those already published for injection molded rPVC.[9, 10] This shows that the wavelength sensitivity of these materials is governed primarily by the nature of the polymer rather than the additives or processing-related factors. In accelerated weathering of plastics under laboratory conditions, it is essential to use a light source with a spectrum similar to that of sunlight. For example, mercury vapor lamps cannot be used as a substitute for a xenon source.[69] Recent advances in PVC technology have contributed to improved service lifetimes of the material exposed to solar UV-B radiation and the anticipated effects of climate change.

Wood-plastic composites

The 2010 global market for wood-plastic composites (WPC) was 2.3million tonnes and, given the short-term projected growth rate of 13.8%, per year this is expected[19] to grow to 4.6 million tonnes by 2016. WPCs are essentially thermoplastic composites (of PE, PP, PVC, and polystyrene (PS)) highly filled with powdered wood. Often, post-consumer plastics are used in their manufacture. Embedding wood fibers in a polymer matrix restricts absorption of moisture and hence avoids fungal growth and biodegradation of the wood fraction.[106] A higher-grade product results when a single type of plastic such as virgin PP is used [71, 133] and the compounding and/or processing operations are carefully controlled[96] to obtain good dispersion of the wood filler.

To improve miscibility of the hydrophilic wood and hydrophobic plastics in fabricating WPCs, compatibilisers are often employed.[65, 109] Good adhesion between the phases was reported, for instance, with maleic anhydride grafted PE and PP.[94, 96] Continued searching for good adhesion-promoters or compatibilisers for specific wood/plastic systems is critical for future growth of this technology. Alternatively, the wood fraction can be chemically functionalized (e.g., acetylated; [73]) for better compatibility. Low processing temperatures (<200°C) have to be used in processing WPCs because the wood component can otherwise thermally degrade. However, WPCs based on waste plastics and wood powder can be processed using conventional equipment into "plastic lumber" that can be handled and worked on using tools designed for wood. WPC is promoted as a 'green' (environmentally friendly) material as it uses waste wood and often post-consumer plastics as well.[15, 24, 149]

Lignin in the wood fraction of WPC absorbs solar UV radiation and undergoes photo-degradation[59] leading to delignification of the wood particles at the surface of the WPC material.[108] Photodegradation is reported to cause discoloration and breakdown of the filler in PP/wood [26] and PE/wood WPCs.[47] These changes render the surfaces hydrophilic, encouraging fungal growth, and biodegradation of the cellulose rich tissue. [40] Absorption of water by wood particles under freeze–thaw cycles causes swelling/shrinkage of the fibres that also destabilizes WPC creating voids or empty spaces in the matrix. These recent findings on WPC parallel what are already known mechanisms of degradation for wood species. Understanding all the degradation pathways involved for WPCs is critical to developing better UV-B stabilizers for the material. The main advantage of WPC is that hydrophilic wood fibres that absorb water and prone to biodegradation are embedded in plastic protecting them from solar UV radiation and environmental biodegradation.

The color, mechanical properties and durability of WPCs vary with the species of wood fiber used. For instance, in WPCs made of high density polyethylene [HDPE] with Douglas Fir and HDPE-hybrid Poplar wood discolored the least (>15%) on exposure to solar-simulated radiation (xenon lamp) compared to HDPE composites with wood species such as White oak and Ponderosa pine. [47]

As expected, the plastic component of WPC also undergoes light-induced degradation. Of the common thermoplastics used in WPCs, polystyrene[93] is the most susceptible. There is some evidence that the presence of wood in PVC- based WPCs may also promote photodegradation of the plastic matrix.[31] Naturally, the same light stabilizers used with plastics are also effective in protecting WPCs; for instance, the use of HALS stabilizers in wood-HDPE[31, 148] and light absorber (benzotriazole type) in wood-PVC[30] composites have been successful. The extent of protection afforded depends on the level of the stabilizer and its dispersion in the polymer matrix.[88] Whether there is an advantage in using a single stabilizer known to be effective in both wood and plastics, to protect WPC is not clear at this time.

Fig. 3 shows the effect of brown-rot fungi acting on a sample of WPC biodegrading the particles of wood exposed at the surface of the composite. A thin layer of plastic (or a cap layer) extruded on to the WPC surface may help seal in these exposed wood particles at the surface, discouraging biodegradation.[134] With a HDPE cap layer, the rate of discoloration from exposure to solar UV radiation was reduced by ≈50% and access of the wood fibers to moisture was also substantially reduced.[100] Blending UV absorbers with a HALS in the HDPE cap layer can further enhance photostability.[79] While several studies have established the effectiveness of cap-layer technology, its techno-economic feasibility in specific product categories remains to be demonstrated.

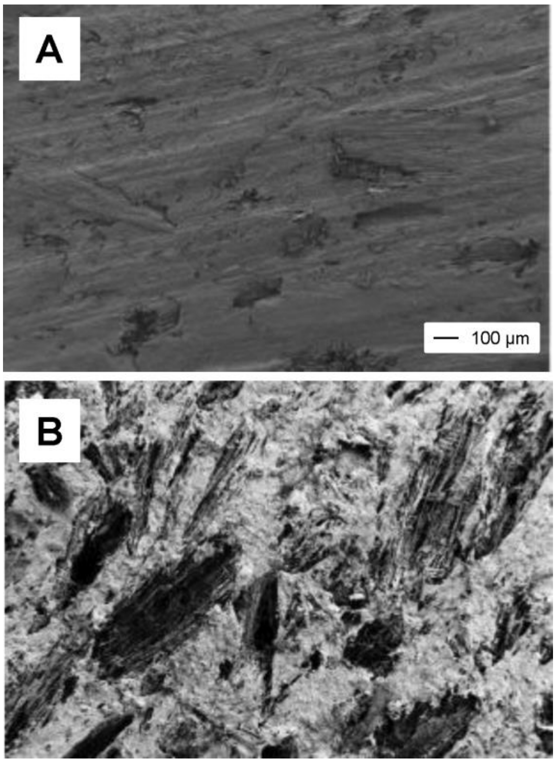

Fig. 3 A. Scanning electron micrograph of a WPC (white oak (60%)/HDPE(40%) control sample (A) and after exposure to *Gloeophyllum trabeum* (Brown rot fungi) for 12 weeks (B). Reproduced with permission from Fabiyi et al.[47]

Biodegradable and compostable plastics such as poly (lactic acid)[122] or poly(3-hydroxybutyrate)[141] have been studied for their potential use in WPC. The perceived sustainability of these potentially fully biodegradable WPCs that return all the carbon into the carbon cycle is attractive. However, the greater cost of these specialized plastics will likely preclude commercialization of such WPCs in spite of the claimed but questionable environmental advantage of biodegradability.

Emerging issue of weathering and microplastics

Weathering of plastics outdoors produces micro-scale plastic fragments that have serious environmental consequences.[12] Microplastics (fragments in the size range of 1 mm to 1 µm) are primarily believed to be derived from weathered, brittle plastic litter and are widely accepted to be a serious ecological concern, especially in the marine environment.[77, 147] The surface cracking of highly weathered plastics is the likely origin of microplastics.[12] Plastic particles, regardless of size, concentrate persistent organic pollutants (POPs).[17] dissolved in the ocean water at very low concentrations. The distribution coefficients (K) of a compound between the plastic and water phase is the ratio of its equilibrium concentration in the plastic and in seawater. For common POPs, values of the K between sea water and plastics are large, ranging from 10^4 to 10^5 in favor of plastic. This means the equilibrium concentration of a POP species can be several orders of magnitude greater in the plastic debris compared to in the seawater. Because of their small size, some of the microplastics are ingested by zooplankton and other marine species,[54] thus providing a pathway for POPs to enter the marine food web.[130] The specific compounds of concern include endocrine disruptors (EDs) such as PCBs, BPA, phthalates, and residual polymer catalysts.

Polypropylene (PP) is commonly found in urban litter and is an important generator of microplastics via surface photodegradation. The wavelength sensitivity of the surface cracking of PP stabilized by HALS was reported recently.[58] The same logarithmic dependence of photodamage on the wavelength of exposure, already reported for various measures of damage, such as discoloration or mechanical properties, was also confirmed for surface cracking. This is the first reported action spectrum for crack formation and is relevant as microplastics originate from surface cracks. However, quantifying surface cracking was indirect and not entirely satisfactory, being based on a correlation between carbonyl index (a spectroscopic quantity) and the degree of cracking. Extrinsic fluorescence techniques using Rhodamine dye, recently used for the first time to study microstructural changes in polymers during UV degradation,[41, 42] hold more promise for quantification of weathering-induced microcracking of plastics.

Higher degrees of crystallinity obtained under extensive weathering are one of the main reasons for embrittlement. On weathering of semi-crystalline plastics (such as PE or PP), it is the amorphous regions that oxidize first because of the lesser solubility and diffusion rates of oxygen in the crystallites. This was recently confirmed for PE[123] using dielectric relaxational spectroscopy, a technique not hitherto used for this purpose. In contrast, Ojeda[112] reported that polypropylene samples underwent a decline (>12%) in crystallinity during natural weathering. The latter observation has not been satisfactorily explained although impurities or accumulation of product during degradation has been suggested as the cause. Research is needed to clarify the relationship between crystallinity changes and exposure to UV radiation during weathering.

Plastics in solar photovoltaic applications

While plastics also are being evaluated as solar thermal absorbers,[81] it is the photovoltaic (P-V) applications that are of greater commercial interest.[74, 105] Research emphasis appears to be divided between the solar UV-damage to light-harvesting semiconductor polymers in organic P-V devices[20, 100, 151] and that of plastic encapsulants used to protect silicon P-V modules.

Recent designs of P-V modules utilize plastics extensively. Generally, two plastic protective laminates or sheets in the modules are affected by solar radiation (Fig. 4). Light transmitted through the transparent front panel reaches the exposed parts of the front sheet and the front surface of the back sheet, discoloring and weakening these after long durations of exposure. The back sheet is often constructed of a multi-layered laminate designed for the service life of the module (20–25 years). These sheets are made of a poly(vinyl fluoride) (PVF) outer layer, a thicker inner core of poly(ethylene terephthalate) (PET) with titanium dioxide (for opacity), and a PVF surface layer (or a PE/EVA tie layer). Of the plastics evaluated over the years, PVF has been selected as the best suited for the application. Long-term exposure can result in discoloration and loss of strength in these sheets and, although accelerated test methods available[20, 67, 84] they are inadequate to reliably predict their service lifetimes. PE and PET degrade under solar UV exposure and undergo yellowing and cracking. The back surface of the back sheet is also affected by diffused UV radiation that, along with high temperatures[83] cause initial damage within ≈5 years of outdoor exposure.[86]

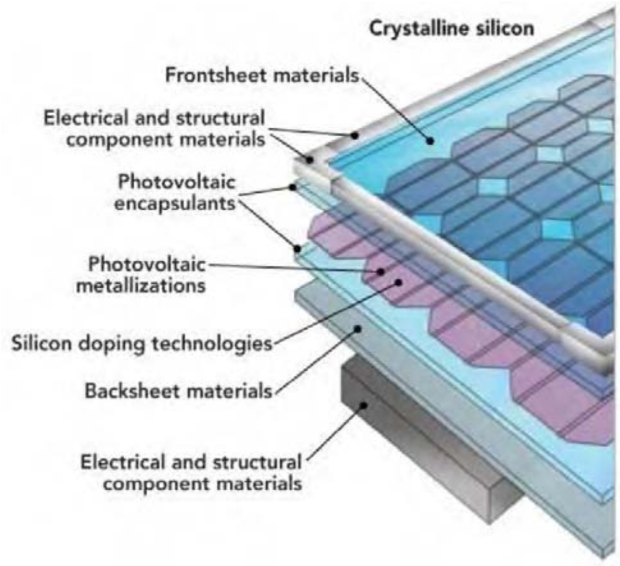

Fig. 4 Structure of a P-V Module showing the back sheet and front sheet material placement. Source: Courtesy of DuPont.

There is an urgent research need to a) develop weather resistant encapsulants as well as accelerated test methods to assess the long-term (> 20-30 years) service lifetimes of P-V modules, reliably. Any increase in UV-B radiation and/or temperature due to climate change will clearly accelerate the degradation, but techniques and standards to reliably quantify the effects reliably are still being developed.[110] The lifetime of protective plastics is a determining factor in implementing large-scale economical P-V technology.

Plastics in greenhouse covers

Plastic films and laminates are the leading greenhouse cladding materials used worldwide. Thin plastic films are sometimes used on conventional glass cladding to modify the spectral quality of light reaching the crops.[80] Plastic panels have different transmission rates for photosynthetically active radiation (PAR, 400–700 nm) and sometimes the plastics incorporate dyes or modifiers[91] to change the transmitted spectrum of solar radiation. The photostability of the dye is a concern in this technology and has not been explored as yet in detail.

Rigid plastics (>10 year service life) commonly used in greenhouses are fibre-reinforced polyester panels, polycarbonate (PC), and acrylics. Flexible cladding (3–4 years of service life) is generally made from PE, ethylene copolymers, and PVC; although PET is also sometimes used. Both classes of cladding undergo discoloration and loss of PAR transmission with weathering during use.[2]

Nanofillers have been evaluated in low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE) greenhouse films to improve mechanical properties and to reduce transmission of UV. Nanoscale oxides of titanium, zinc oxide, and silica were evaluated for this purpose.[43] Nano-zinc oxide fillers improve weatherability of the films *via* UV-absorption or shielding, without affecting their transparency for PAR wavelengths. With certain varieties of crops, some degree of transparency to UV radiation might be needed to ensure a greater quality produce (see Chapter 3) and plastic films can be designed to accommodate this need. The market for durable greenhouse films is large enough for specialty chemical companies (Clariant, Swizerland) to offer tailor-made light stabilization solutions designed for greenhouse films.[33] While the potential for durable but UV-resistant greenhouse films based on nano-composites clearly exists the lifetime cost of their use has not been reported.

Dependence of solar UV radiation damage to greenhouse films on the dose of solar UV-B radiation is of interest in developing lifetime assessments. Dehbi and colleagues[38, 39] reported a U-shaped (nonlinear) dependence of yellow discoloration with duration of exposure for LDPE greenhouse films, in both natural and accelerated weathering. However, this form of dose–response behaviour is unexpected and atypical and is likely an artifact of the layered structure of the film. Oreski and colleagues[114] investigated the weathering changes in stabilized EVA copolymer greenhouse films (200 μm) and showed that only a thin surface layer was degraded. Even in thinner films (30 μm) of EVA, the mechanical properties were not significantly affected at 1,000 h of accelerated weathering exposure at 60 W/m^2 of UV irradiance (300–400 nm) at 40°C. Present-day stabilizer technology is clearly adequate for greenhouse film applications. Energy costs of maintaining greenhouse temperatures vary with the choice of cladding. In a new modelling study, Al-Madhouri and colleagues[6] found that the low emissivity of PVC is a better choice than LDPE in conserving heat in greenhouses. The search continues for a single plastic material that combines long-term resistance to solar UV radiation, transmittance of PAR, and thermal insulation, and is ideally suited for greenhouses.

Nanofiller in photostabilisation of plastics

The bulk of reported work on nanofilled polymers involves polymer-based coatings, especially clear coats used in protecting exterior surfaces from solar UV damage (these are assessed below).

Redhwi[125, 126] studied three nano-composites of LDPE (with Clay, ZnO, and Silica at 5 % (wt)) and found that natural resistance of the plastic to weathering was not compromised by the presence of the nanofillers except in the case of nanosilica. In studies on nanocomposite systems, surface-modified rutile titania (40–100 nm) in LDPE[57] was reported to control the loss in tensile properties relative to unfilled samples in accelerated weathering studies. Nanofillers generally need to be either surface-treated or a compatibiliser must be used in the formulation to ensure that high levels of dispersion are achieved throughout the material. While some work has been carried out on this topic,[87] further information is needed across the wide range of filler and/or plastics. The stability of the compatibilisers or modifiers to UV radiation also has not been studied in sufficient detail.

In general, the inclusion of nanoscale fillers should impart increased photostability to polymer coatings (including wood topcoats) and bulk polymers. Because variables, such as the particle size distribution and dispersion effectiveness are involved, quantitative effects are difficult to compare even for the same nanofillers in identical polymer matrices. Different combinations of these have been used in different studies. It appears that, in some systems at least, nanofillers yield at least the same level of protection as conventional fillers, but at a lower volume fraction and can therefore be an economical choice. However, further work is needed to elucidate the conditions under which they act as photostabilizers.

Kingston et al.[87] recently reviewed the potential for release of nanofillers from several nano-composites filled with multi-wall carbon nanotubes (MWCNT) and concluded that the potential for release of MWCNT with typical intended consumer use is expected to be small. It is not known if weathering of the composite surfaces facilitates the release of nanofiller particles from filled-coatings or composites. Release of nanoscale fillers from composites during their use is an emerging environmental concern and is being investigated.

Temperature effects in solar UV-damage of materials

At higher ambient temperatures the light-induced degradation rates of materials accelerate. In the case of wood, heat alone often does not result in significant degradation; yet higher temperatures accelerate the photo-degradation process. In modelling effects of temperature in weathering studies, ambient temperatures are typically used. However, because of the absorption of solar radiation, especially the infrared radiation, the surface temperature of the sample is often higher by as much as 10–20°C (depending on the material) and should be used in more realistic weathering models. A sophisticated heat transfer model that allows the estimation of sample surface temperatures from metrological data (without resorting to expensive field measurements) has been developed and validated.[23] Its availability will not only refine the modelling of damage estimates but also contribute to the assessment of stabilizers.

The surface cracking of light-stabilized PP exposed to xenon lamp radiation was recently reported.[58] In this first quantitative study of light-induced crack formation, the activation energy estimated for this process was 20 kJ/mole. However, models based on Arrhenius equation[68]or the reciprocity rule are inadequate in describing the case of concurrent light-induced and thermal (photo-thermal) degradation of PP.[53] The lack of a satisfactory general quantitative model is a major drawback in predicting the rates of degradation and service life in plastics exposed to solar UV radiation where heat build-up also increases the temperature of the material. This deficiency is particularly apparent in P-V device technology.

The temperature dependence of UV radiation-induced photodegradation was recently demonstrated experimentally via the exposure of wood from conifers and deciduous species to UV-B.[136] However, as a mercury vapor lamp that also emits UV-C radiation was used as the source in this study, the results are not pertinent natural weathering. Increase in temperature from 30°C to 80°C increased light induced color changes by 33-57% in pine, spruce, ash, and poplar wood,[119] and the effect is more pronounced at greater humidity.[135] The high temperatures used in the laboratory accelerated weathering tests reported by Persze and Tolvaj,[119] do not correspond to realistic temperatures of storage or use of wood.

Wood as a building material

In North America 25% of the windows are made of wood with nearly 9 million units made in 2010. The overriding market trend for building materials in general is the increasing demand for "green" or sustainable materials of construction.[89, 107, 127, 145] Exposed wood products are common in buildings, and these are generally surface- coated to ensure durability. A wide range of protective finishes such as paints, varnishes, stains, or water repellents are used for this purpose.[46] Recent life-cycle analyses (LCA) confirm wood to be an environmentally friendly building material.[66, 116]

Photodegradation of wood

Lignin in wood is a potent chromophore that readily absorbs UV radiation and undergoes ready photodegradation. This results in rapid color changes[135, 137, 154], lignin degradation[3, 117, 137] and loss in microtensile strength.[142] As with plastics, the oxidative degradation process in wood also increases the carbonyl index (the relative spectral signal from carbonyl groups in its infra-red spectrum) as a result of lignin degradation.[121] The fundamental measures in weathering are the efficiency of the photoprocess, the photodamage/mole of available photons and the action spectrum.[11] The action spectrum for yellowing of mechanical pulp (newsprint paper) under exposure to simulated solar radiation was re-investigated recently in a rigorous laboratory study. [70] The action spectrum for yellowing showed a logarithmic dependence of yellowing efficiency on wavelength as previously reported for newsprint paper.[11] These recent findings are in line with and confirm the known data on photodamage to wood.

As with plastics, solar UV radiation typically penetrates only the surface layer of wood. Photodegradation of surface layers monitored by microtensile measurements[142, 153] shows the damage is limited to about a 250-µm layer for Spruce wood exposed to simulated sunlight. Scanning electron microscopy showed some cellular damage at greater depths, but this was not supported by tensile property changes.

The role of wood extractives in UV stabilization

Extractives are naturally-occurring compounds that can be extracted from wood using common solvents such as acetone, ether and methanol. Natural wood extractives, being good absorbers of solar UV radiation, protect the wood from photodegradation.[29] Extractives in wood generally include phenolic compounds, stilbenes, and flavonoids that act as antioxidants and light stabilizers. Nzokou and Kamden[111] found the extractives to act as antioxidants and a stabilizer against degradation by UV radiation, during artificial weathering of *Prunus serotina*, *Quercus rubra*, and *Pinus resinosa*. Chang and colleagues[29] also showed that extractives slow down the rate of wood degradation in *Cryptomeria japon*ica and *Acacia confuse* heartwood. Wood/LLDPE composites prepared with extractive-free wood (extractives removed by solvent extraction) showed poorer UV radiation stability compared to un-extracted wood fiber.[131] In contrast to the above, Sharratt and colleagues;[130] however, reported that discoloration of Scots pine (*Pinus sylvestris*) exposed to simulated sunlight exposure, was unaffected by the presence of extractives. Consistent with this observation of UV-stabilizer activity of extractives, textile dyes derived from plants have very good UV-protective properties.[64]

Drawbacks of extractives as stabilizers, however, are their water solubility and ready leachability from wood. While heat treatment, at least in the case of *Merbau* heartwood, appears to help prevent this[72], a general solution to the problem is not available. Wood extractives, depending on the species, could be a new source of light stabilizers that can be further developed and refined to guard both wood and WPCs against damage caused by solar UV radiation.

Stabilizing wood against UV radiation

Improved protection of wood against solar UV radiation is afforded by coating the surface with layers containing light stabilizers[129] such as HALS (or synergistic combinations of stabilizers[51]) or inorganic fillers. Coating and surface modifications (as with cap layers already referred to in connection with WPC) also reduced moisture pick-up and therefore increase fungal resistance[37] of wood.

A wide range of protective surface coverings or finishes such as paints, varnishes, stains, or water repellents[45] are now commercially available. Transparent coatings that are not UV stabilized merely protect the wood against moisture but are not effective in controlling light-induced damage.[143] In such finishes, the interface (between wood and the coating) is degraded by UV-B radiation transmitted through the coating. This influences the coating performance.[36] However, coatings that are hydrophilic (e.g., waterborne acrylic) must also be avoided as they promote the diffusion of water into the wood.[140] Moisture in wood can facilitate biodegradation by fungi such as white-rot fungi (Fig.5).

Using conventional light stabilizers in clear coats on wood can be an effective stabilization technique. For instance, the generation of carbonyl groups by photodegradation of the underlying wood, is reduced by incorporating 2% of a conventional light absorber (Tinuvin-1130 or hydroxyphenylbenzotriazole) in the polyurethane surface coatings.[32] Treatment of Yellow Cedar wood surface with a low molecular weight phenol formaldehyde resin, containing 2% Lignostab-

1198, a HALS, improved the weathering resistance.[46] A low-cost wax coating was also found to control light-induced yellowing of Norway spruce wood.[95] Of the waxes studied, high loadings (wax content 11.7%) of emulsion of montan wax was the most effective.

The effectiveness of clear coats can be further improved by photo-stabilizing the underlying wood substrate itself prior to the application of coatings.[36, 118, 143] Chemically bonding UV absorbers to the wood is effective for many wood species.[45, 62] Pretreatment with a reactive UV-absorber 2-hydroxy-4(2,3-epoxypropoxy)-benzophenone with epoxy functionalized soybean oil improved photostability of Scots pine wood.[113] Surface modifications involving UV stabilizers may hold promise in protecting high-cost wood species from photodamage.

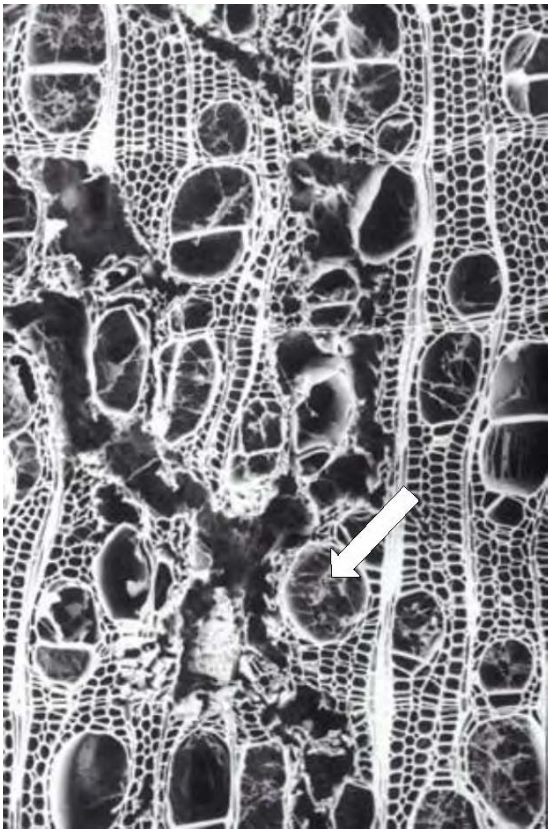

Fig. 5 Cross section of Oak Wood being biodegraded by white rot fungi. Biodegraded cells and fungal hyphae within other cells can be seen. (100 X). Reproduced with permission from Robert A. Blanchette, Pathology and Wood Microscopy Research Laboratory, University of Minnesota, MN (USA).

Changing the surface layer of the wood substrate by chemical reaction (as opposed to using a protective clear coat) can also retard photo-degradation.[44] This can be cost-effective, as only a thin surface layer of wood needs to be chemically altered. Esterification using an anhydride reagent is a popular route to surface modification. Bhat et al.[22] reported that acetylation of *Acacia mangium* and *Acacia* hybrid woods with succinic anhydride better controlled UV-induced discoloration and mechanical loss compared to surface propylation. However, esterification only partially controls photo-yellowing and lignin degradation in Rubberwood.[129] In contrast to unmodified wood, esterified wood showed photo-bleaching.[102, 129] Aromatic esters [via vinyl benzoate reaction] also performed satisfactorily in controlling discoloration.[78] A novel process for benzoylation of wood meal was reported,[150] but the method uses ionic liquids (salts that are liquids <100 °C) and is therefore likely to be too expensive for commercial use. The same is true of surface treatment approaches that rely on silylation (using methoxysilanes), despite their effectiveness in stabilizing wood, being as yet too expensive for commercial use.[18]

Of the approaches available, the use of clear coats that are impervious to moisture but stabilized with conventional HALS or other stabilizers is the most effective (and also the most economical) approach for wood. It is also relatively environmentally friendly compared to other methods.

Use of nanofillers to protect wood against UV radiation

A majority of the studies reviewed suggest that nanoscale fillers in the topcoat or wood surface improve the UV stability of wood. While the economic feasibility of using nanofillers in wood coatings is not clear as yet, their performance is equal or better than conventional fillers at comparable volume fractions is supported by the recent research. Three strategies for stabilization have been reported: incorporating nanofillers in topcoats, applying nanofiller directly to wood, and generating nanofillers in the wood.

Photostabilization of water-based polyurethane coatings intended for use on wood substrates, with 10-nm Ceria (CeO_2) nanoparticles[49, 128] at a level of 0.4–1.4% has been reported. Nano-Ceria was also reported to stabilize PP.[21] A similar improvement in controlling discoloration (and other surface damage such as reduction in gloss) was obtained with 7 nm nano-silica particles[103] at 1–5 wt.% incorporated into polyurethane coating. The same was reported for 50-nm nano-ZnO[124] in the same class of coating and for a 20-nm grade of the nanofiller at 1–2 wt.% in an acrylic wood stain.[34] However, using 0.5–1.0 wt.% of 20-nm rutile, a crystalline form of nano-titania, in similar coatings showed a decrease in photo-stability compared to base polymer, in terms of discoloration under accelerated weathering.

Acrylic water-based coatings for wood, containing nano-titania (NT) as well as nano-ZnO[34] have also been evaluated for control of discoloration, loss of gloss, and carbonyl group formation indicative of degradation. Fufa et al.[55, 56] found NT in the topcoat of wood cladding to be only marginally better than the base coating (with no NT) in controlling discoloration and carbonyl formation in Norway spruce. However, a very low fraction of only 1 wt.% (based on solids) of filler was used in that study. A 50-µm thick clear coat with 1.14 wt.% of NT filler afforded a much higher level of protection compared to that from a comparable coating with benzotriazole light absorbers.[52] Direct deposition of rutile nanoparticles on hardwood surface (without a coating) is also an option; this is achieved by hydrothermal processing[95] Such coatings are thicker and higher in concentration of NT particles, yielding excellent resistance against discoloration. Nanoparticles can also be chemically generated in situ on wood and bamboo surfaces[95] and this greatly enhances the material's photostability. This was demonstrated with Chinese hardwood where the in-situ generation was followed by silylation treatment to increase hydrophobicity. Wang and colleagues[144] studied NT coatings on Chinese fir wood followed by silylation. However, such two-step processes, especially those involving silylation, are likely to be too expensive for large-scale commercial use.

Role of fabric in protection against UV radiation

Personal protection afforded by clothing against the damaging effects of solar UV radiation is considerable and depends on fiber composition, (natural, synthetic or mixed fibers), fabric construction (porosity, weave and thickness) and dyeing (natural or synthetic dyes and their UV-absorbing properties.[60] In addition, outdoor uses of fabric such as in tents, awnings, shading, and sunshade fabrics also provide a protective role to humans from solar radiation. Clothing is in fact one of the best ways of protecting people against solar UV radiation[99] as even where the fabric materials themselves undergo limited UV-induced degradation they continue to provide excellent protection. The effectiveness of fabrics in this regard is quantified using the "ultraviolet protection factor" or UPF of the fabric. UPF is the ratio of the minimum erythemal dose of solar UV radiation for skin protected by fabric to that unprotected.[35] The percentage of effective UV radiation transmittance at each UPF value range is given in Table 1. For instance a cotton T-shirt provides a UPF of 3-5 (dry) and even lower when wet while denim has a UPF 1700. Dark colored fabrics have a higher UPF compared to light-colored ones.[90]

Several features of fabrics determine its UPF: (a) the porosity of the material or how open the structure is will be inversely proportional to the UPF; (b) the absorption of UV by the fabric material; (c) dyes, chemical reactants[148], or UV stabilizers[82]applied to the fabric; and (d) moisture level of the fabric.[146]

Table 1 The Relationship between UPF and fraction of erythemally effective UV transmitted through the material. (From Australian/ New Zealand Standard: AS/NZS 4399 (1996). Sun Protective Clothing: Evaluation and classification.)

UPF range	UV radiation protection category	Effective UV radiation transmission %)
15–24	Good protection	6.7–4.2
25–39	Very good protection	4.1–2.6
40–50, 50+	Excellent protection	<2.5, <1%

Of these, the porosity or tightness of the weave is the dominant factor in obtaining UV radiation protection, followed by the ability of fibers to absorb UV radiation. Grifoni et al.[63] compared the UV protection afforded by natural-fiber fabrics (cotton, hemp, flax and ramie) and concluded that thicker fabrics with denser weaves (with a cover factor, CF > 94%) such as drapery fabrics usually showed UPF >50. Cover factor is the ratio of the area covered by the yarns to the whole area of the fabric. Cotton fabrics afforded excellent protection from UV radiation as confirmed in other studies.[82] Lighter textile-grade fabrics, however, showed high UPF values only when the porosity was low (Cover factor >94%). Different natural fibers have about the same UV absorbance, and the difference in the performance of corresponding fabrics is mostly determined by cover factor and dyeing. Commercial sun-protective garments (UPF 50+ that transmit <1% of UV radiation) perform by reducing their porosity or “open areas” in the weave of the fabric and using UV absorbers. Even these, when wet (with water filling the spaces) do not scatter but transmit UV, reducing their effective UPF value.

The UPF of different fabric materials varies as follows:

Cotton >Polyester> Nylon >Elastane[60]

Chemical modification of fiber surfaces can increase the UPF ratings. A particularly successful approach is the use of inorganic oxides (including nanoscale particles[101] or zinc oxide in polyester[27, 152] and in cotton[1] and with titania-silica[48], alumina or nanosilica[98] particles in cotton, yielded very high UPF values in the hundreds (UPF > +50). While the untreated thick (tightly woven) fabric often has high UPF values to afford excellent protection, the use of surface modification technologies allows even a lighter-weight fabric to deliver the same high level of UV protection.

Layer-by-layer (LBL) deposition of nanolayers of three brightner compounds also increased the UPF of cotton fibers (UPF >40) and improved durability in laundering as well.[97] Optical whiteners absorb UV radiation and re-emit as blue radiation (typically 420-470 nm). LBL has also been used to deposit nano-alumina on cotton.[139] Despite the impressive performance of LBL technologies, they are expensive and are not near commercialization at this time. Chitosan metal complexes have also been used as organic stabilizer coatings on textile fibers but whilst these improve the antibacterial properties significantly they only provide a moderate improvement in UPF.[61]

Glazing and protection against UV radiation

Window glass (glazing) filters out the solar UV-B radiation but allows some UV-A radiation to pass through; the transmitted fraction depends on the type of glazing used. In buildings and in automobiles where some of the solar radiation is screened by glass, sunlight reaching into the cabin can still cause discoloration of materials and bleaching of dyes. In spite of the lower efficiency of UV-A wavelengths (compared to UV-B) in discoloration, the relatively greater amounts of the former in the terrestrial solar spectrum can still affect exposed fabric and other materials. Individuals, however, are protected from the UV-B radiation by almost all the different types of glass used on residential, commercial and automobile applications. Reported values for transmission of UV-A by different glazing are summarized below (Table 2[138]).

Table 2. Percentage Transmission of UV-A Radiation by different types of glazing materials

Type of Glazing	Thickness[a] (mm)	Percentage Transmission
Residential windows		
Double glazed clear glass	3.0/3.0	57
Double glazed tinted glass	3.0/3.0	20-33
Double glazed laminated glass	3.0/6.0	0.5
Double glazed UV-blocking glass	3.0/3.0	0.1
Automobile windows		
Laminated windshield glass	-	2-3
Tempered glass in rear and side window	-	33-48
Grey privacy glass	-	8
Moon-roof glass	-	2

[a] The two numbers refer to the two sheets of glass in double-glazed windows.

Thermal performance of windows can be improved dramatically by incorporating monolithic or granular aerogel in the interspace between panes in double-glazed windows.[85] According to Buratti[25] the rate of heat transfer decreased by 23% in aluminium-framed windows using aerogel technology. An associated benefit is that the presence of aerogel also cuts down the radiation transmitted, especially UV-A and UV-B radiation in sunlight.

References

1 Abd El-Hady MM, Farouk A, Sharaf S, 2013, Flame retardancy and UV protection of cotton based fabrics using nano-ZnO and polycarboxylic acids, *Carb. Polymers*, **92**, 400-406.

2 Abdel-Ghany AM, Al-Helal IM, 2011, Solar energy utilization by a greenhouse: General relations, *Renew. Energy*, **36**, 189–196.

3 Agresti G, G, Bonifazi L, Calienno G, Capobianco A, Lo Monaco C, Pelosi R, Picchio R, Serranti S, 2013, Surface investigation of photo-degraded wood by colour monitoring, infrared spectroscopy, and hyperspectral imaging, *J. Spectros.*

4 Akcros, 2010, Akcros USA announces new series of stabilizer products for PVC, *Addit. Polymers.*, **10**, 1-2.

5 Akovali G, 2012, Plastic materials: polyvinyl chloride (PVC), in *Woodhead Publishing Series in Civil and Structural Engineering* eds.: Pacheco-Torgal F, Jalali S, Fucic A, Woodhead Publishing, pp. 23-53.

6 Al-Mahdouri A, Baneshi M, Gonome H, Okajima J, Maruyama S, 2013, ????, *Sol. Energ. Mat. Sol. Cells*, **96**, 21-32.

7 Al-Salem SM, 2009, Influence of natural and accelerated weathering on various formulations of linear low density polyethylene (LLDPE) films, *Material Design*, **30**, 1729-1736.

8 Amar A, Parisi AV, 2013, Spectral response of solvent-cast polyvinyl chloride (PVC) thin film used as a long-term UV dosimeter, *J. Photochem. Photobiol. B.*, **125**, 115-120.

9 Andrady AL, Searle ND, 1995, Photoyellowing of mechanical pulps II Activation spectra for light-Induced yellowing of newsprint paper by polychromatic radiation, *Tech. Assoc. Pulp Paper Ind. J.*, **78**, 131-138.

10 Andrady AL, 1996, Wavelength sensitivity of common polymers: A Review, *Adv. Polymer.Sci.*, **128**, 45-94.

11 Andrady AL, Hamid SH, Hu X, Torikai A, 1998, Effects of increased solar ultraviolet radiation on materials, *J. Photochem. Photobiol. A.*, **46**, 96-103.

12 Andrady AL, 2011, Microplastics in the marine environment, *Mar. Poll. Bull.*, **8**, 1596-1605.

13 Arkema, 2010, Arkema unveils new impact modifier for window profiles, collaborates with Purac, *Addit. Polymers.*, **2010**, 2-3.

14 Arkema, 2011, PVC processing aid from Arkema Inc sets new standards, *Addit. Polymers.*, **2011**, 2-3.

15 Ayrilmis N, Kaymakci A, 2013, Fast growing biomass as reinforcing filler in thermoplastic composites: Paulownia elongata wood, *Indust. Crops Product.*, **43**, 457-464.
16 Bais AF, McKenzie RL, Aucamp PJ, Ilyas M, Madronich S, Bernhard G, Tourpali K, 2015, Ozone depletion and climate change: Impacts on UV radiation, *Photochem. Photobiol. Sci.*, **14**, This issue.
17 Bakir A, Rowland SJ, Thompson RC, 2014, Enhanced desorption of persistent organic pollutants from microplastics under simulated physiological conditions, *Environ. Pollut.*, **85**, 16-23.
18 Baur SI, Easteal AJ, 2013, Improved photo-protection of wood by chemical modification with silanes: NMR and ESR studies, *Polym. Adv. Technol.*, **24**, 97-103.
19 BCC Research Market Forecasting, 2011, Global market for wood-plastic composites to pass 46 million metric tons by 2016, http://bccresearch.blogspot.ca/2011/11/global-market-for-wood-plastic.html#.VC6DtxYd7WU, accessed August, 2014.
20 Bedeloglu A, Demir A, Bozkurt Y, Sariciftci NS, 2010, Photovoltaic properties of polymer based organic solar cells adapted for non-transparent substrates, *Renew. Energy*, **35**.
21 Bezati F, Massardier V, Balcaen J, Froelich D, 2011, A study on the dispersion, preparation, characterization and photo-degradation of polypropylene traced with rare earth oxides, *Polymer Deg. Stab.*, **96**, 51-59.
22 Bhat I, Khalil A, Awang KB, Bakare IO, Issam AM, 2010, Effect of weathering on physical, mechanical and morphological properties of chemically modified wood materials, *Material Design*, **31**.
23 Bijl P, Heikkilä A, Syrjälä S, Aarva A, Poikonen A, 2011, Modelling of sample surface temperature in an outdoor weathering test, *Polymer Test.*, **30**.
24 Binhussain MA, El-Tonsy MM, 2013, Palm leave and plastic waste wood composite for out-door structures, *Construct. Build. Mater.*, **47**, 1431-1435.
25 Buratti C, Moretti E, 2012, Glazing systems with silica aerogel for energy savings in buildings, *Appl. Energy*, **98**, 396-403.
26 Butylina S, Hyvärinen M, Kärki T, 2012, Accelerated weathering of wood–polypropylene composites containing minerals, *Composites Part A: Appl. Sci. Manufact.*, **43**, 2087-2094.
27 Çakır BA, Budama L, Topel Ö, Hoda N, 2012, Synthesis of ZnO nanoparticles using PS-b-PAA reverse micelle cores for UV protective, self-cleaning and antibacterial textile applications, *Colloid. Surfac. A*, **414**, 132-139.
28 Celina MC, 2013, Review of polymer oxidation and its relationship with materials performance and lifetime prediction, *Polymer Deg. Stab.*, **98**, 2419-2429.
29 Chang TC, Chang H, Wu CL, Lin HY, Chang ST, 2010, Stabilizing effect of extractives on the photo-oxidation of Acacia confusa woo, *Polymer Deg. Stab.*, **95**, 1518-1522.
30 Chaochanchaikul K, Sombatsompop N, 2011, Stabilizations of molecular structures and mechanical properties of PVC and wood/PVC composites by Tinuvin and TiO_2 stabilizers, *Polymer Eng. Sci.*, **51**, 1354-1365.
31 Chaochanchaikul K, Rosarpitak V, Sombatsompop N, 2013, Photodegradation profiles of PVC compound and wood/PVC composites under UV weathering, *Express Polymer Lett.*, **7**, 146-160.
32 Chou PL, Chang JT, Yeh TF, Chang S, 2008, Characterizing the conservation effect of clear coatings on photodegradation of wood, *Biosource Technol.*, **99**, 1073-1079.
33 Clariant, 2013, Clariant introduces stabilizers for UV protection of greenhouse films, *Addit. Polymers.*, **2013**, 3-4.
34 Cristea MV, Riedl B, Blanchet P, 2011, Effect of addition of nanosized UV absorbers on the physico-mechanical and thermal properties of an exterior waterborne stain for wood, *Prog. Org. Coat.*, **72**, 755-762.
35 Das B, 2010, UV radiation protective clothing, *Open Textile J.*, **3**, 14-21.
36 Dawson BSW, Singh AP, Kroese HW, Schwitzer MA, S. Gallagher, Riddiough SJ, Wu S, 2008, Enhancing exterior performance of clear coatings through photostabilisation of wooden surfaces Part 2: Coating and weathering performance, *J. Coat. Technol. Res.*, **5**, 207-219.
37 De Filpo G, Palermo AM, Rachiele F, Nicoletta FP, 2013, Preventing fungal growth in wood by titanium dioxide nanoparticles, *Int. Biodet. Biodeg.*, **85**, 217-222.
38 Dehbi A, Bouaza A, Hamou A, Youssef B, Saiter JM, 2010, Artificial ageing of tri-layer polyethylene film used as greenhouse cover under the effect of the temperature and the UV-A simultaneously, *Mat. Design*, **31**, 864-869.
39 Dehbi A, Hamid A, Mourad I, Bouaza A, 2011, Degradation assessment of LDPE multilayer films used as a green house cover: Natural and artificial aging Impacts, *J. Appl. Polymer. Sci.*, **124**, 2702-2716.
40 Dittenber DB, Ganga Ra HVS, 2012, Critical review of recent publications on use of natural composites in infrastructure, *Composites Part A: Appl. Sci. Manufact.*, **43**.

41 Douminge L, Mallarino S, Cohendoz S, Feaugas X, Bernard J, 2010, Extrinsic fluorescence as a sensitive method for studying photo-degradation of high density polyethylene Part 1, *Curr. Appl. Phys.*, **10**, 1211-1215.

42 Douminge L, Feaugas X, Bernard J, Mallarino S, 2013, Extrinsic fluorescence as a sensitive method for studying photo-degradation of high density polyethylene correlated with mechanical stresses, *Curr. Appl. Phys.*, **13**, 1751-1757.

43 Espejo C, Arribas A, Monzó F, Díez. PP, 2012, Nanocomposite films with enhanced radiometric properties for greenhouse covering applications, *J. Coat. Technol. Res.*, **5**, 2017-209.

44 Evans PD, 2009, Review of the weathering and photostability of modified wood, *Wood Mat. Sci. Eng.*, **1**, 2-13.

45 Evans PD, 2012, Weathering of wood and wood composites, in *Handboook of wood chemistry and wood composite,* ed.: Row RM, Taylor and Francis, CRC pp. 151-213.

46 Evans PD, Kraushaar Gibson S, Cullis I, Liu C, Sèbe G, 2013, Photostabilization of wood using low molecular weight phenol formaldehyde resin and hindered amine light stabilizer, *Polymer Deg. Stab.*, **98**, 158-168.

47 Fabilyi JS, McDonald AG, Wolcott MP, Griffiths PR, 2008, Wood plastic composites weathering: Visual appearance and chemical changes, *Polymer Deg. Stab.*, **93**, 1405-1414.

48 Fakin D, Veronovski N, Ojstršek A, Božič M, 2012, Synthesis of TiO_2–SiO_2 colloid and its performance in reactive dyeing of cotton fabrics, *Carb. Polymers*, **88**, 992-1001.

49 Fauchadour D, Jeanson T, Bousseau JN, Echalier B, 2005, Nanoparticles of cerium oxide, application to coating technologies, *Paint. Coat. Ind.*, **21**, 88-93.

50 FerroCorp, 2014, Ferro and PolyOne target LDPE and PVC foams with K debuts, *Addit. Polymers.*, **1**, 4-5.

51 Forsthuber B, Grüll G, 2010, The effects of HALS in the prevention of photo-degradation of acrylic clear topcoats and wooden surfaces, *Polymer Deg. Stab.*, **95**, 746-755.

52 Forsthuber B, Schaller C, Grull G, 2013, Evaluation of the photo stabilising efficiency of clear coatings comprising organic UV absorbers and mineral UV screeners on wood surface, *Wood Sci. Technol.*, **47**, 281-297.

53 François-Heude A, Richaud E, Desnoux E, Colin X, 2014, Influence of temperature, UV-light wavelength and intensity on polypropylene photothermal oxidation, *Polymer Deg. Stab.*, **100**, 10-20.

54 Frias JPGL, Otero V, Sobral P, 2014, Evidence of microplastics in samples of zooplankton from Portuguese coastal waters, *Mar. Environ. Res.*, **95**, 89-95.

55 Fufa SM, Jelle BP, Hovde PJ, 2013, Weathering performance of spruce coated with water based acrylic paint modified with TiO_2 and clay nanoparticles, *Prog. Org. Coat.*, **76**, 1543-1548.

56 Fufa SM, Jelle BP, Hovde PJ, 2013, Effects of TiO_2 and clay nanoparticles loading on weathering performance of coated wood, *Prog. Org. Coat.*, **76**, 1425-1429.

57 Gaggino R, 2012, Water-resistant panels made from recycled plastics and resin, *Construct. Build. Mater.*, **35**, 468-482.

58 Geburtig A, Wachtendorf V, 2010, Determination of the spectral sensitivity and temperature dependence of polypropylene crack formation caused by UV-irradiation, *Polymer Deg. Stab.*, **95**, 2118-2123.

59 Ghaffar SH, Fan M, 2013, Structural analysis for lignin characteristics in biomass straw, *Biomass Bioenergy*, **57**, 264-279.

60 Gies P, McLennan A, 2012, Everyday and high-UPF sun-protective clothing, *Melanom. Lett.*, **30**, 7-8.

61 Gouda M, Keshk SM, 2010, Evaluation of multifunctional properties of cotton fabric based on metal/chitosan film, *Carb. Polymers*, **80**.

62 Grelier S, Castellan A, Podgorski L, 2007, Use of low molecular weight modified polystyrene to prevent photodegradation of clear softwoods for outdoor use, *Polymer Deg. Stab.*, **92**, 1520-1527.

63 Grifoni D, Bacci L, Zipoli G, Albanese L, Sabatini F, 2011, The role of natural dyes in the UV protection of fabrics made of vegetable fibres, *Dyes Pigments*, **91**, 279-285.

64 Grifoni D, Bacci L, Lonardo Sd, Pinelli P, Scardigli S, Camilli S, Sabatini F, Zipoli G, Romani A, 2014, UV protective properties of cotton and flax fabrics dyed with multifunctional plant extracts, *Dyes Pigments*, **105**, 89-96.

65 Guo C, Li L, Wang Q, 2010, Investigation on the compatibilizing effect of m-isopropenyl-a,a-dimethylbenzyl isocyanate grafted polypropylene on polypropylene and wood flour composites, *Wood Sci. Technol.*, **46**, 257-270.

66 Gustavsson L, Joelsson A, Sathre R, 2010, Life cycle primary energy use and carbon emission of an eight-storey wood-framed apartment building, *Energy Build.*, **42**, 230-242.

67 Haillant O, 2011, Accelerated weathering testing principles to estimate the service life of organic PV modules, *Sol. Energ. Mat. Sol. Cells*, **95**, 1284-1292.

68 Haillant O, Dumbleton D, Zielnik A, 2011, An Arrhenius approach to estimating organic photovoltaic module weathering acceleration factors, *Sol. Energ. Mat. Sol. Cells*, **95**, 1889-1895.

69 Heikkilä A, Kärhä P, Tanskanen A, Kaunismaa M, Koskela T, Kaurola J, Ture T, Syrjälä S, 2009, Characterizing a UV chamber with mercury lamps for assessment of comparability to natural UV conditions, *Polymer Test.*, **28**, 57-65.

70 Heikkilä A, Kärhä P, 2014, Photoyellowing revisited: Determination of an action spectrum of newspaper, *Polymer Deg. Stab.*, **99**, 190-195.

71 Homkhiew C, Ratanawilai T, Thongruang W, 2014, Effects of natural weathering on the properties of recycled polypropylene composites reinforced with rubberwood flour. , *Indust. Crops Product.*, **56**, 52-59.

72 Hu C, Jiang G, Xiao M, Zhou J, Yi Z, 2012, Effects of heat treatment on water-soluble extractives and color changes of merbau heartwood, *J. Wood. Sci.*, **58**, 465-469.

73 Hung K-C, Chen Y-L, Wu J-H, 2012, Natural weathering properties of acetylated bamboo plastic composites, *Polymer Deg. Stab.*, **97**, 1680-1685.

74 Imai T, Takamatsu S, Shiraishi K, Marumoto K, Itoh T, 2012, Photovoltaic textiles manufactured with precision die coating, *Procedia Eng.*, **47**, 502-505.

75 IPCC, 2010, Intergovernmental Panel on Climate Change Working Group I Contribution to the IPCC Fifth Assessment Report Climate Change 2013: The Physical Science Basis, Report No., University Press, Cambridge, United Kingdom and New York, NY, U.S.A

76 ISP, 2010, International Specialty Products reveals new additives family for high-performance PVC applications, *Addit. Polymers.*, **2010**, 1-2.

77 Ivar do Sul JA, Costa MF, 2014, The present and future of microplastic pollution in the marine environment, *Environ. Pollut.*, **185**, 352-364.

78 Jebrane M, Sèbe G, Cullis I, Evans PD, 2009, Photostabilisation of wood using aromatic vinyl esters, *Polymer Deg. Stab.*, **94**, 151-157.

79 Jin S, Stark NM, Matuana LM, 2013, Influence of a stabilized cap layer on the photodegradation of coextruded high density polyethylene/wood-flour composites, *J. Vinyl Addit.Technol.*, **19**, 239-249.

80 Johannes FJM, Reisinger G, Hofmann T, Hinken J, H.Tantau, A.Ulbrich, Lambrecht S, Elsner BV, Schurr U, 2012, Glass–film-combination: Opto-physical properties and energy saving potential of a novel greenhouse glazing systems, *Energy Build.*, **50**, 298-307.

81 Kahlen S, Wallner GM, Lang RW, 2010, Aging behavior of polymeric solar absorber materials—Part 1 Engineering plastics, *Solar Energy*, **84**, 1567-1576.

82 Kan C, Yam LS, 2014, Effect of stretching on ultraviolet protection of cotton and cotton/coolmax blended weft knitted fabric in a wet state, *Materials* **7**, 58-74.

83 Kempe M, Wohlgemuth J, 2013, Evaluation of Temperature and Humidity on PV Module Component Degradation, in *Proceedings of the 39th IEEE Photovoltaic Specialists Conference, June 16–21, 2013*, Tampa Convention Center in Tampa Bay, FL.

84 Kempe MD, 2010, Ultraviolet light test and evaluation methods for encapsulants of photovoltaic modules, *Sol. Energ. Mat. Sol. Cells*, **94**, 246-253.

85 Kim JT, Todorovic MS, 2013, Tuning control of buildings glazing's transmittance dependence on the solar radiation wavelength to optimize daylighting and building's energy efficiency, *Energy Build.*, **63**, 108-118.

86 Kingston C, Zepp R, Andrady AL, Boverfof D, Fehir R, Hawkins D, Roberts J, Sayre P, Shelton B, Sultan Y, Vejins V, Whlleben W, 2014, Release characteristics of selected carbon nanotube polymer composites, *Carbon*, **68**, 33-57.

87 Kouini B, Serier A, 2012, Properties of polypropylene/polyamide nanocomposites prepared by melt processing with a PP-g-MAH compatibilizer, *Mat. Design*, **34**, 313-318.

88 Krehula LK, Katančić Z, Siročić AP, Hrnjak-Murgić Z, 2014, Weathering of high-density polyethylene-wood plastic composites, *J. Wood. Chem. Technol.*, **34**, 39-54.

89 Kubba S, 2012, Green Building Materials and Products, in *Handbook of Green Building Design and Construction* ed.: Kubba S, Butterworth-Heinemann, Boston, pp. 227-311.

90 Kullavanijaya P, Lim HW, 2005, Photoprotection, *J. Am. Acad. Dermatol*, **52**, 937-958.

91 Lamnatou C, Chemisana D, 2013, Solar radiation manipulations and their role in greenhouse claddings: Fluorescent solar concentrators, photoselective and other materials, *Renew. Sustain. Energy Rev.*, **27**, 175-190.

92 Lee-Taylor J, Madronich S, Fischer C, Mayer B, 2010, A Climatology of UV Radiation, 1979– 2000, 65S –65N, in UV Radiation in Global Climate Change: Measurements, Modeling and Effects on Ecosystems, eds.: Gao W, Schmoldt D, Slusser JR, Springer-Verlag and Tsinghua University Press, pp. 1-20.

93 Lee CH, Hung KC, Chen YL, 2012, Effects of polymeric matrix on accelerated UV weathering properties of wood-plastic composites, *Holzforschung.*, **66**, 981-987.

94 Lei Y, Wu Q, 2012, Wood plastic composites based on microfibrillar blends of high density polyethylene/poly(ethylene terephthalate), *Biores. Technol.*, **101**, 3665-3671.

95 Lesar B, Pavli M, Petri M, Seve A, Skapin M, Humar M, 2011, Wax treatment of wood slows photodegradation, *Polymer Deg. Stab.*, **96**, 1271-1278.

96 Leu SY, Yang TH, Lo SF, Yang TH, 2012, Optimized material composition to improve the physical and mechanical properties of extruded wood–plastic composites (WPCs), *Construct. Build. Mater.*, **29**, 120-127.

97 Li J, Yu H, Sun Q, Liu Y, Cui Y, Lu Y, 2010, Growth of TiO_2 coating on wood surface using controlled hydrothermal method at low temperatures, *Appl. Sur. Sci.*, **256**, 5046-5050.

98 Liu X, Song R, Yu W, Pan N, 2012, Developing UV-protective cotton fabrics based on SiO_x nanoparticles, *Fiber. Polym.*, **13**, 489-494.

99 Maged HZ, Mamdouh BEH, El-Naggar MA, Fathalla A, Nisreen MA, 2009, Novel UV-protective formulations for cotton, PET fabrics and their blend utilizing irradiation technique, *Eur. Polymer J.*, **45**, 2926-2934.

100 Manceau M, Rivaton A, Gardette JL, Guillerez S, Lemaître N, 2011, Light-induced degradation of the P3HT-based solar cells active layer, *Sol. Energ. Mat. Sol. Cells*, **95**, 1315-1325.

101 Mihailović D, Šaponjić Z, Radoičić M, Radetić T, Jovančić P, Nedeljković J, Radetić M, 2010, Functionalization of polyester fabrics with alginates and TiO_2 nanoparticles, *Carb. Polymers*, **79**, 526-532.

102 Mitsui K, 2010, Acetylation of wood causes photobleaching, *J. Photochem. Photobiol. B.*, **101**, 210-214.

103 Mohammad RA, Mohseni M, Mirabedini SM, Tabatabaei MH, 2012, Surface analysis and anti-graffiti behavior of a weathered polyurethane-based coating embedded with hydrophobic nano silica, *Appl. Sur. Sci.*, **258**, 4391-4396.

104 Moretti E, Zinzi M, Belloni E, 2014, Polycarbonate panels for buildings: Experimental investigation of thermal and optical performance, *Energy Build.*, **70**, 23-35.

105 Moulé AJ, 2010, Power from plastic, *Solid State Mat. Sci.*, **14**, 123-130.

106 Najafi SK, 2013, Use of recycled plastics in wood plastic composites—a review, *Waste Manag.*, **33**, 1898-1905.

107 Nässén J, Hedenus S, Karlsson S, Holmberg J, 2012, Concrete vs. wood in buildings – An energy system approach, *Build. Environ.*, **51**, 361-369.

108 Naumann A, Stephan I, Noll M, 2012, Material resistance of weathered wood-plastic composites against fungal decay, *Int. Biodet. Biodeg.*, **75**, 28-35.

109 Nörnberg B, Borchardt E, Luinstra GA, Fromm J, 2014, Wood plastic composites from poly(propylene carbonate) and poplar wood flour—Mechanical, thermal and morphological properties, *Eur. Polymer J.*, **51**, 167-176.

110 NREL, 2013, Photovoltaic Module Qualification Plus Testing National Renewable Energy Laboratory National Renewable Energy. Laboratory Report No. NREL/TP-5200-60950 Golden, CO, December 2013, p. 30

111 Nzokou P, Kamdem DP, 2006, Influence of wood extractives on the photo-discoloration of wood surfaces exposed to artificial weathering, *Col. Res. Applic.*, **31**, 425-234.

112 Ojeda T, 2011, Degradability of linear polyolefins under natural weathering, *Polymer Deg. Stab.*, **96**, 703-707.

113 Olsson S, M J, Westin M, Östmark E, 2012, Grafting of 2-hydroxy-4 (2, 3-epoxypropoxy)-benzophenone and epoxidized soybean oil to wood: Reaction conditions and effects on the color stability of Scots pine, *Polymer Deg. Stab.*, **97**, 1779-1786.

114 Oreski G, Wallner GM, Lang RW, 2009, Ageing characterization of commercial ethylene copolymer greenhouse films by analytical and mechanical methods, *Biosys. Eng.*, **103**, 489-496.

115 Pablos JL, Abrusci C, Marín I, López-Marín J, Catalina F, Espí E, Corrales T, 2010, Photodegradation of polyethylenes: Comparative effect of Fe and Ca-stearates as pro-oxidant additives, *Polymer Deg. Stab.*, **95**, 2057-2064.

116 Pajchrowski G, Noskowiak A, Lewandowska A, Strykowski W, 2014, Wood as a building material in the light of environmental assessment of full life cycle of four buildings, *Construct. Build. Mater.*, **15**, 428-436.

117 Pandey KK, Vuorinen T, 2008, Comparative study of photodegradation of wood by a UV laser and xenon light source, *Polymer Deg. Stab.*, **93**, 2138-2146.

118 Pandey KK, Srinivasa K, 2013, Study of UV resistance and natural weathering of coatings on chemically modified wood, International Research Group on Wood Protection Report No., Stockholm, Sweden

119 Persze L, Tolvaj L, 2012, Photodegradation of wood at elevated temperature: Colour change, *J. Photochem. Photobiol. B.*, **10844-47**.

120 Plastics Europe, 2012, Plastics Facts 2012, Plastics Europe, www.plastics europe.org, accessed August, 2014.

121 Popescu CM, Popescu MC, Vasile C, 2011, Structural analysis of photodegraded lime wood by means of FT-IR and 2D IR correlation spectroscopy, *Int. J. Biol. Macromol.*, **48**, 667-675.

122 Qiang T, Yu D, Zhang A, Gao H, Li Z, Liu Z, Chen W, Han Z, 2014, Life cycle assessment on polylactide-based wood plastic composites toughened with polyhydroxyalkanoates, *J. Cleaner Product.*, **66**, 139-145.

123 Ramanujam M, Wachtendorf V, Purohit PJ, Mix R, Schönhals A, Friedrich JF, 2012, A detailed dielectric relaxation spectroscopy study of artificial UV weathered low density polyethylene, *Thermochem. Acta*, **530**, 73-78.

124 Rashvand M, Ranjbar Z, Rastegar S, 2011, Nano zinc oxide as a UV-stabilizer for aromatic polyurethane coatings, *Prog. Org. Coat.*, **71**, 362-368.

125 Redhwi HH, Siddiqui MN, Andrady AL, Hussain S, 2013, Durability of LDPE nanocomposite with clay silica, and zinc oxide II. Weatherability of the nanocomposits, *Polymer Comp.*, **34**, 1878-1883.

126 Redhwi HH, Siddiqui MN, Andrady AL, Hussain S, 2013, Durability of LDPE nanocomposites with clay Silica, and zinc oxide-Part 1: Mechanical properties of the nanocomposite materials, *J. Nanocomp. Mater.*, **2013**, 1-6.

127 Rowell RM, 2012, *Handboook of wood chemistry and wood composite*, Taylor and Francis, CRC Press.

128 Saadat-Monfared A, Mohseni M, 2014, Polyurethane nanocomposite films containing nano-cerium oxide as UV absorber; Part 2: Structural and mechanical studies upon UV exposure, *Colloid. Surfac. A*, **441**, 752-757.

129 Salla J, Pandey KK, Prakash GK, Mahadevan KM, 2012, Photobleaching and dimensional stability of rubberwood esterified by fatty acid chlorides, *J. Wood. Chem. Technol.*, **32**, 121-136.

130 Setälä O, Lehtinen FV, Lehtiniemi M, 2014, Ingestion and transfer of microplastics in the planktonic food web, *Environ. Pollut.*, **185**, 77-83.

131 Sharratt V, Hill CA, Kint DP, 2009, A study of early colour change due to simulated accelerated sunlight exposure in Scots pine (*Pinus sylvestris*), *Polymer Deg. Stab.*, **94**, 1589-1594.

132 Sil D, Chakrabarti S, 2010, Photocatalytic degradation of PVC–ZnO composite film under tropical sunlight and artificial UV radiation: A comparative study, *Solar Energy*, **84**, 476-485.

133 Sobczak L, Lang RW, Haider A, 2012, Polypropylene composites with natural fibers and wood – General mechanical property profiles, *Composit. Sci. Technol.*, **72**, 550-557.

134 Stark NM, Matuana LM, 2009, Coextrusion of WPCs with a clear cap layer to improve color stability, in *4th Wood Fibre Polymer Composites International Symposium* Institut Technologique, Bordeaux, France.

135 Tolvaj L, Mitsui K, 2010, Correlation between hue angle and lightness of light irradiated wood, *Polymer Deg. Stab.*, **95**, 638-642.

136 Tolvaj L, Persze L, Albert L, 2011, Thermal degradation of wood during photodegradation, *J. Photochem. Photobiol. B.*, **105**, 90-93.

137 Tolvaj L, Varga D, 2012, Photodegradation of timber of three hardwood species caused by different light sources, *Acta Silvatic. Lignaria Hung.*, **8**, 145-156.

138 Tuchinda C, Srivannaboon S, Lim HW, 2006, Photoprotection by window glass, automobile glass, and sunglasses, *J. Am. Acad. Dermatol*, **54**, 845-854.

139 Uğur SS, Sarıışık M, Aktaş HA, 2011, Nano-Al_2O_3 multilayer film deposition on cotton fabrics by layer-by-layer deposition method, *Mater. Res. Bull.*, **46**, 1202-1206.

140 van Meel PA, Erich SJF, Huinink HP, Kopinga K, Jong J, Adan OCG, 2011, Moisture transport in coated wood, *Prog. Org. Coat.*, **72**, 686-694.

141 Vidal R, Martinez P, Garrain D, 2009, Life cycle assessment of composite materials made of recycled thermoplastics combined with rice husks and cotton linters, *Int. J. Life Cycle Assess.*, **14**, 73-82.

142 Volkmer T, Arietano L, Plummer C, Strautmann J, Noël M, 2013, Loss of tensile strength in cellulose tissue on the surface of spruce (*Picea abies*) caused by natural photodegradation and delignification, *Polymer Deg. Stab.*, **98**, 1118-1125.

143 Vollmer S, Evans PD, 2013, Performance of clear coatings on modified wood exposed to the weather for 2 years in Australia, *Int. Wood Prod. J.*, **4**, 177-182.

144 Wang Q, Hauser PJ, 2010, Developing a novel UV protection process for cotton based on layer-by-layer self-assembly, *Carb. Polymers*, **81**, 491-496.
145 Wang X, Liu S, Chang H, Liu J, 2014, Sol-gel deposition of TiO_2 nanocoatings on wood surfaces with enhanced hydrophobicity and photostability, *Photostabil. Wood Fiber Sci.*, **46**, 109-117.
146 Wilson CA, Bevin NK, Laing RM, Niven BE, 2008, Solar protection - effect of selected fabric and use characteristics on ultraviolet transmission, *Textile Res. J.*, **78**, 95-104.
147 Wright SL, Thompson RC, Galloway T, 2013, The physical impacts of microplastics on marine organisms: A review, *Environ. Pollut.*, **178**, 483-492.
148 Xie K, Wang Y, Xu L, 2010, Modification of cellulose with reactive polyhedral oligomericsilsesquioxane and nano-crosslinking effect on color properties of dyed cellulose materials, *Carb. Polymers*, **80**, 481-485.
149 Yemele MCN, Koubaa A, Cloutier A, Soulounganga P, Wolcott M, 2010, Growth of ZnO nanofilms on wood with improved photostability, *Holzforschung.*, **64**, 385-390.
150 Yuan T, Zhang LM, Xu F, Sun RC, 2013, Enhanced photostability and thermal stability of wood by benzoylation in an ionic liquid system, *Indust. Crops Product.*, **53**, 123-128.
151 Zhao Z, Rice L, Efstathiadis H, Haldar P, 2013, Annealing and thickness related performance and degradation of polymer solar cells, *Microelec. Reliab.*, **53**, 123-128.
152 Zhou Z, Zhao Y, Cai Z, 2010, Low-temperature growth of ZnO nanorods on PET fabrics with two-step hydrothermal method, *Appl. Sur. Sci.*, **256**, 4724-4728.
153 Živković V, Arnold M, Pandey KK, Richter K, Turkulin H, 2013, Novel approach in analysis of light source effects to spectral sensitivity of fir wood surfaces, in *6th European Weathering Symposium: Natural and Artificial Ageing of Polymers* (Ed.: Reichert T), Gesellschaft fuer Umweltsimulation, Bratislava, Slovačka, p. 643363.
154 Živković V, Arnold M, Radmanović K, Richter K, Turkulin H, 2014, Spectral sensitivity in the photodegradation of fir wood (*Abies alba* Mill) surfaces: Colour changes in natural weathering, *Wood Sci. Technol.*, **48**, 239-252.

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Questions and Answers about the Environmental Effects of the Ozone Layer Depletion and Climate Change: 2014 Update

Environmental Effects Assessment Panel: 2014

United Nations Environment Programme

Pieter J Aucamp & Robyn Lucas

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This document provides some answers to commonly asked questions about the environmental effects of ozone depletion

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Cover page photo by Dr Pieter J Aucamp with the question***: UV exposure has a major effect on the human eyes. How does it affect the eyes of animals?***

FREQUENTLY ASKED QUESTIONS ABOUT THE ENVIRONMENTAL EFFECTS OF OZONE DEPLETION

Contents

Abbreviations/acronyms used in this document

Abbreviation/ Acronym	Full name
CDOM	Coloured Dissolved Organic Matter
CDR	Carbon Dioxide Reduction
CFC	Chlorofluorocarbon
DOM	Dissolved Organic Matter
DU	Dobson Unit, for measuring total column of ozone in the atmosphere
EESC	Equivalent Effective Stratospheric Chlorine
GHG	Greenhouse gas
GWP	Global Warming Potential
HCFC	Hydrochlorofluorocarbon
HFC	Hydrofluorocarbon
ODS	Ozone depleting substance
PFC	Perfluorocarbon
SAM	Southern Annular Mode
SRM	Solar Radiation Management
sza	Solar Zenith Angle
TOMS	Total Ozone Mapping Spectrometer (satellite-based instrument designed to measure total ozone amount)
UV	Ultraviolet
UV-A	UV radiation in the wavelength range from 315 to 400 nm
UV-B	UV radiation in the wavelength range from 280 to 315 nm
UV-C	UV radiation in the wavelength range from 100 to 280 nm
UVI	UV Index

INTRODUCTION

In the mid-1970s it was discovered that some man-made products destroy ozone molecules in the stratosphere. Ozone filters out damaging solar ultraviolet (UV) radiation. The destruction of stratospheric ozone thus leads to higher levels of UV radiation at the surface of the Earth and this can cause damage to ecosystems and to materials such as plastics. It may cause an increase in the risk of some human diseases, for example, skin cancers and cataracts.

The discovery of the role of the synthetic ozone-depleting chemicals, such as the chlorofluorocarbons (CFCs), stimulated increased research and monitoring. Computer models predicted a disaster if nothing was done to protect the ozone layer. Based on this scientific information, the nations of the world took action in 1985 with the Vienna Convention for the Protection of the Ozone Layer, followed by the Montreal Protocol on Substances that Deplete the Ozone Layer in 1987. The Convention and Protocol have been amended and adjusted several times since 1987 as new knowledge has become available.

The Meeting of the Parties to the Montreal Protocol appointed three Assessment Panels to regularly review research findings and progress. These panels are the Scientific Assessment Panel, the Technological and Economic Assessment Panel and the Environmental Effects Assessment Panel. Each panel covers a designated area with a natural degree of overlap. The main reports of the Panels are published every four years, as required by the Meeting of the Parties. All three reports have an executive summary that is distributed more widely than the entire reports. It has become customary to add a set of questions and answers – mainly for non-expert readers – to these executive summaries. This document contains the questions and answers prepared by the experts of the Environmental Effects Assessment Panel. They refer mainly to the environmental effects of ozone depletion and its interactions with climate change, based on the 2014 report of this Panel, but also on information from previous assessments and from the 2014 report of the Scientific Assessment Panel[1]. Readers who need further details on any question should consult the full reports for a more complete scientific discussion. All of these reports can be found on the UNEP website: http://ozone.unep.org .

1 Reference: Twenty Questions and Answers about the Ozone Layer 2014 Update, Scientific Assessment of Ozone Depletion 2014, United Nations Environment Programme, Nairobi.

1. HOW IS OZONE PRODUCED AND DESTROYED?

The ozone molecule (O_3) contains three atoms of oxygen and is mainly formed by the action of UV radiation from the sun on oxygen molecules (diatomic oxygen, O_2) in the upper part of Earth's atmosphere (called the stratosphere). Ozone is also produced locally near Earth's surface (in the troposphere) from the action of UV radiation on some air pollutants.

About 90% of all ozone molecules are found in the stratosphere, a region that begins about 10-20 kilometres above Earth's surface and extends up to about 50 kilometres. Most of this ozone is found in the lower stratosphere in what is commonly known as the "ozone layer." The stratospheric ozone layer protects life on Earth by absorbing most of the harmful UV radiation from the Sun. The remaining 10% of ozone is in the troposphere, which is the lowest region of the atmosphere, between Earth's surface and the stratosphere.

The concentration of ozone varies from about 12 parts per million in the stratospheric ozone layer to about 20 parts per billion near Earth's surface.

Figure 1.1 illustrates the production and destruction of stratospheric ozone. Atomic oxygen (O) is formed when UV radiation in sunlight interacts with oxygen molecules (O_2). Atoms of O react with molecules of O_2 to form an ozone molecule (O_3). Ozone is destroyed naturally in the upper stratosphere by the UV radiation from the sun. These reactions are most important in the stratosphere above tropical and middle latitudes, where UV radiation is most intense. For each ozone molecule that is destroyed, an oxygen atom and an oxygen molecule are formed. Some of these recombine to produce ozone again. These naturally occurring reactions of destruction and production of ozone are balanced so that the ozone amount in the stratosphere remains constant.

Ozone is a very strong oxidising agent and reacts with many chemicals including organic substances. In addition to the processes described above, human activities and natural processes can emit large amounts of gases containing chlorine (Cl), bromine (Br) and fluorine (F) that eventually reach the stratosphere. When exposed to UV radiation from the Sun, these halogen-containing gases are converted to more reactive gases, such as chlorine monoxide (ClO) and bromine monoxide (BrO). These reactive gases participate in "catalytic" reaction cycles that efficiently destroy ozone in the stratosphere (Figure 1.1).

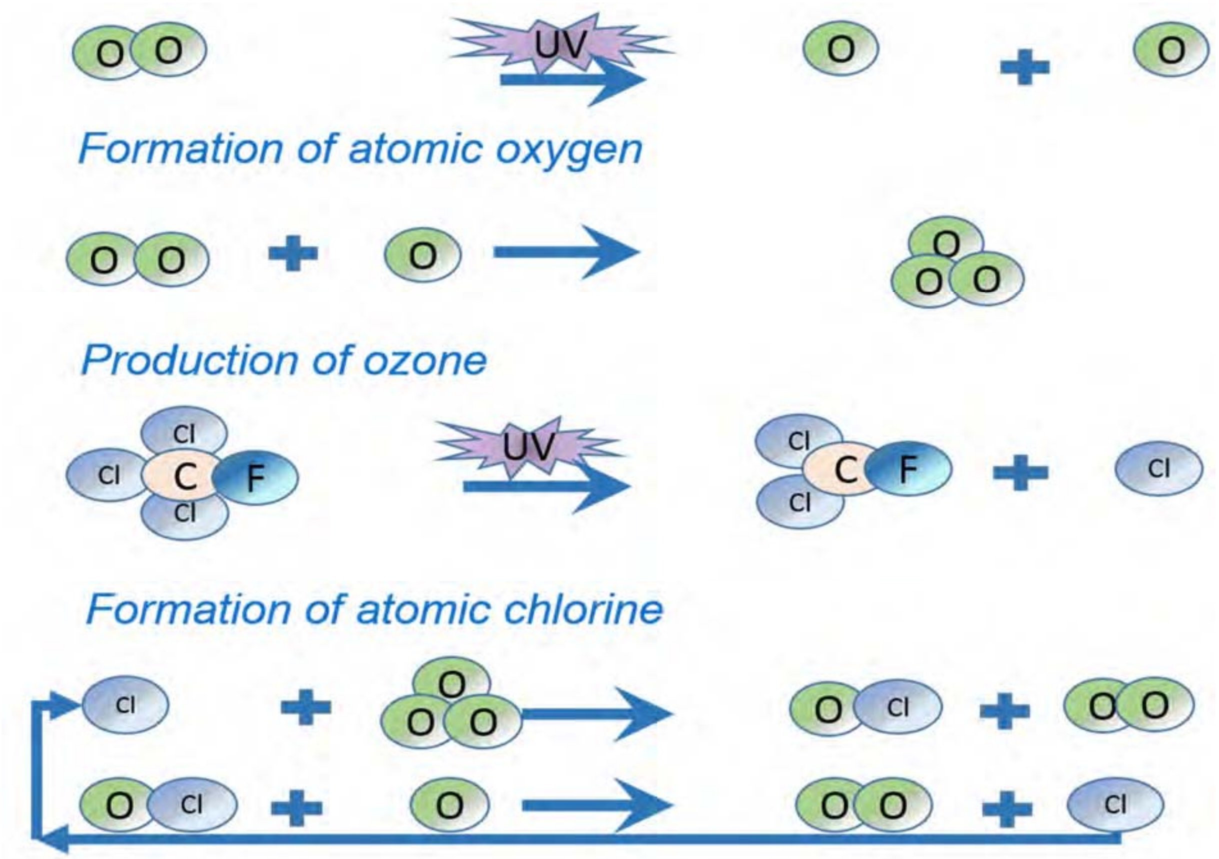
The destruction of ozone by halogens involves two separate chemical reactions. The net or overall result is that atomic oxygen (O) and ozone (O_3) are combined, to form two oxygen molecules (O_2). In Figure 1.1, the cycle begins with ClO or Cl. Cl reacts with (and thereby destroys) ozone and forms ClO. This then reacts with O to generate O_2 and regenerate Cl. Because Cl or ClO is reformed each time an ozone molecule is destroyed, chlorine is considered to be a catalyst for ozone destruction. Similar reactions occur with bromine derivatives and other compounds such as nitrogen oxides.

The relative potency of the different halogens depends largely on the stability of the compounds. Hydrogen fluoride (HF) is very stable, so fluorocarbons have no known impact on ozone. The atmospheric lifetimes of the iodine compounds are extremely short and they do not play an important role in the ozone destruction processes.

Chlorine-containing compounds from natural sources, such as volcanic eruptions, are usually "washed out" of the atmosphere before they can reach the stratosphere. They can however destroy ozone in the troposphere.

The total amount of ozone above any point on Earth is measured in Dobson Units (DU). An ozone column amount of 300 DU, which is a typical global average, corresponds to a 3 mm layer of pure ozone. Ozone column amounts vary seasonally and with latitude, and can sometimes reach values nearly twice as large as the global average. During the springtime Antarctic Ozone "Hole", ozone amounts of less than 100 DU may occur.

Most of the atmospheric column of ozone is in the stratosphere (see Box 1), where the intensity of UV radiation is greater than closer to Earth's surface. At any location, between 5 and 10% of the ozone column is in the troposphere, where it may be harmful to human and ecosystem health. For example, high concentrations of ozone can lead to respiratory problems and decreased crop productivity. In polluted environments, ozone production in photochemical smog can lead to increases from its background levels of ~25 ppb (parts per billion) to in excess of 100 ppb. For this reason, in many large cities, ozone is routinely measured, and health warnings are issued whenever the concentration exceeds 100 ppb.



Destruction of Ozone – The last two reactions are repeated many times.

Figure 1.1: Formation and destruction of ozone

Box 1. Troposphere *versus* Stratosphere

The troposphere is the region of the atmosphere extending from the surface of the Earth to an altitude of approximately 15 km, but ranging from less than 10 km in Polar Regions to about 20 km in the tropics. Temperature decreases with altitude in the troposphere typically at a rate of approximately 6°C/km. This promotes turbulent mixing so that any gases there are uniformly mixed. The upper limit of the troposphere is called the tropopause, which is the altitude at which temperature no longer decreases with altitude. At altitudes above this point, absorption by ozone of incoming sunlight (especially UV radiation), and of outgoing infrared radiation from Earth's surface cause the temperature gradient to stabilise or to show an increase in temperature with increasing altitude. Such temperature gradients inhibit the vertical mixing, resulting in a layered (or "stratified") structure. In this region of the atmosphere, gases are no longer uniformly mixed. Peak ozone amounts occur at altitudes near 25 km, and the stratosphere extends to an altitude of about 50 km (Figure 1.2).

The maximum altitudes of clouds, of jet aircraft flight paths, and of the highest mountains are all approximately 10 km. Turbulent mixing in the troposphere leads to convective motion, condensation and cloud formation, and precipitation.

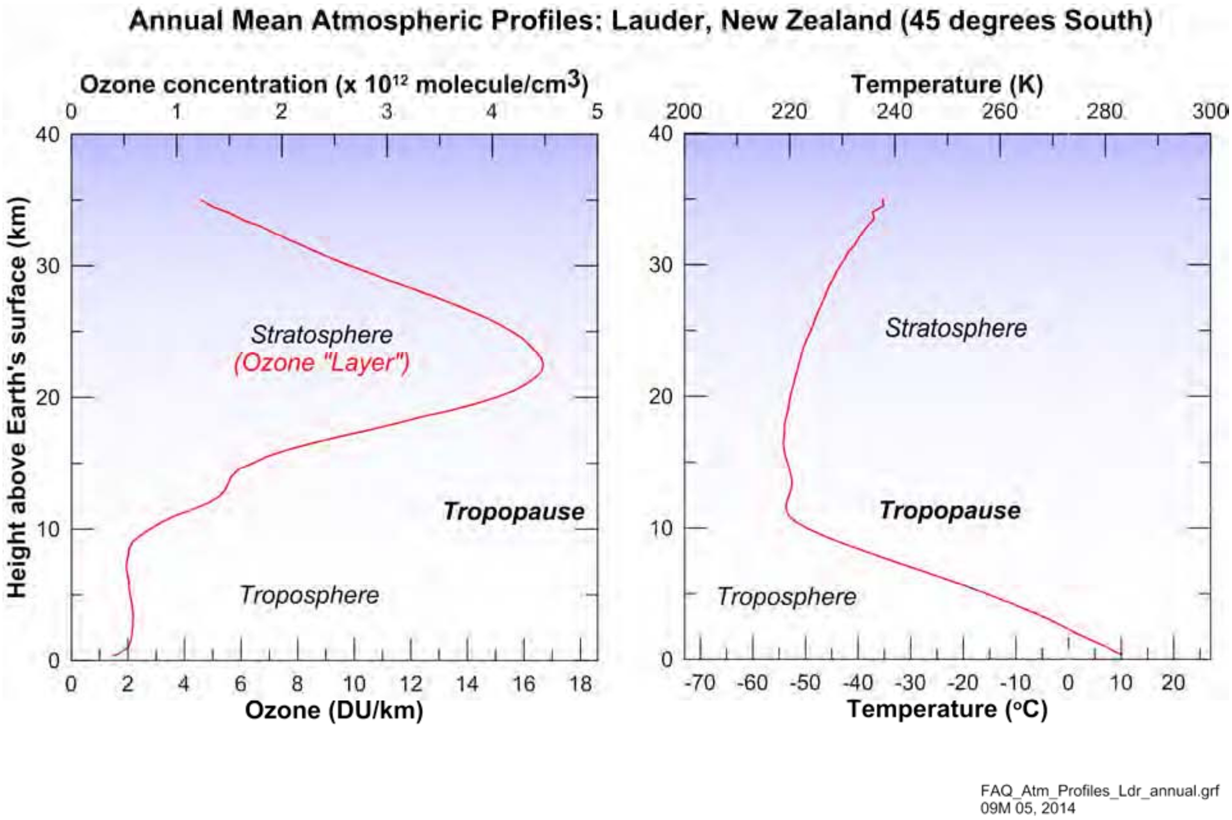


Figure 1.2: Atmospheric profiles of ozone and temperature measured with instruments carried by balloons. Figure provided by Dr R McKenzie.

2. ARE THERE INTERACTIONS BETWEEN OZONE AND CLIMATE CHANGE?

The relationship between ozone and climate change is complex as depicted in Figure 2.1 and explained on the next pages.

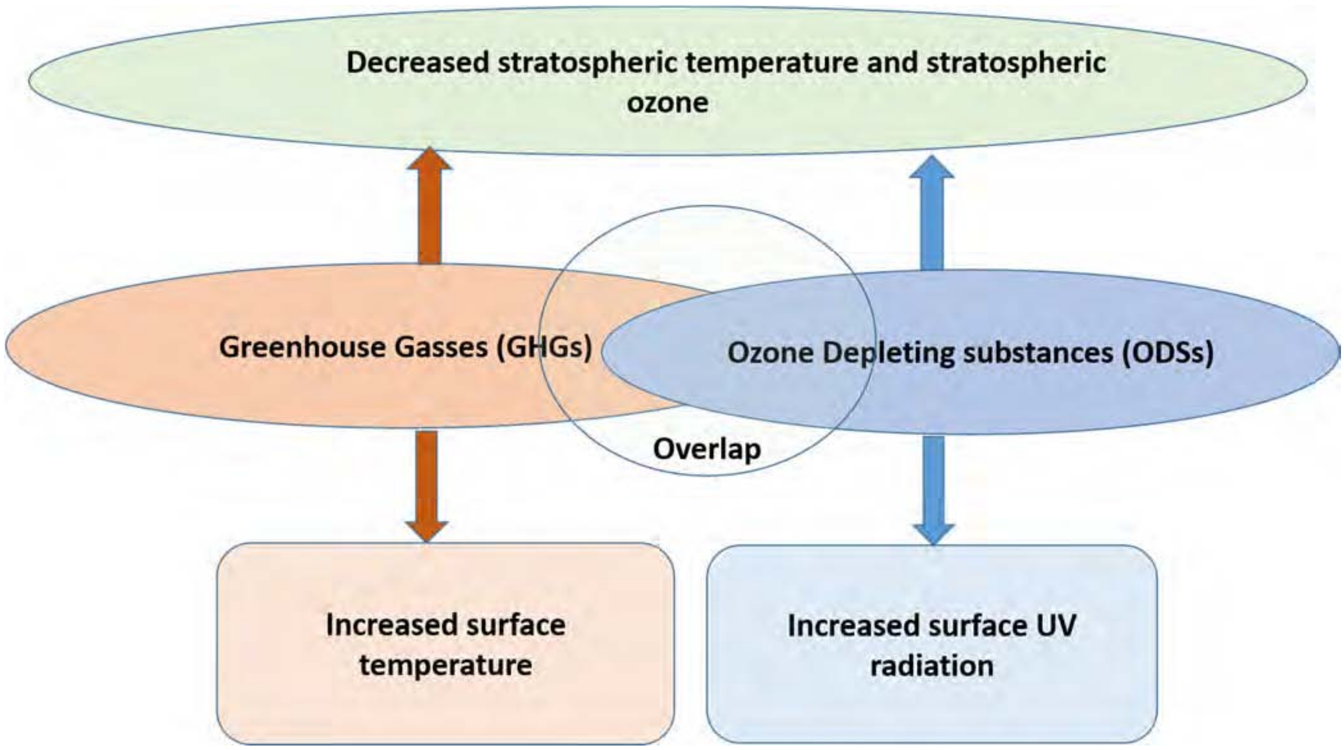


Figure 2.1. Schematic of ozone focused stratospheric chemistry-climate interactions. Links between components of the chemistry-climate system are indicated with arrows.

a. Is ozone depletion affected by climate change?

Climate change will affect ozone depletion through changes in atmospheric conditions that alter the chemical production and loss of stratospheric ozone. The interactions are complex. Climate change is expected to decrease temperatures and water vapour abundances in the stratosphere.

Ozone, the chlorofluorocarbons (CFCs), and their substitutes, are greenhouse gases (GHGs) that have a relatively small (± 13%) contribution to climate change. Several other gases that are involved in the chemistry of ozone depletion are also active greenhouse gases. They include water vapour, methane, and nitrous oxide. Increases in these gases will ultimately lead to increases in stratospheric gases that destroy ozone. Changes in solar output and future volcanic eruptions (the latter through injection into the atmosphere of particulates and gases that form an active surface for ozone depletion) will influence both climate change and ozone depletion.

While recent ozone depletion has been dominated by chlorine and bromine in the stratosphere, in the longer term (~100 years) it seems likely that the impact of climate change will dominate, through the effects of changes in atmospheric circulation and chemistry. Increases in GHGs over the first half of the current century may contribute to a colder stratosphere, leading to a decrease in the rate of destruction of ozone outside Polar Regions. In Polar Regions however, the lower temperatures may lead to some increases in polar stratospheric clouds that can lead to exacerbation of ozone depletion. The temperature changes are also leading to changes in atmospheric circulation. These changes may aid the mixing of long-lived CFCs from the troposphere to the stratosphere that will increase their rate of photochemical destruction. This can lead to more severe ozone depletion in the short term but will contribute to faster ultimate recovery of ozone. Changes in polar ozone can also lead to changes in circulation patterns in the lower atmosphere, which in turn affect surface climate. The effects of climate change on UV radiation are twofold: those that influence total ozone directly, and those that depend on changes in other variables (such as clouds, aerosols or snow cover) that influence solar UV indirectly. This is further complicated by the notion that decreasing the water vapour in the stratosphere will cause cooling of the Earth's surface, competing with the present warming.

b. Has stratospheric ozone depletion had an influence on climate change?

Stratospheric ozone depletion has an influence on climate change since both ozone and the compounds responsible for its depletion are active greenhouse gases.

Halocarbons such as CFCs have contributed to positive direct radiative forcing and associated increases in global average surface temperature. Ozone depletion due to increasing concentrations of ozone depleting substances (ODSs) has an indirect cooling effect. Warming due the existence of ODSs and cooling associated with ozone depletion are two distinct climate forcing mechanisms that do not simply offset one another. Bromine-containing gases currently contribute much more to cooling than to warming, whereas CFCs and hydrochlorofluorocarbons (HCFCs) contribute more to warming than to cooling. Hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs) contribute only to warming. The indirect cooling effect of ODSs is projected to cease upon ozone layer recovery.

Actions taken under the Montreal Protocol resulted in the replacement of CFCs with HCFCs, HFCs, and other substances or methods of fulfilling their main uses, e.g. as coolants. Because these replacement chemicals/compounds generally have lower global warming potentials (GWPs), and because total halocarbon emissions have decreased due to the Montreal Protocol and its amendments and adjustments, their contribution to climate change has been reduced. Ammonia and those hydrocarbons used as halocarbon substitutes are very likely to have a negligible effect on global climate.

Substitutes for ODSs in air conditioning, refrigeration, and foam blowing, such as HFCs, PFCs, and other gases such as hydrocarbons, are not expected to have a significant effect on global tropospheric chemistry.

c. How is ozone depletion influencing Southern Hemisphere climate?

Ozone depletion changes the distribution of atmospheric heat resulting in distinct alterations to Southern Hemisphere atmospheric circulation and climate factors such as precipitation and temperature.

Stratospheric ozone depletion and resultant cooling over Antarctica has caused the tropopause to lift allowing the polar westerly jet stream to shift southwards (Figure 2.2). The speed of both the polar jet and the westerly winds has also increased, keeping most of Antarctica cold as the rest of the world warms. This shift in the westerly's and their increased strength has changed atmospheric and oceanic circulation throughout the Southern Hemisphere by creating a more positive phase of the Southern Annular Mode (SAM). The SAM index describes the difference in sea-level pressure between the latitudes of 40˚S and 60˚S. Over the past century, increasing greenhouse gases and then ozone depletion over Antarctica have both pushed the SAM towards a more positive phase and the SAM index is now at its highest level for at least 1000 years. Positive SAM anomalies are characterised by stronger sub polar westerly winds positioned further south over the continental landmass, colder Antarctic temperatures and low atmospheric pressure over the icecap. As a result, high latitude precipitation has increased and the mid-latitude dry zone has moved south as shown (Figure 2.2). The resultant changes to precipitation and temperature and some of their ecosystem impacts are just emerging. In addition to increased wind across the Southern Ocean and colder temperatures across Antarctica, these include warmer and wetter summers in Southern Africa, SE South America, SE Australia and E New Zealand and warmer drier summers in Patagonia. In southernmost South America these drier conditions have been linked to slower growth of trees, while in New Zealand the wetter summers have led to increased tree growth.

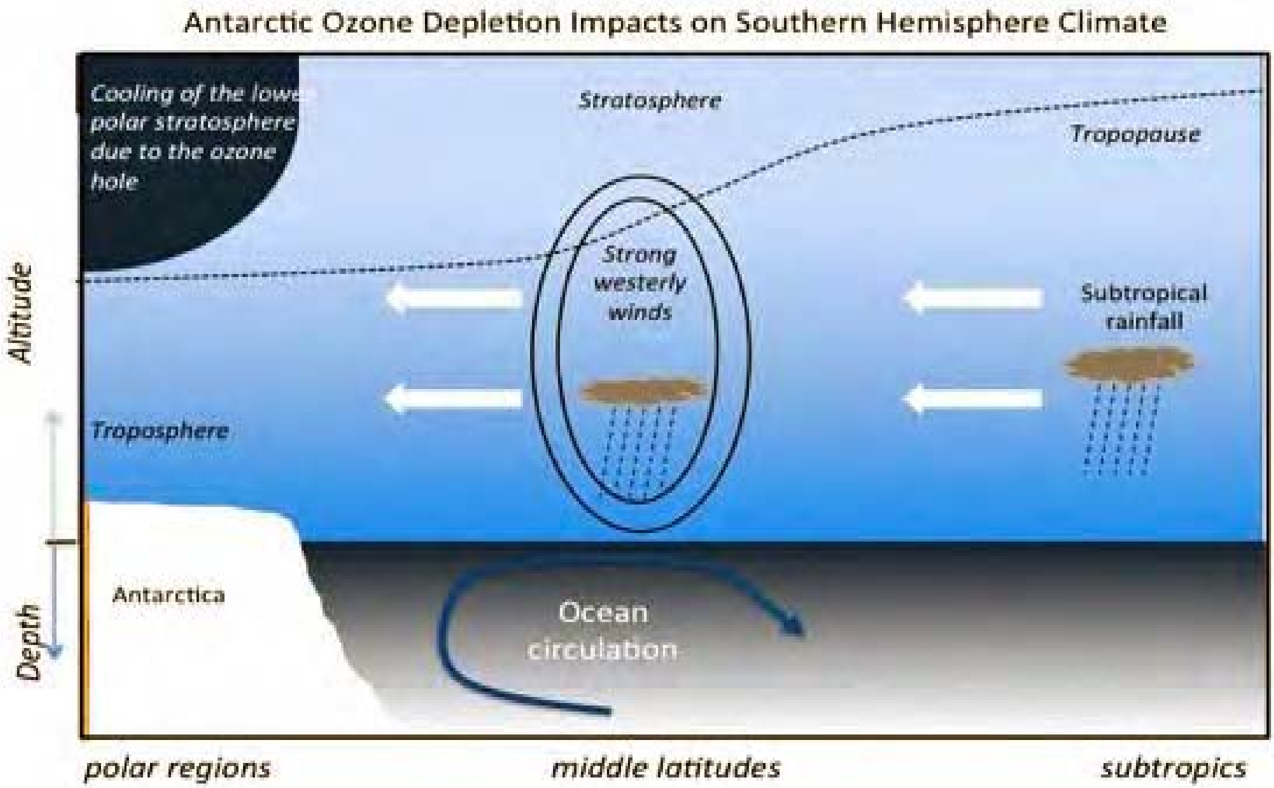


Figure 2.2 Schematic illustration of Southern Hemisphere climate impacts in the austral summer associated with Antarctic ozone depletion. This ozone depletion has cooled the Antarctic stratosphere, shifting the mid-latitude westerly jet pole ward with associated rainfall impacts (shown by the white arrows). These changes in rainfall have been observed in Australia, New Zealand, Africa and South America. The wind changes have also strengthened the subtropical rotating ocean currents and overturning circulation in the ocean (shown by the blue arrow). Figure provided by David J. Erickson III and Sharon Robinson.

3. WHAT IS THE RELATIONSHIP BETWEEN OZONE AND SOLAR UV RADIATION?

There is an inverse relationship between the concentration of ozone and the amount of UV radiation transmitted through the atmosphere since ozone absorbs some of the UV radiation. The main benefit of ozone is that it absorbs UV radiation from sunlight so that the intensity of UV radiation at Earth's surface is dramatically lower than at the top of the atmosphere. If there were no ozone present, the intensities of UV-B radiation at ground level would be increased by orders of magnitude, leading to substantial harmful environmental impacts.

Only a small fraction of the radiation emitted by the Sun is in the UV range. This range extends from 100 to 400 nm and is divided into three bands: UV-A (400 – 315 nm), UV-B (315 – 280 nm) and UV-C (280 – 100 nm). As the Sun's radiation passes vertically through the atmosphere, all the UV-C and approximately 90% of the UV-B is absorbed by ozone and oxygen molecules in the stratosphere. UV-A radiation is less affected by the atmosphere. Therefore, the UV radiation reaching Earth's surface is composed mainly of UV-A with a small UV-B component (Figure 3).

The amount and variability of the UV-B component depends on the solar elevation angle, which defines the path-length through the atmosphere, and also on the amount of ozone. A decrease in the concentration of ozone in the atmosphere results in increased UV-B radiation at the surface of the Earth. UV-B radiation is much more biologically active than UV-A radiation and can have either beneficial or detrimental effects on living organisms. Changes in the amount of UV-B radiation (for example due to stratospheric ozone depletion) are very important for ecosystems, materials and humans.

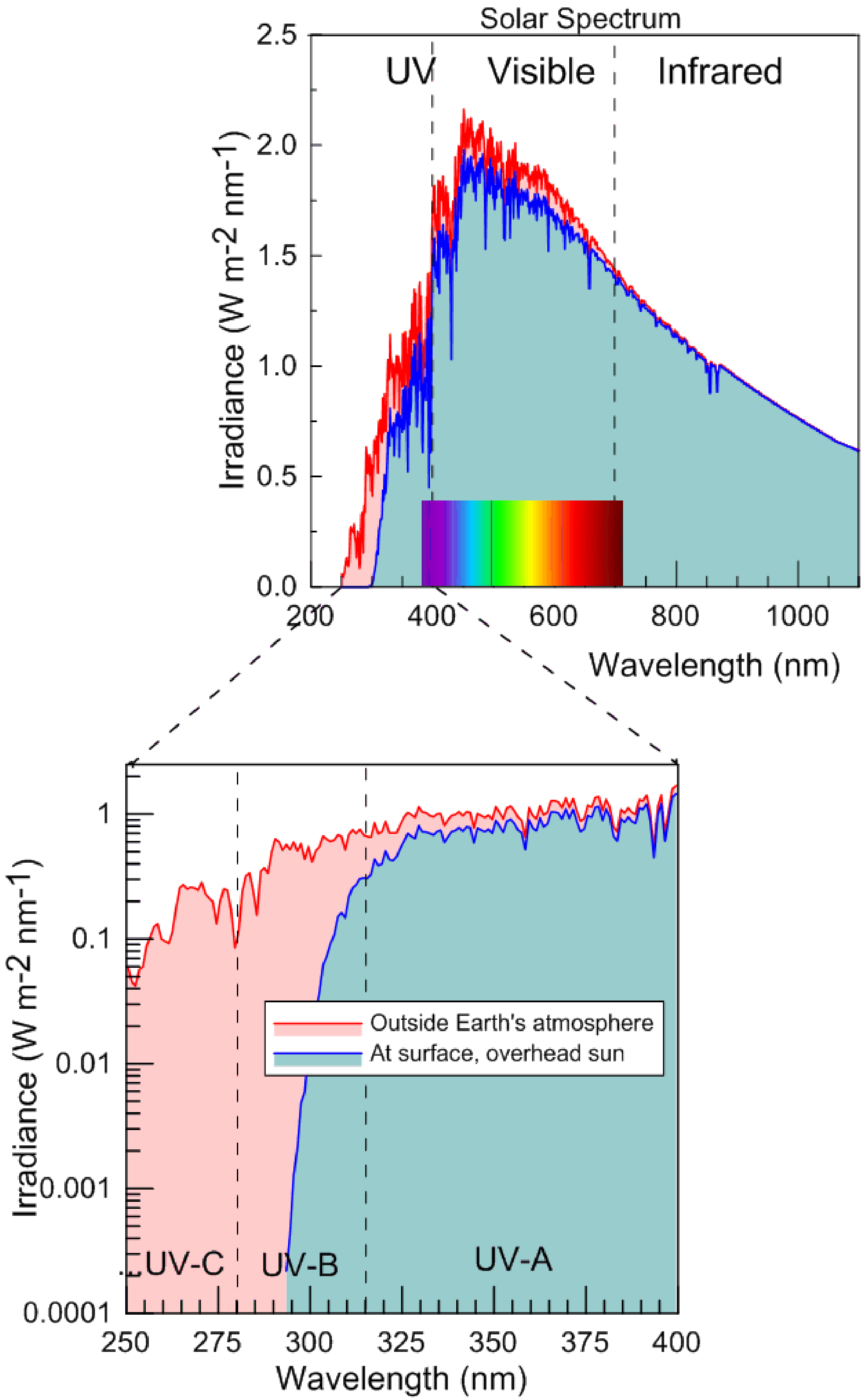


Figure 3: Absorption of UV radiation by ozone. The blue curve shows that ozone absorption increases rapidly at shorter wavelengths so that at wavelengths less than 300 nm, less than 1% of the radiation is transmitted. Figure provided by Dr R McKenzie.

4. WHY IS THERE CONCERN ABOUT UV RADIATION?

The high photon energies at UV-B wavelengths are capable of breaking molecular bonds in DNA, which is the building block of life. Damage to this molecule can result in multiple health effects, including skin cancers. UV radiation can adversely affect agricultural and aquatic productivity as well as air quality. It can also reduce the effective lifespan of materials such as plastics and paint products. Some UV radiation is however beneficial for human health such as in the production of vitamin D and for killing pests and pathogens.

UV-B radiation makes up only a small proportion of the UV radiation reaching Earth's surface, because it is largely absorbed by stratospheric ozone. However, UV-B radiation is the most biologically damaging as the high photon energies are sufficient to break molecular bonds. The longer wavelength UV-A is less damaging, but is implicated in some adverse effects, including skin damage. Ozone has only a minor effect on UV-A radiation.

For many, but not all, environmental effects and biological processes, the damaging effect of UV radiation increases as the wavelength decreases (and hence the energy per individual photon increases).

Table 4. Approximate contributions (Wm^{-2}) to solar energy from UV-A and UV-B radiation at selected ozone amounts for overhead sun (sza=0) and for sza=60 °. All for an Earth-Sun separation of 1 Astronomical Unit (the mean distance between the Earth and the Sun i.e., close to the equinoxes), cloudless skies, no aerosols, and assuming a value for the solar constant of 1365 W m^{-2}. (See also Question 6 for an explanation of sza).

Solar zenith angle (sza)	Ozone levels (Dobson Units)	Solar Energy Contribution (Wm^{-2})	
		UV-B (280-315 nm)	UV-A (315-400 nm)
Extra-terrestrial		20.8	85.1
Earth surface, sza= 0	300	3.82	65.1
Earth surface, sza=60,	450	0.60	26.3
Earth surface, sza=60	300	0.90	26.7
Earth surface, sza=60	100	1.89	27.2

5. WHAT IS THE UV INDEX?

The UV Index (UVI) describes the level of solar UV radiation at the Earth's surface relevant to sunburn in humans (erythema).

Information about the intensity of UV radiation is provided to the public in terms of the internationally adopted UVI colour-scale, along with appropriate health warnings, as shown in Table 5. The colours corresponding to the various ranges are standardised throughout the world.

The UVI can be measured directly with instruments designed specifically to measure sun burning UV radiation. For clear-sky conditions, the UVI can be calculated approximately from knowledge of the ozone and the solar zenith angle (also known as solar elevation angle; see Question 6 for more detail). However, the UVI at a specific location and time depends strongly on the cloud cover and on the amount of aerosols. Other influential factors include the seasonally varying Sun-Earth separation, the altitude, and surface reflection. When the surface is snow-covered, the UVI can be up to 60% greater than for snow-free surfaces. Several countries provide daily forecasts of the UVI that take predicted changes in ozone and cloud cover into account. Further details about the UVI can be found at
www.unep.org/PDF/Solar_Index_Guide.pdf

Table 5: The UV Index and related colours as used by the World Health Organization

Exposure Category	UVI Range
Low	**< 3**
Moderate	**3 to 5**
High	**6 to 7**
Very High	**8 to 10**
Extreme	**>11**

6. WHEN AND WHERE SHOULD THERE BE CONCERN ABOUT EXPOSURE TO UV RADIATION?

The effects of UV radiation depend on how much is received. Therefore it is important to understand how exposure to UV radiation varies, due to both variation in levels at Earth's surface and to human activities.

The main determinants of surface UV radiation are the elevation of the Sun above the horizon – known as the solar zenith angle (sza) (Figure 6.1), and the amount of ozone in the atmosphere. Consequently, the highest UVI values occur in the tropics, where ozone amounts are at their lowest (apart from the Antarctic "ozone hole"), and where the sun is directly overhead at noon. UV radiation is also influenced by seasonal changes in Sun-Earth separation (closest in Dec/Jan), altitude, and surface reflection (albedo). The variation in the UVI as a function of the solar zenith angle and the ozone amount is illustrated in Figure 6.2.

In addition to this variation in estimated clear-sky UVI, there are a range of modifiers of the UVI at Earth's surface. Clouds and aerosols can reduce levels of UV radiation by more than 50%; and on average they block about 30% of the clear-sky radiation. However, scattering from clouds that are in the direct beam of the sunlight, but which do not obscure it, can lead to significant shorter term enhancements in levels of UV radiation. For aquatic systems, the transmitted UV radiation also depends on the clarity of water, with coloured dissolved organic matter (CDOM) being an important attenuator.

Most organisms that are exposed to UV radiation have their own means of blocking it to reduce the dose received (e.g., melanin in human skin, or flavonoids in some plant species).

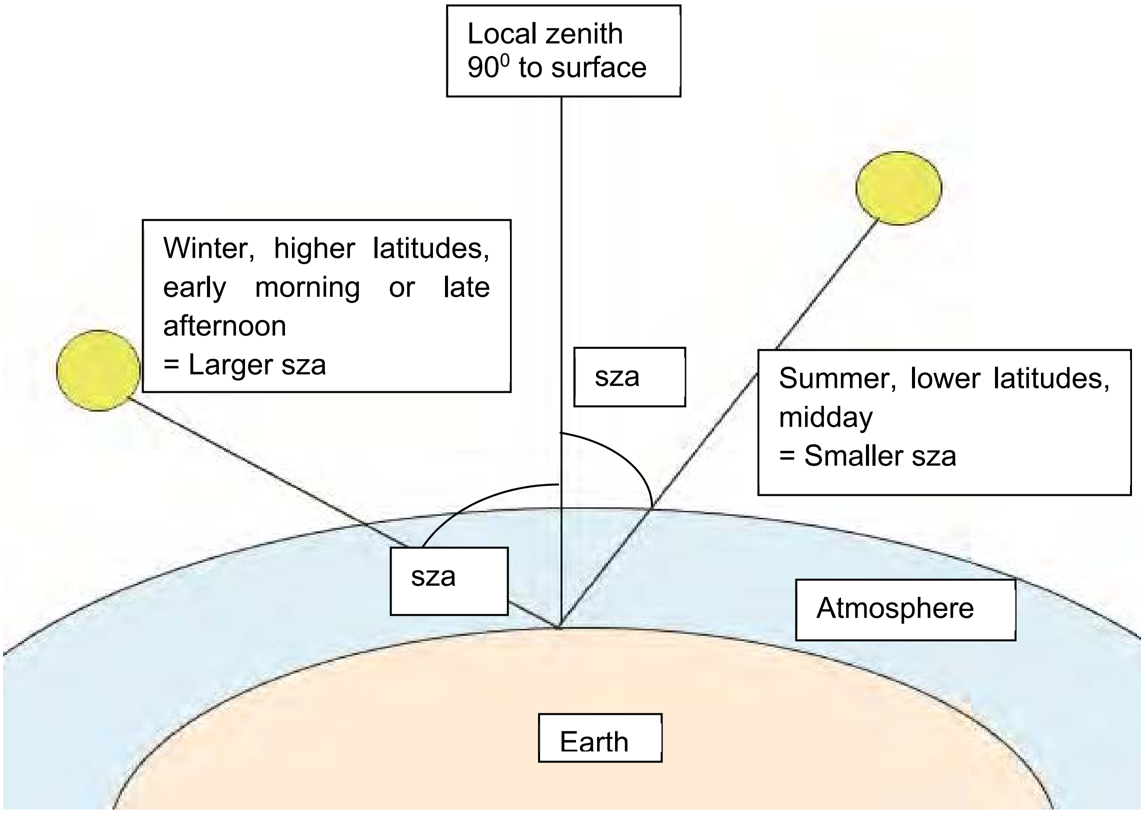


Figure 6.1: The solar zenith angle (sza) is the angle between the theoretical perpendicular position of the Sun and the incoming rays from the Sun

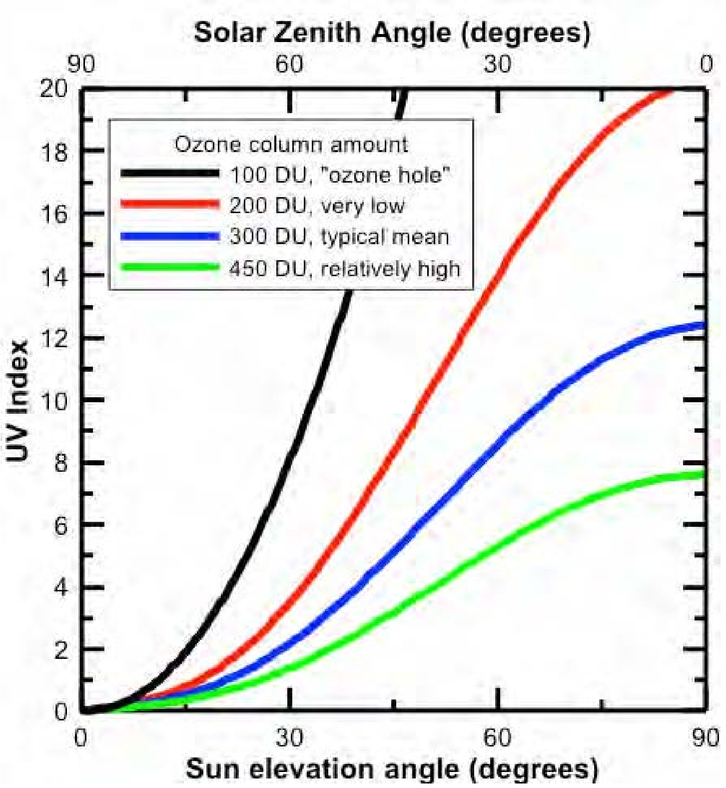


Figure 6.2: Variation of the clear-sky UVI in relation to solar elevation. The coloured lines represent different ozone concentrations, measured in Dobson Units (DU), Figure provided by Dr R L McKenzie, NIWA.

The maximum UVI for any location on the globe is illustrated in the map below (Figure 6.3). The UVI has significantly higher summer maxima in the Southern Hemisphere compared with corresponding latitudes in the Northern Hemisphere. In the tropics at sea level the UVI can exceed 16 and a peak terrestrial value of 25 has occurred at high altitudes e.g. Altiplano region of South America (Figure 6.3). Recently a value of 35 has been measured in Chile. Generally, peak UVI values decrease with increasing latitude and in Polar Regions; UVI values tend to be much lower, and are zero during the polar winter night. However, the Antarctic region, which is affected by the Antarctic “ozone hole”, is a notable exception. Peaks there can exceed an UVI of 16. Outside the protective layer of Earth’s atmosphere (altitude > 50 km), the UVI can exceed 300.

The higher the UVI, the greater the potential for damage, and the less exposure time it takes for harm to occur. For fair-skinned individuals a UVI of more than 10 can cause sunburn from an exposure of about 15 minutes.

High levels of UV radiation can have a wide range of environmental impacts. For any particular process, the impact depends on the difference in absorption of the different wavelengths. For example, effects on human skin erythema (sunburn) will be proportional to the dose of erythemally active UV radiation.

In humans, high levels of exposure to UV radiation can lead to skin-damage (e.g., sunburn) skin cancer and eye damage (e.g., cataract). However, some exposure to UV radiation is required to maintain adequate levels of vitamin D. UV radiation can also affect other animals, plants, aquatic organisms, and whole ecosystems. It influences air quality through the production of photochemical smog, and the degradation rates of materials such as paints and plastics. These are discussed further in subsequent FAQs.

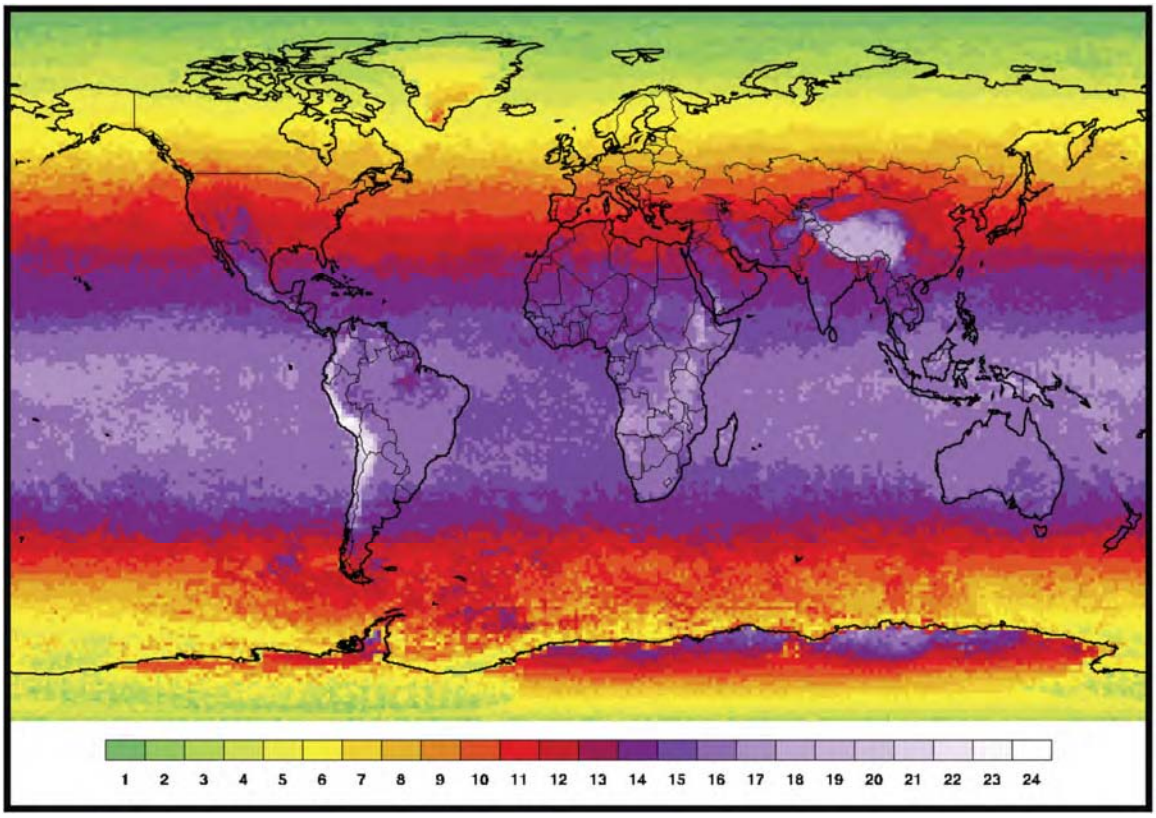


Figure 6.3: Average values for the maximum UVI at each point on the globe derived from the total ozone monitoring satellite (TOMS) measurements over several years. Figure provided by Ben Liley, NIWA Lauder (note that the colours used to depict the UVI here are different to those provided in Table 5)

7. HOW IS UV RADIATION EXPECTED TO CHANGE IN THE FUTURE?

Due to the combined effects of ozone recovery, and changes in cloud cover induced by increasing greenhouse gases, relatively modest changes in UV radiation are expected in the future.

In the Antarctic region, significant reductions in mean noontime UVI values are expected due to the continuing recovery of ozone, especially during the springtime "ozone hole" period. By the end of the 21st century, these future reductions in UVI due to projected ozone increases will be comparable with the increases that occurred due to ozone depletion in the past, as shown in the bottom panels of Figure 7. Other changes in UVI induced by climate change effects are also potentially important. For example, projected increases in cloud cover and reductions in surface reflectivity due to ice-melt in the Arctic, and in the margins of the Antarctic continent, are expected to continue to contribute to reductions in UVI (see middle panels of Figure 7). However, there is only low confidence in these estimates of effects. Outside Polar Regions, future changes are likely to be dominated by changes in aerosol extinctions, particularly in densely populated areas. For example, large increases in UVI are projected for parts of Asia, to counterbalance the large reductions in UVI that probably occurred there over the past few decades (see upper panels of Figure 7). Because of uncertainties in both the projected amounts of aerosols, and their optical properties, these aerosol effects are uncertain. For that reason, we do not provide an estimate of the sum of the individual effects.

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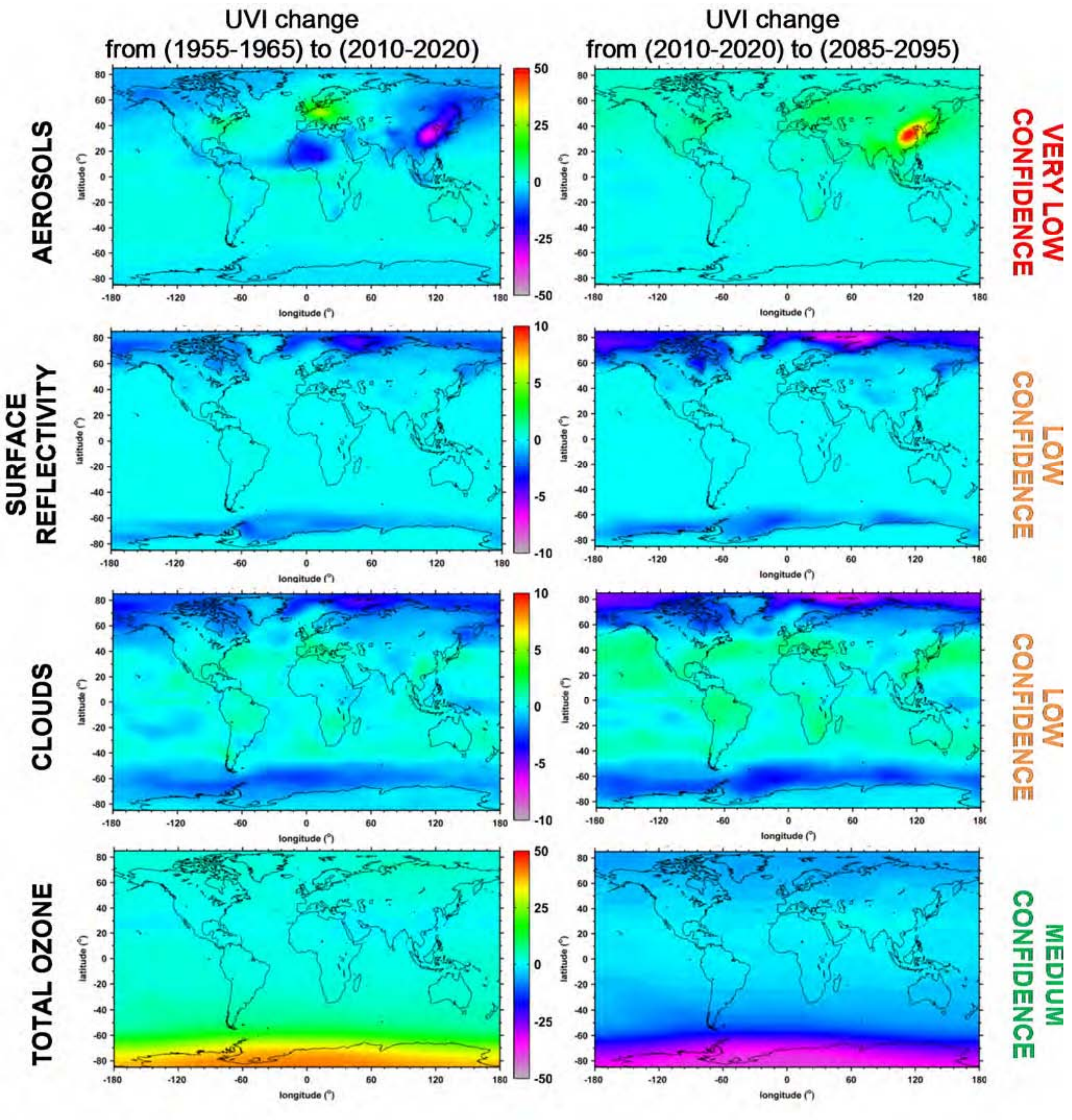

Figure 7. Calculated percentage changes per year in noontime UVI relative to the "present" (i.e., 2010-2020). The left column shows simulated changes since 1955-1965. The right column shows the simulated changes expected from the present to the period 2085-2095. Effects of aerosols, surface reflectivity, cloudiness and total ozone on UVI are shown in each row, with our assessment of the confidence in the UVI projections. Note the different colour-scales for each row.

8. HOW IS UV RADIATION BAD FOR MY HEALTH?

Exposure to solar UV radiation damages the skin and eyes. These effects can be acute after intense exposure or chronic after long-term exposure.

Sunburn is the major immediate (acute) outcome in the skin of over-exposure to sunlight. The dose of solar UV-B radiation required to induce sunburn varies considerably from one individual to another, largely depending on the pigment in their skin. Six categories of skin type are commonly used to describe sensitivity to sunlight (see Table 8).

Exposure of the unprotected eye to intense UV-B radiation causes sunburn of the superficial layers of the eye or the inner surface of the eyelids, resulting in photoconjunctivitis, or affecting the cornea, resulting in photokeratitis. This can cause pain and blindness for a few hours to a day or two. Protection of the eye is needed under conditions of high ambient UV radiation or where there are highly reflective surfaces, such as snow or white sand. Sunburn occurs because energy from UV radiation damages DNA and other molecules in the skin or eyes.

The inflammatory response that occurs to manage this damage includes increased blood flow to the area and release of chemicals that stimulate nerve fibres, leading to redness and pain, respectively. Damage to the DNA of skin cells can result in their destruction; peeling of the skin may occur if DNA damage is severe and affects a large number of skin cells.

Exposure to UV radiation suppresses the generation of cell-mediated immune responses (Box 8). Higher exposure to UV radiation around the time of vaccination may result in a lower immune response, at least in some individuals. UV irradiation can cause immune suppression that allows the reactivation of some viruses. For example sun exposure can trigger the reactivation of latent herpes simplex virus infection and the reappearance of vesicles (cold sores or fever blisters) in the skin (Figure 8.1).

Table 8: Skin types commonly used to categorise sensitivity of the skin following exposure to UV radiation.

Skin phototype	Sun sensitivity	Sunburn/tan
I	Extremely sensitive	Always burns, never tans
II	Very sensitive	Burns readily, tans slowly and with difficulty
III	Moderately sensitive	Can burn after high exposure, tans slowly
IV	Relatively tolerant	Burns rarely, tans easily
V	Variable	Can burn easily, difficult to assess as pigment is present already
VI	Relatively insensitive	Rarely burns

The major harmful effect of chronic (long-term) exposure of the skin to sunlight, and/or intermittent episodes of sun burning, is the development of skin cancers, including non-melanoma skin cancers and melanoma (Figure 8.2). Repeated DNA damage from exposure to UV radiation results in mutations in specific tumour-related genes, including those required for DNA repair. Immune suppression induced by exposure to UV radiation (Box 8) allows the abnormal tumour cells to develop and form skin cancers.

The non-melanoma skin cancers are divided into squamous cell carcinoma and basal cell carcinoma (Figure 8.2), and are the most common cancers in many countries. Incidence is highest in fair-skinned populations living in sunny climates, and increases with increasing age. The majority of these tumours are found on the face and head - the sites most consistently exposed to the sun. Non-melanoma skin cancers are generally readily treatable and are rarely fatal but both the tumours and the treatment may be disfiguring. The number of new cases of non-melanoma skin cancer occurring each year has increased significantly in many countries over the past 40 years or so, particularly in fair-skinned populations.

Melanomas of the skin (Figure 8.2) are much more dangerous than the non-melanoma skin cancers, with a significant risk of death if not treated at an early stage. They arise from the cells that form the pigment (melanin) that determines skin colour. While non-melanoma skin cancers predominantly occur in older adults, melanoma can develop in people of all ages. For example, it is the most commonly reported cancer in women age 17-33 years in Australia. Melanoma occurs mainly in fair-skinned populations, and, while high levels of sun exposure at any age increase the risk of melanoma, high dose exposure and/or sunburn in childhood may be particularly important. In people with fair skin, melanoma occurs most frequently on the back in men and on the legs in women. In people with dark skin, melanoma is more common on the soles of the feet than on the sun-exposed areas of the body. The incidence of melanoma has increased in many countries in recent decades, but current figures indicate a levelling-off or even a decrease in younger age groups in countries with strong sun protection programs.

Over the long term, sun exposure also causes photoageing of the skin, seen as wrinkling and freckling of the skin and the development of moles (naevi), brown spots (solar lentigines) and crusty lesions of the skin called actinic keratoses. UV radiation in both the UV-A and UV-B wavelengths are responsible, causing mutations in DNA and loss of the elastic fibres in the skin. Some of these changes, particularly actinic keratoses and numerous moles, are associated with an increased risk of skin cancers.

Chronic exposure of the eye to UV radiation increases the risk of pterygium (surfer’s eye) and cataract, both of which are irreversible. Pterygium is an invasive growth on the surface of the eye that may impair vision and require surgery (sometimes repeatedly). Cataracts are extremely common in older people and are at least partly caused by chronic exposure of the eye to UV radiation. Clouding of the lens of the eye progresses slowly and painlessly, leading to an increasing loss of vision and eventually blindness, if not treated surgically.

Immune suppression resulting from chronic exposure to UV radiation may underlie the involvement of certain human papillomavirus types (that typically cause warts) in the formation of squamous cell carcinomas.

Box 8: UV-induced immune suppression

When UV radiation reaches the skin, it is absorbed by specific molecules called chromophores. These initiate a cascade of events affecting the immune system that result in a decreased ability to respond to "foreign" challenges, such as invading microorganisms or tumour proteins, encountered within a short period of the exposure. The production of a range of immune mediators is altered, and specialised lymphocytes called T regulatory cells are induced. All of these changes lead to long-term suppression of immune responses to the specific challenge.

Figure 8.1: Cold sores caused by reactivation of latent herpes simplex virus following exposure to solar UV-B radiation. Photograph supplied by Professor M. Norval (University of Edinburgh, Scotland).

Figure 8.2: Examples of the 3 major types of skin cancer. Photograph supplied by Professor M. Norval (University of Edinburgh, Scotland).

9. HOW WILL CLIMATE CHANGE AFFECT EXPOSURE OF HUMANS TO UV RADIATION?

The effects of climate change on the amount of UV radiation reaching Earth's surface will be small. However warming temperatures and changes in precipitation patterns may affect the amount of time people spend outdoors and their use of sun protection, and thus the dose of UV radiation to which they are exposed.

The risk of developing skin cancers, eye diseases and immune suppression depends on the dose of UV radiation reaching the relevant tissues. This in turn depends on the amount of UV radiation reaching Earth's surface and on the sun exposure behaviour of the individual: time spent in the sun and use of sun protection such as clothing, hats, sunscreen and sunglasses. As noted in previous sections, the effects of climate change on the amount of UV radiation reaching Earth's surface will be small. The major uncertainty is whether people will spend more or less time outdoors in the sun, and expose more or less skin to the sun, as temperatures rise, but humidity, storms, floods and droughts also increase. Trends in fashion, holiday locations and leisure activities will also be important in determining the amount of exposure to UV radiation that people receive in future years. There is some evidence that skin cancers develop more rapidly when ambient temperatures are higher, but the relevance of this finding to health effects of climate change is unclear at present.

Altered levels of immune suppression, due to changes in the received dose of UV radiation may change vulnerability to infectious diseases and allergic diseases that also have changed in geographic and/or seasonal distribution as a result of climate change. At this time, the direction and magnitude of any such effects are highly speculative.

10. HOW IS UV RADIATION GOOD FOR MY HEALTH?

The best known benefit of exposure to solar UV radiation is production of vitamin D in the skin. In most regions of the world, humans obtain most of their vitamin D requirements from sun exposure. Many health benefits have been proposed for vitamin D. Exposure to UV radiation may also have beneficial effects through non-vitamin D pathways. Solar UV radiation can kill viruses, bacteria, and protozoan parasites in surface waters, making them safer to drink.

Vitamin D is the precursor of a hormone that is essential in humans for the maintenance of good health, particularly of the musculoskeletal and immune systems. Although the diet of humans contains some items rich in vitamin D, such as oily fish and eggs, most vitamin D in the majority of people is produced by exposure of the skin to solar UV radiation (Figure 10). Vitamin D is synthesised most effectively when the sun is at its height in the summer months and in the middle of the day; little or none is synthesised in the early morning and late afternoon, or in mid-winter at latitudes higher than about 40 degrees (for example, Boston, USA 42°N; Madrid, Spain 40°N; Christchurch, New Zealand 43°S). Individuals with dark skin usually require more sun exposure than those with fair skin to make the same amount of vitamin D, and the production is less efficient in older people.

It is important for many aspects of human health to maintain a sufficient level of vitamin D in the body. An assessment of this can be made by measuring the concentration of a vitamin D metabolite [25-hydroxyvitamin D, 25(OH)D] in the blood. There is considerable controversy around the optimal blood level of 25(OH)D, although a level of more than 50nmol/L (20ng/ml) is commonly recommended.

The active form of vitamin D is required in the body to maintain blood levels of calcium within a narrow range. The bones are a major store of calcium; vitamin D deficiency can result in release of calcium from the bones to maintain blood calcium levels, leading to defects in the bone that result in the diseases of rickets in children and osteomalacia in adults. There is controversial evidence currently that vitamin D deficiency may also increase the risk of a range of non-skeletal disorders. These include some internal cancers such as colorectal cancer, autoimmune diseases such as multiple sclerosis and type 1 diabetes, infections such as tuberculosis and influenza, and cardiovascular diseases such as hypertension. While some reports indicate that vitamin D supplementation decreases the risk of fractures, and possibly colorectal cancer, it has yet to be confirmed that increased exposure to solar UV-B radiation, affecting vitamin D status, can modulate the risk of these diseases.

In addition to the possible protective effect of higher vitamin D status on the development of some autoimmune diseases, there is emerging evidence that sun exposure itself may have beneficial effects through non-vitamin D pathways. In some autoimmune diseases, there is over-activity of certain T lymphocytes in the immune system against specific elements of the body's own tissues. Through the immunosuppression pathways, sun exposure and vitamin D may reduce this response, thus providing protection.

UV-B radiation is a potent disinfectant and naturally sterilises surface waters that may contain pathogenic microorganisms. Many people rely on surface waters for their drinking supplies, and the safety of these may depend on the dose of UV-B radiation (see also Question 14).

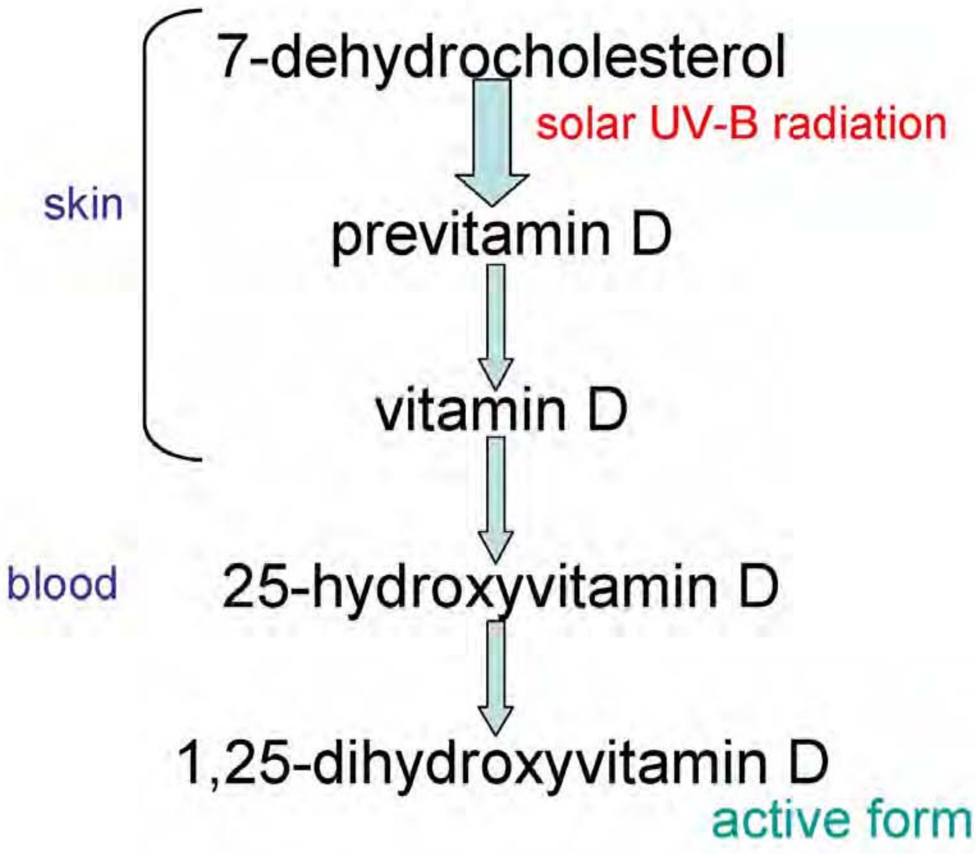

Figure 10. Simplified metabolic pathway leading to production of the active form of vitamin D which binds to receptors on target cells, thus initiating a variety of genetic and cellular responses.

11. HOW MUCH EXPOSURE TO SOLAR UV RADIATION SHOULD I HAVE?

Optimal sun exposure maximizes the beneficial effects and minimizes the adverse effects of exposure to UV radiation. Levels of UV radiation vary according to location (latitude, altitude and environment), season, time of day, cloudiness and levels of air pollution. People vary in their sensitivity to UV radiation, for both the beneficial and adverse effects of sun exposure, through differences in skin colour and a range of other genetically determined factors. There is no "one-size-fits-all" recommendation, but some guidance is given below.

The intensity of UV-B radiation from the sun is highest at low latitude, in summer and during the hours around noon (about 11 am until 3M). Many news outlets and government websites report the daily UV Index (UVI) and issue alerts when high values are predicted.

If you are outside, it is most important to avoid sunburn. The time taken to reach this point depends on many factors, including your ability to tan in response to exposure to the sun. The face is the most common place for skin cancers to develop, so when outside for more than brief casual exposures, wear a hat and protect your eyes. Hats with brims more than 10 cm wide are recommended for head and neck protection, and can reduce exposure of the eyes by up to 50%. The hood of a jacket and headwear with side-flaps can provide protection from UV-B irradiation to the side of the face and eyes. Wrap-around sunglasses are better at protecting the entire eye than conventional sunglasses with open sides (see Figures 11.1 and 11.2).

Vitamin D is made most efficiently in the middle of the day, but this is also the time when UV radiation is most intense and there is the greatest risk of sunburn. Brief casual exposures during the central hours of the day may not require sun protection; however sun protection is recommended when outside for longer periods, including during the middle of the day, if the forecast UVI is 3 or greater. Some textiles are highly effective at blocking the penetration of UV rays, but others are less so. If you can easily see through the fabric when you hold it up to the light, it is likely to be less effective at screening UV radiation. Sunscreens are effective but need to be applied at the stated concentration and re-applied frequently, especially after swimming. Often they are applied too sparingly. It is advisable to use a sunscreen with a SPF (sun protection factor) rating of at least 15 which provides protection against the sunburn caused by UV-B radiation, and which also includes protection against UV-A radiation (graded by up to 5 stars). It is particularly important to protect children from sunburn, episodes of which could lead to increased risk of skin cancer development in adulthood. People with darker skin need higher exposure to UV-B radiation to develop sunburn, and also to make vitamin D, than people with fairer skin.

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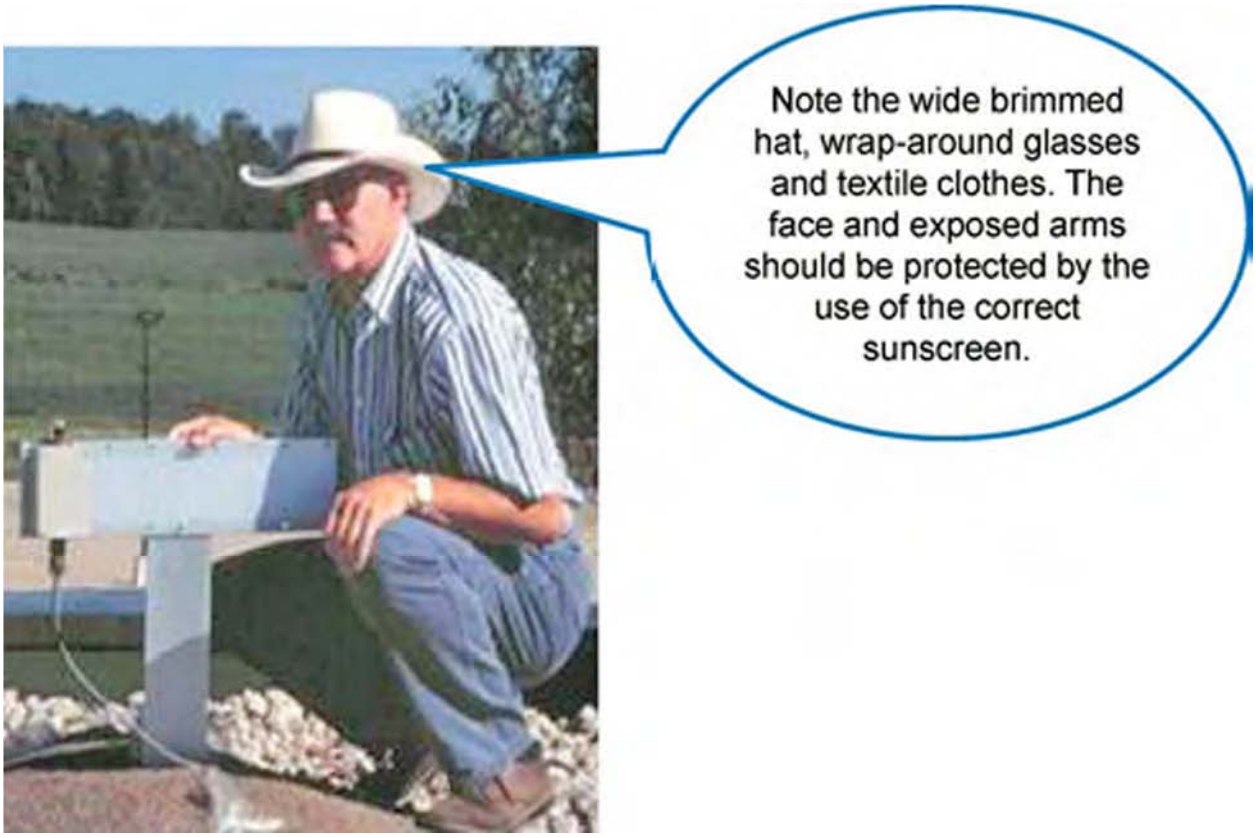

Figure 11.1. Wearing the correct clothing and the use of sunscreen can protect against UV radiation. (Photograph supplied by Dr A. Cullen, University of Waterloo, Canada.)

Figure 11.2. Wearing the correct clothing and the use of sunscreen can protect against UV radiation. (Photograph supplied by Mary Norval)

12. ARE THE REPLACEMENTS FOR OZONE DEPLETING SUBSTANCES SAFE FOR HEALTH AND THE ENVIRONMENT?

The replacements for ozone depleting substances (ODSs) are tested for safety to health and the environment before they are approved for use and so far few problems have been found. Originally CFCs were thought to be safe for the environment, so there is always the possibility that safety issues could emerge the longer a product is used, the greater the volume that is produced, the more uses that are found, or with new findings about the environment. For example, when HFCs were proposed as substitutes for CFCs, the global warming potentials of such compounds were only just being conceptualized. Once such properties were recognized, it was realised that these compounds could only be a short-term solution and that they too would need to be replaced. Thus, there is a requirement to avoid complacency and to manage these substances responsibly.

The Significant New Alternatives Program (SNAP) of the U.S. Environmental Protection Agency (EPA) evaluates alternatives for ozone depleting substances prior to their use. Anyone planning to market or produce a substitute in the U.S. must provide notice to EPA of their intent, as well as providing health and safety information, before introducing it. Normally the health and safety information will include information on chemical and physical properties, flammability and basic toxicological information, and more recently, global warming potential. The SNAP program reviews the information in the context of the proposed use and issues one of four decisions: acceptable; acceptable subject to use conditions; acceptable subject to narrowed use limits; and unacceptable. The information on a particular compound is continually updated so that compounds may be proposed for additional uses or additional information may be added to the portfolio for a particular use and this could change the decision originally issued by the SNAP program.

The HFCs and HCFCs that are replacements for the CFCs have a smaller effect on the ozone layer. The HFCs and HCFCs are largely degraded before reaching the stratosphere. HFCs and HCFCs break down relatively rapidly into several products including the persistent substances such as trifluoroacetic acid (TFA) and chlorodifluoroacetic acid. These compounds are washed from the atmosphere by precipitation and reach surface waters, along with other chemicals washed from the soil. In locations where there is little or no outflow and high evaporation (seasonal wetlands and salt lakes), the concentrations of these products are expected to increase over time. The effects of increased concentrations of naturally occurring mineral salts and other materials is likely to be greater and more biologically significant than those of breakdown products of the HFCs and HCFCs.

TFA, a final degradation product of some HFCs and HCFCs, is very resistant to breakdown, and amounts deposited in flowing surface water will ultimately accumulate in the oceans. Based on estimates of current and future use of HFCs and HCFCs, additional inputs to the ocean will add only fractionally (less than 0.1%) to amounts already present from natural sources such as undersea vents and volcanic activity (Figure 12).

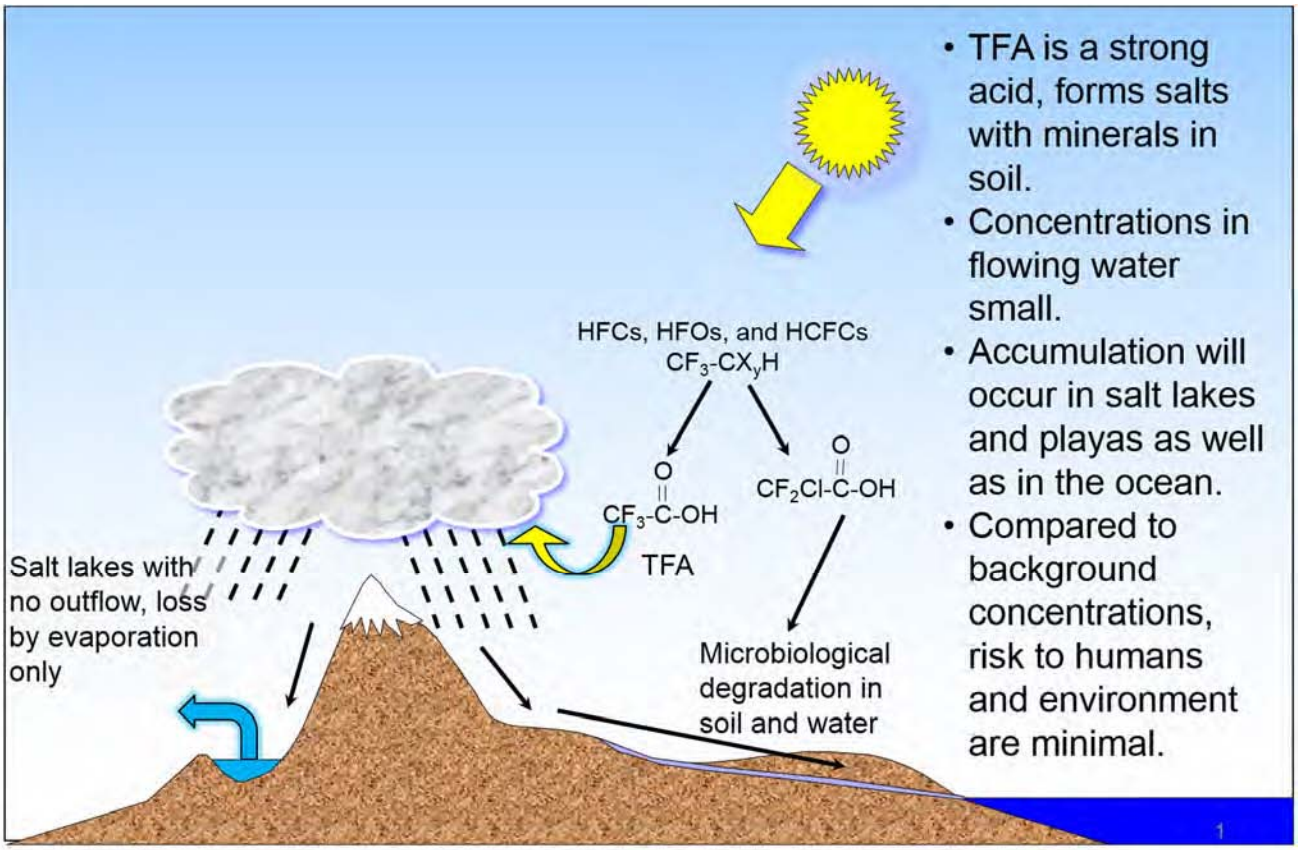

Figure 12. Illustration of the formation of trifluoroacetic acid (TFA) from HFCs and HCFCs in the lower atmosphere and the movement of the TFA into surface waters and the oceans. Figure provided by Keith Solomon.

13. WHAT EFFECTS DOES UV-B RADIATION HAVE ON NATURAL TERRESTRIAL ECOSYSTEMS, CROPS AND FORESTS?

UV-B radiation causes a wide range of responses in terrestrial ecosystems. Animals can move to avoid UV-B radiation but plants cannot. However, most plants (including agricultural and forest species) have mechanisms that provide some shielding from UV radiation. In some cases, increases in UV radiation are detrimental, for example, reducing production. However, some plant species have increased resistance to insect feeders when exposed to UV radiation, with a net result of decreased feeding on agricultural plants and greater productivity.

a. How do plants protect themselves from UV-B radiation?

Only a small portion of the UV-B radiation striking a plant penetrates into the inner tissues. The outer surface of the plant can be protected by light coloured hairs or waxes that reflect the UV-B radiation (Figure 13.1). Thicker leaves and stems (e.g. in succulents) also reduce the proportion of inner tissues exposed to UV-B radiation. In the majority of plant species tested, UV-B radiation induces the synthesis of compounds that act as sunscreens and prevent UV-B radiation from reaching sensitive biological components within the leaves. These protective screening compounds can be found inside the cells or bound to the cell walls (Figure 13.1). Even where screening of UV radiation is incomplete, plants have several mechanisms for repairing damage to vital biomolecules such as DNA, including one that uses sunlight to drive the repair reactions. This suite of protective mechanisms means that in general plants are able to protect themselves from increases in UV-B radiation especially if the plants are native to high radiation environments such as the tropics or high mountains (Figure 13.2).

The present rate of global change is so rapid, however, that evolution may not keep up with it, particularly in high latitudes where temperature and UV-B radiation have increased dramatically over recent decades. In Antarctica and the southern tip of South America, plants adapted to environments with relatively low levels of UV-B radiation have been affected by the increased levels of UV-B radiation due to ozone depletion (see Figure 13.1). Although the negative impact of UV-B radiation on plant productivity is usually relatively small (about 6%), some species are more affected than others. Over time, these differences between species may lead to changes in terrestrial ecosystems, especially in regions like Antarctica where UV-B radiation is likely to remain elevated for many more decades (Figure 13.2).

Another group of plants that may be more sensitive to UV-B radiation are agricultural plants that humans have moved from areas of low UV-B to high UV-B radiation e.g. from temperate to tropical regions. This is analogous to light-skinned humans moving to high radiation environments and becoming susceptible to higher rates of sun damage (see Question 8) or light skinned cattle being moved to tropical areas and being affected by UV-induced eye damage. Some varieties of these crops are UV-B-sensitive and produce reduced yields following an increase in UV-B radiation. It is possible to breed and genetically engineer UV-B tolerant crops so that crop losses are reduced.

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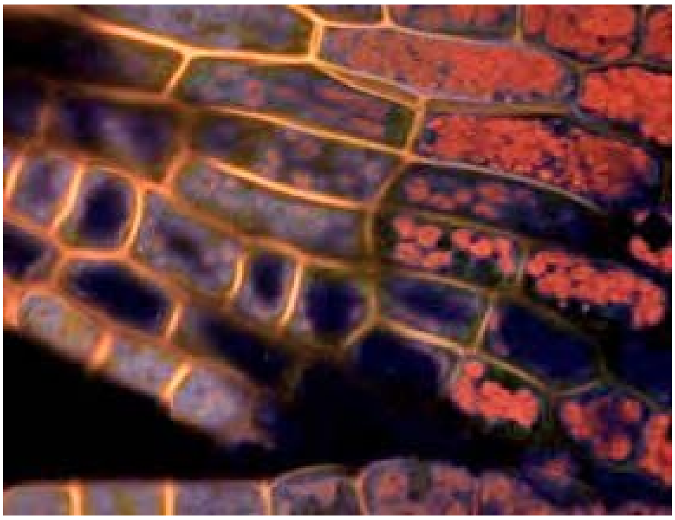

Figure 13.1 Wax on the surface of cabbage plants protects the underlying leaf from high UV radiation (left). If UV radiation penetrates the leaf it can be removed by sunscreen compounds bound to the cell walls, highlighted in orange in this micrograph (right). Photographs Prof. S. Robinson and Dr L. Clarke, University of Wollongong, Australia.

Figure 13.2: Impacts of UV-B radiation on terrestrial ecosystems. Ozone depletion has led to higher UV fluxes over Antarctica with negative effects on some species of Antarctic plants, such as the mosses seen growing along this icy stream (RH panel). An example of the chemical structure of protective molecules produced by plants in response to UV radiation is shown in the centre. These compounds include the red pigments seen in lettuces (top left panel), while those shielded from UV are mostly green. Similarly, Antarctic mosses (bottom left) shielded by small stones are green (centre), while the plants around them produce protective red pigments. These compounds can be important components of our foods. (Photograph of lettuce from Prof. N. Paul, University of Lancaster, UK, others Prof. S. Robinson, University of Wollongong, Australia).

b. How is UV-B radiation beneficial to agriculture and food production?

Some protective molecules produced by plants in response to natural UV-B radiation, are important in our food and medicinal plants. They can enhance the colour and flavour of food and increase its antioxidant activity. Such compounds are increasingly important to the food industry and horticulturalists often seek to enhance production by ensuring plants are exposed to sufficient UV-B radiation.

Some of these changes in plant biochemistry induced by UV- B radiation can have further effects in agriculture, for example by influencing the interactions between crop plants and herbivorous insects. Under enhanced UV-B radiation, sunscreen compounds both protect the plant from the UV-B radiation directly and deter insects from eating the plant (herbivory). The change in biochemical composition can make the plant less attractive as food for herbivores (including for insect pests). The negative effect of UV-B radiation on the food supply of plant-eating insects can be substantial. Some of the reduced consumption is due to direct effects of UV-B radiation on insects and some due to the changes in plant tissues induced by the UV-B radiation. This means that if UV-B radiation is higher, insects generally eat less plant material. In an agricultural context this may mean less insecticide is needed to deter agricultural pests. These effects on palatability also impact the food supply of animals at an ecosystem level.

Another example of positive effects of UV radiation in the environment is UV vision which is used extensively by a wide range of invertebrates and vertebrates, including birds, fish, insects, spiders, and other taxa, for critical life processes including mate selection and location of food resources. Some invertebrates are specifically able to detect and respond to UV-B radiation under natural conditions.

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c. How far does UV penetrate - does it affect soil processes

In addition to changing the palatability of plants, UV-induced compounds alter the speed at which leaf litter is broken down in the soil and thus the recycling of nutrients in the soil. Therefore UV radiation has impacts that go beyond individual plants and can affect ecosystem processes. Changes to plant composition, induced by UV-B radiation, have impacts on the animals and microbes (bacteria and fungi) that rely on plant matter for food.

Sunscreen compounds and structural alterations, which allow leaves to withstand UV-B radiation while attached to the plant, can make leaves more fibrous and tougher to break down once they form leaf litter. UV-B radiation changes the composition of the microbes in the soil and this can also influence how easily leaf litter is broken down. When plant litter is directly exposed to sunlight, it is degraded photochemically (photodegradation).

The changes that occur at the plant level can influence underground decomposition. Decomposition of dead plant material (leaf litter) is a vital process, since it recycles carbon and nutrients making them available to growing plants. UV radiation affects decomposition indirectly via changes to leaf biochemistry and microbial diversity and directly through photodegradation.

Changes to both microbial and photodegradation breakdown processes have important consequences for future carbon sequestration and nutrient cycling.

14. WHAT ARE THE INTERACTIVE EFFECTS OF UV RADIATION AND CLIMATE CHANGE ON AQUATIC ECOSYSTEMS AND ORGANISMS?

UV radiation can affect aquatic ecosystems and the metabolism of aquatic organisms both through direct exposure and via secondary effects from photochemical changes of nutrients and organic matter. Many of these effects interact with the changes induced by climate change.

In the open water, the incoming solar radiation is attenuated and thus the part of the ecosystem that is affected is close to the surface. Most aquatic systems are stratified with an upper mixing layer where the photosynthesis occurs. Here the biomass is increasing and nutrients are consumed. In the layers below are organisms and organic matter that are consumed and nutrients are mineralised. This results in an upper sun-exposed, low-nutrient layer and a lower dark layer high in nutrients. The exchange between the layers is limited, depending on the strength of the temperature or salinity difference that separates the layers.

As planktonic organisms circulate within the layers, the intensity of UV radiation to which the organisms are exposed will depend on the depth of the upper layer and the UV attenuation. Both these factors are affected by climate change.

Increased temperature and increased fresh water inflow from melting glaciers and sea ice reduce the depth of the upper layer and thus the plankton organisms will be exposed to more UV radiation. It also makes the stability of the separation of the layers stronger, reducing the transport of nutrient to the upper layer.

On the other hand, climate change will increase the runoff of UV-absorbing dissolved organic matter (DOM) from land, reducing the UV intensity in lakes and in coastal waters. In addition, climate change reduces the area covered by sea ice in polar areas, and reduces the thickness of the ice. Still another consequence from increased concentration of CO_2 in the atmosphere is that more CO_2 will dissolve in water and acidify it. One important consequence is that production of calcified outer scales, which protect the inner parts of some organisms from UV radiation, will be harmed. These functions show that interactions between UV radiation and climate change are numerous and not yet fully understood.

Different organisms have different sensitivity for UV radiation, either through inherent differences in basic metabolism or through differences in their UV protection capacity (production of screening pigments or mechanisms to repair lesions). Thus exposure to UV radiation will change the species composition. This might propagate through higher levels in the food chain. Typically smaller organisms will be more susceptible than larger ones. Many protections against UV radiation are not constant but are induced and produced when organisms are exposed. Organisms living under low-UV conditions (for example in coastal areas with high concentration of DOM) are more sensitive than organisms from off-shore that are acclimatised to higher levels of UV radiation.

Temperature increases and changes in nutrient concentration as a result of climate change might modify both the repair rate and the production of UV-absorbing compounds. This is because some of them, such as mycosporine-like amino acids (MAA), contain nitrogen, which commonly is a limiting nutrient in marine waters.

15. WHAT ARE THE INTERACTIVE EFFECTS OF UV RADIATION AND CLIMATE CHANGE ON WATER QUALITY?

Climate change, involving increases in temperature and the frequency and intensity of precipitation, is altering ice and snow cover as well as the UV transparency and mixing regimes of inland and oceanic waters. These changes are influencing the exposure of aquatic organisms to UV radiation, altering the structure and function of aquatic food webs, and decreasing the ability of solar UV radiation to disinfect pathogens and parasites of humans and wildlife.

Most groups of aquatic organisms are susceptible to the negative sub lethal as well as lethal effects of solar UV radiation. In addition, there is increasing recognition that parasites and pathogens of humans and wildlife are sensitive to damage by solar UV radiation. Thus UV radiation in natural sunlight has the beneficial effect of disinfecting surface waters by killing free-living stages of parasites and pathogens (Figure 15.1). Exposure to sunlight can decrease viral infections in Atlantic salmon by many orders of magnitude, as well as decrease fungal infections in both amphibians and important zooplankton grazers. Thus aquatic food webs are being altered by both direct UV damage and by solar UV disinfection of parasites and pathogens.

Climate change is leading to a warmer and wetter world on average, though extreme events and regional variation that result in extreme droughts and floods are major concerns. Increasing concentrations of the tea-coloured dissolved organic matter (DOM), washed in from terrestrial ecosystems, can also decrease the UV transparency of surface waters following rain and runoff events (Fig. 15.2). Heavy precipitation events also wash more parasites and pathogens into surface waters and drinking water supplies. The outbreaks of infectious diseases that often follow extreme precipitation events are likely related to these increases in runoff as well as to decreases in water transparency. Higher concentrations of DOM in many regions of Europe and North America are leading to an increase in the cost of water purification as treatment facilities often have to be upgraded.

Both warmer and wetter conditions associated with climate change are increasing the strength of vertical temperature gradients, or "thermal stratification" in lakes and oceans. Reductions in winter snow cover, later freeze dates in early winter and earlier ice-out dates in freshwater and marine environments are causing longer periods of exposure to solar UV radiation as well as more intense thermal stratification. The surface temperatures of large lakes and oceans are getting warmer, and deeper waters in lakes are often getting cooler. The wind-mixed warmer surface waters are also often shallower as a result of the increased thermal stratification. In regions where the shallower mixed layer are caused by increases in DOM and subsequent decreases in water transparency, the effectiveness of disinfection by solar UV irradiation is reduced. Good examples include reductions in the viability of human parasites such as *Cryptosporidium* as well as decreases in potentially lethal fungal pathogens of both amphibians and zooplankton with increasing UV exposure (Figure 15.1). The reductions in light levels at deeper depths will, at the same time, also lead to oxygen depletion and larger and more frequent "dead zones". In contrast, in regions where the shallower mixed waters are caused by warming air temperatures, water transparency is increasing (Figure 15.2), natural solar disinfection is more effective, and oxygen depletion is less likely. These changes in thermal stratification, UV exposure, and oxygen depletion, are influencing the frequency and intensity of harmful algal blooms (HABs), the distribution and abundance of fish species, and the plankton and other species that comprise the critically important lower levels of the food web.

Figure 15.1 Microphotographs of two parasites that are sensitive to disinfection by solar UV radiation. Cryptosporidium parvum (top) is a protozoan parasite of humans, and Metschnikowia bicuspidata (bottom) is a fungal parasite seen here inside of its host, the important freshwater zooplankton grazer Daphnia (body length ~ 1 mm). The Daphnia on the lower left is parasitized while that on the upper right is healthy and not parasitized. (Photo credits: Cryptosporidium by Sandi Connelly, Metschnikowia by Meghan Duffy)

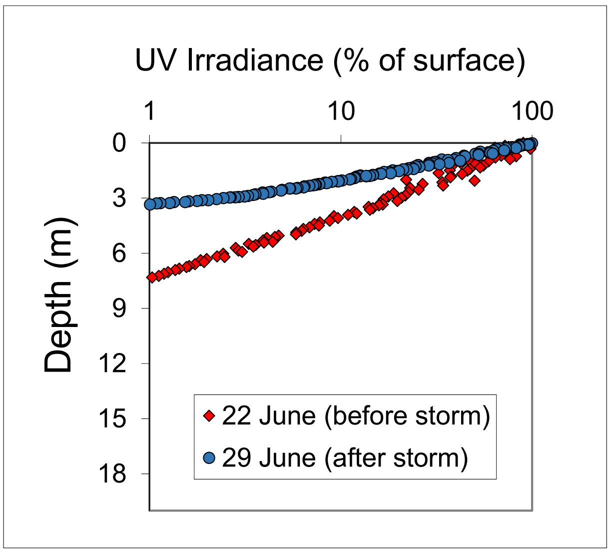

Figure 15.2. An example of the reduction in underwater UV transparency following a heavy precipitation event. This event in June, 2006 dropped 200 mm of rain in the vicinity of Lake Giles in eastern Pennsylvania within a week. Figure adapted from Rose et al. 2012. Limnology and Oceanography 57: 1867.

16. DOES EXPOSURE TO SOLAR UV RADIATION ALTER THE USEFUL LIFETIME OF BUILDING MATERIALS?

Solar UV radiation decreases the useful lifetime of some plastics and wood materials used in building construction.

The useful life of wood, plastic and wood-plastic composite products used in the exterior of buildings is determined primarily by degradation caused by exposure to solar UV radiation. The affected products include structural and decorative wood products as well the cladding (siding), exposed plastic pipes, plastic roofing membranes and plastic glazing. Figure 16.1 shows the cross-section of a PVC plastic window frame used in residential buildings. These plastics are easily degraded by UV-B radiation resulting in uneven discoloration, surface release of fillers or 'chalking', reduced impact strength and development of surface cracks. Acceptable lifetimes are possible only because very efficient UV-stabilizers are incorporated as additives.

Wood used in building applications undergoes UV-induced degradation of the cellulose, rendering the surface increasingly hydrophilic. This encourages colonization of the surface by fungal species that can break down the wood. (Figure 16.2). Absorbed water can stress and damage the wood during freeze-thaw cycles. Wood used in outdoor applications is either chemically treated or surface coated with polymer-based paints to mitigate this problem. The coatings themselves deteriorate and have to be replaced several times during the service life of the wood. This is also true of the wood-plastic composites where the wood fraction is photolabile.

The photodegradation processes in wood and plastic progress faster at higher levels of UV-B radiation and at higher temperatures. Therefore, the 2 - 6°C increase in surface temperatures suggested by the climate models will shorten their service lives even further. Possible synergistic effects of the combination of UV radiation and higher temperatures are not fully understood for both plastics and wood materials. The effects will be most severe in places with high rainfall and high air pollution, both of which tend to accelerate the degradation.

Any increase in UV-B radiation as a result of a decrease in the stratospheric ozone layer will increase the rates of degradation, shortening the service lifetime. However, with both wood and plastics, this can be compensated for by either using higher amounts of UV-stabilizer levels or using better UV-resistant alternatives. Even taking into account the potential for a few degrees increase in ambient temperatures, available high-efficient stabilizers should be able to maintain service lifetimes at the present levels. (Figure 16.3). Dark-coloured plastics exposed to sunlight reach a much higher bulk temperature under present conditions compared to white or light-coloured plastics, but can still be effectively stabilized. There are also classes of plastics, varieties of wood and better surface coatings available that can be substituted for existing materials as well.

There is invariably a cost associated with mitigating the effects of increased levels of solar UV radiation and/or increased temperature due to climate change. In such situations the cost of some plastic and wood products in construction will rise.

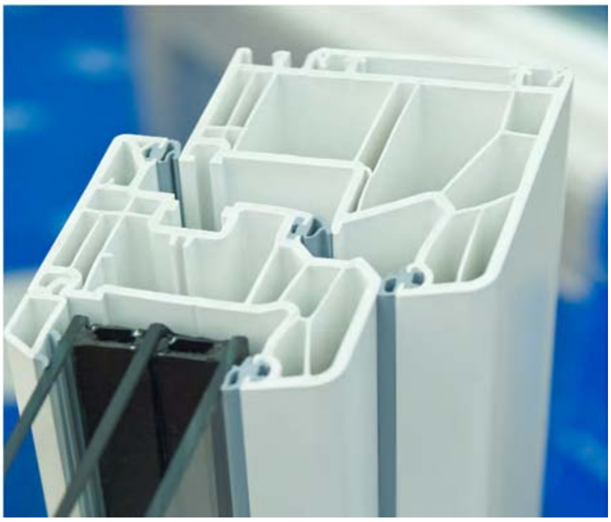

Figure 16.1. Cross-section of a rigid PVC window frame used in residential building. PVC is the most-used plastic in building construction where it is used in residential siding, pipes, window frames and gutters. Rigid PVC meant for outdoor use has rutile titanium dioxide mineral powder incorporated in it. This oxide absorbs solar UV radiation and helps reduce the light-induced yellowing, chalking and weakening of the plastic material. Picture supplied by Anthony L. Andrady.

Figure 16.2. Unprotected wood surfaces that are damaged by solar UVR can easily undergo biodegradation by wood-rot fungi. The light induced damage renders the surface more hydrophilic making it easier for bacteria and fungi to degrade the material. Coating the wood can often control the deterioration of wood by solar radiation. Adding UV stabilizers to the coating can make it even more effective in protecting the wood. Picture supplied by Anthony L. Andrady.

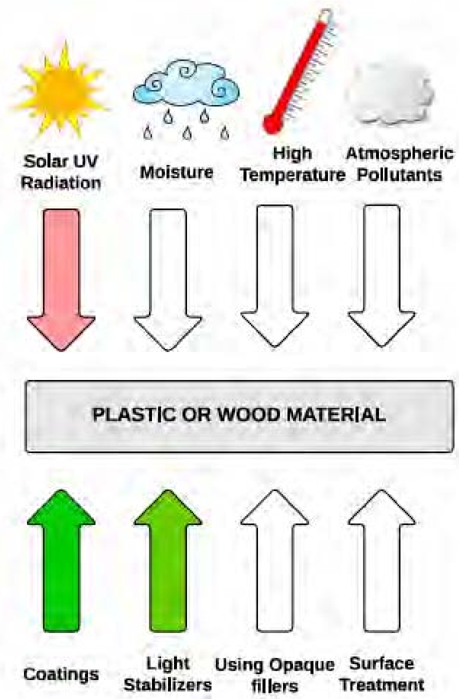

Figure 16.3. The main agencies that promote the environmental degradation of materials used outdoors are shown in the upper part of the figure. The most important of these is solar UV Radiation. The techniques used to mitigate these effects are shown in the lower part of the figure with the two primary strategies of using light-stabilizers and coatings highlighted as they are the most effective in protecting the wood.

17. WILL THE USEFUL OUTDOOR SERVICE LIFETIME OF A MATERIAL AT ONE LOCATION BE APPLICABLE FOR ITS USE AT A DIFFERENT LOCATION?

Generally, any estimate of the service lifetime of a material used outdoors, determined for one geographical location, will not be the same at a different location. This is because the levels of UV radiation and temperature the major determinants of service lifetime are different at different locations.

Damage induced by UV radiation to outdoor materials, such as plastics and paints, is primarily governed by the cumulative dose received over the course of their lifetimes. As previously noted, solar UV radiation at Earth's surface is primarily UV-A with a small proportion of UV-B, and the annual dose of UV radiation depends on location. Thus, latitudes within the tropics, where the noon solar elevation gets close to the zenith throughout the year, receive much higher annual doses of UV radiation than high latitude sites, where winter doses of UV radiation are small compared with summer doses. Generally, the closer the site is to the equator, the greater the annual dose of UV radiation, and therefore the shorter the serviceable lifetime of the material. This may be exacerbated if damage is accelerated at higher temperatures.

Figure 17 shows a compilation of UV-A and UV-B data (and their ratios) from a selection of sites where the highest quality UV measurements are available.

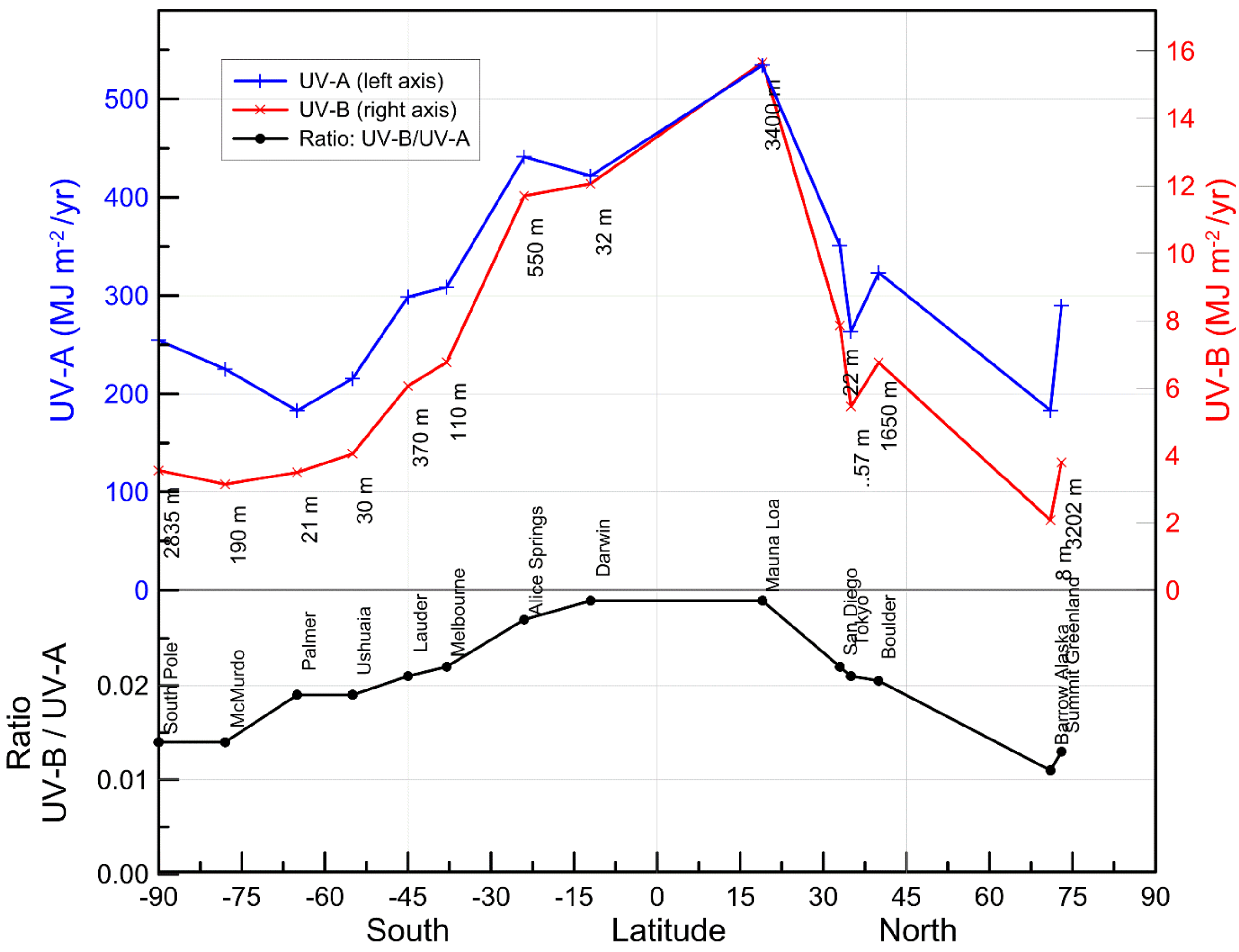

Figure 17. Latitudinal variability in UV-A and UV-B radiation. Altitudes of locations are shown. Although doses of UV radiation are larger in the Southern Hemisphere (SH) than at corresponding latitudes in the Northern Hemisphere (NH), the difference is much less marked than for the peak irradiances, which can be 40% greater in the SH compared with the NH. Generally, the annual dose decreases with latitude, with stronger latitudinal gradients in the UV-B region than in the UV-A region, even allowing for differences in altitude between these sites, which can account for differences of approximately 5% per 1000m (i.e., 15% more UV at Mauna Loa and 10% more at Boulder). Most of these sites are relatively clean, but aerosol extinctions have a significant effect at some, such as Tokyo. These results imply that UV doses in the latitude greater than 30° in each hemisphere generally are significantly less than for sites within the latitude range from 30° S to 30° N, a range which corresponds to half the area of the globe.

18. TO WHAT EXTENT IS UV RADIATION TRANSMITTED THROUGH MATERIALS?

Solar UV-B radiation is blocked by glass as well as by most fabric materials but UV-A is transmitted to varying extents.

About 5% of the solar radiation reaching Earth's surface is within the UV wavelengths. Protecting ourselves, and objects of value, from the damaging effects of the UV radiation is important. Some materials effectively block the UV radiation and provide such protection.

All types of glass very effectively screen out the UV-B radiation, the most damaging spectral region in sunlight. The same is not true of UV-A; different grades of glass transmit UV-A to different degrees. Laminated glass in double-glazed laminated glass windows or used in vehicles as windshields or windows is most effective, allowing less than 2% of the UV-A radiation to pass through. Clear glass or tinted glass windows allow 20-53% of UV-A radiation to pass through depending on the type and thickness.

Fabrics are also good filters of UV radiation depending on how tightly woven they are and the textile type. A tighter weave results in less free space through which UV rays can pass. Generally, cotton (grey or bleached) offers more protection than synthetic fibres at the same tightness of weave. Wet fabrics where the interstices are filled with water are less protective.

Fabrics can be dyed or made of particle-filled synthetic fibres to obtain even better protection from both UV-A and UV-B radiation.

19. HOW DOES OZONE DEPLETION AFFECT AIR POLLUTION AND VICE VERSA?

Variations in stratospheric ozone and climate change will modify concentrations of pollutants in the atmosphere, which play a significant role in the health of both humans and Earth's environment.

Globally, outdoor air pollution is estimated to lead to 850,000 premature deaths each year, mostly from respiratory and cardiovascular diseases. The cost of crop damage in the U.S. from air pollution is estimated to be 6.1 billion dollars annually. In some locations, air pollution is made worse by interactions between UV radiation and changes in climate. These problems are expected to continue and worsen in the future, thus increasing risks to humans directly and to the supply of food.

Variations in stratospheric ozone and climate change are important drivers of changes in the production and fate of air pollutants. Solar UV radiation provides the energy for many of the chemical transformations that occur in the atmosphere. Solar UV irradiation changes the chemistry or breaks down a number of important atmospheric gases, e.g., nitrogen dioxide, formaldehyde, and ozone. These processes will be altered by anything that changes the amount of UV radiation such as attenuation by clouds and particulate pollutants in the air, both of which will be affected by changes in climate. Decreased stratospheric ozone and increasing temperature from climate change are expected to lead to greater concentrations of ozone close to the surface of the Earth in polluted regions, resulting in an increased mortality rate that could exceed that resulting from climate-related increases in storms and flooding. The quality of the air in less-polluted areas is expected to improve but will not fully offset the damage in polluted regions, in terms of human disease burden.

20. WHAT IS GEOENGINEERING?

Geoengineering is described as technologies that aim to alter the climate system in order to counter climate change.

The Intergovernmental Panel on Climate Change (IPCC) set up a panel to investigate geoengineering in 2011 with the results detailed in the latest IPCC report. The technologies can be divided into two groups (Figure 20):

Carbon Dioxide Reduction (CDR) that would result in slower, or even reverse, projected increases in future CO_2 concentrations by accelerating the natural removal of atmospheric CO_2 and increasing the storage of carbon in reservoirs. The main removal methods are:

A. Ocean fertilization: Adding nutrients to the ocean which increases oceanic productivity in the surface ocean and transports a fraction of the resulting biogenic carbon downward,

B. Alkalinity addition to the ocean: Adding alkalinity from solid minerals to the ocean, which causes more atmospheric CO_2 to dissolve in the ocean,

C. Accelerated weathering: Increasing the weathering rate of silicate rocks and transporting the dissolved carbonate minerals to the ocean,

D. Direct air capture: Capturing atmospheric CO_2 chemically, and storing it either underground or in the ocean,

E. Biomass energy with carbon capture: Burning biomass at electric power plants with carbon capture, and the captured CO_2 is stored either underground or in the ocean, and

F. Afforestation: Capturing CO_2 through afforestation and reforestation to be stored in land ecosystems.

Solar Radiation Management (SRM) that would counter the warming associated with increasing greenhouse gasses by reducing the amount of sunlight absorbed. The main methods are:

G. Deployment of space mirrors: Placing reflectors into space to reflect solar radiation,

H. Stratospheric aerosol injection: Injecting aerosols in the stratosphere, e.g. sulphur dioxide,

I. Marine cloud brightening: Seeding marine clouds to make them more reflective,

J. Ocean brightening with microbubbles: Producing microbubbles at the ocean surface to make it more reflective,

K. Crop brightening: Growing more reflective crops, and

L. Whitening rooftops: Painting roofs and other built structures in light colours.

The CDR methods will not influence the surface UV radiation but the SRM methods will, depending on the specific method used. The first three should reduce the amount of solar radiation reaching Earth's surface but the last three will increase the UV radiation received by an object by reflecting radiation to the sides of the object.

Stratospheric sulphate aerosols from volcanic eruptions and natural emissions deplete stratospheric ozone. Stratospheric aerosols introduced for SRM are expected to have the same effect and the resulting ozone depletion will increase the amount of UV radiation reaching the surface of the Earth, with potential damage to terrestrial and marine ecosystems and to human health.

The IPCC evaluation of geoengineering came to the following conclusion: "*CDR methods have biogeochemical and technological limitations to their potential on a global scale. There is insufficient knowledge to quantify how much CO_2 emissions could be partially offset by CDR on a century timescale. Modelling indicates that SRM methods, if realizable, have the potential to substantially offset a global temperature rise, but they would also modify the global water cycle, and would not reduce ocean acidification. If SRM were terminated for any reason, there is high confidence that global surface temperatures would rise very rapidly to values consistent with the greenhouse gas forcing. CDR and SRM methods carry side effects and long-term consequences on a global scale.*"

Figure 21: Overview of some proposed geoengineering methods that have been suggested.

Reference: Summary for Policymakers, The Physical Science Basis, Working Group I Contribution to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, 2013.

21. WHAT WOULD HAVE HAPPENED WITHOUT THE MONTREAL PROTOCOL?

Without the successful and continued implementation of the Montreal Protocol and its subsequent amendments and adjustments, stratospheric ozone would have continued to decline globally, and levels of UV-B radiation would have consequently continued to increase dramatically, leading to severe environmental effects.

The objective of the Montreal Protocol is the protection of the ozone layer through control of the global production and consumption of Ozone Depleting Substances (ODSs). Projections of the future quantities of ODSs expressed as equivalent effective stratospheric chlorine (EESC) values are shown below (Figure 21.1) for the mid-latitude stratosphere for the scenarios of no Protocol and the 1987 Montreal Protocol and its subsequent amendments and adjustments. EESC is a relative measure of the potential for stratospheric ozone depletion that combines the contributions of chlorine and bromine from surface observations of concentrations of ODSs in the stratosphere. Without the Protocol, EESC values have been projected to increase significantly in the 21st century (Black curve). Only with the Copenhagen (1992) and subsequent Amendments and Adjustments did projected and measured EESC values show a long-term decrease.

Since there is an inverse relationship between the amount of ozone and the amount of UV radiation reaching Earth’s surface one can expect the levels of UV radiation on the surface to decline as is illustrated in figure 21.2 using the UVI as indicator.

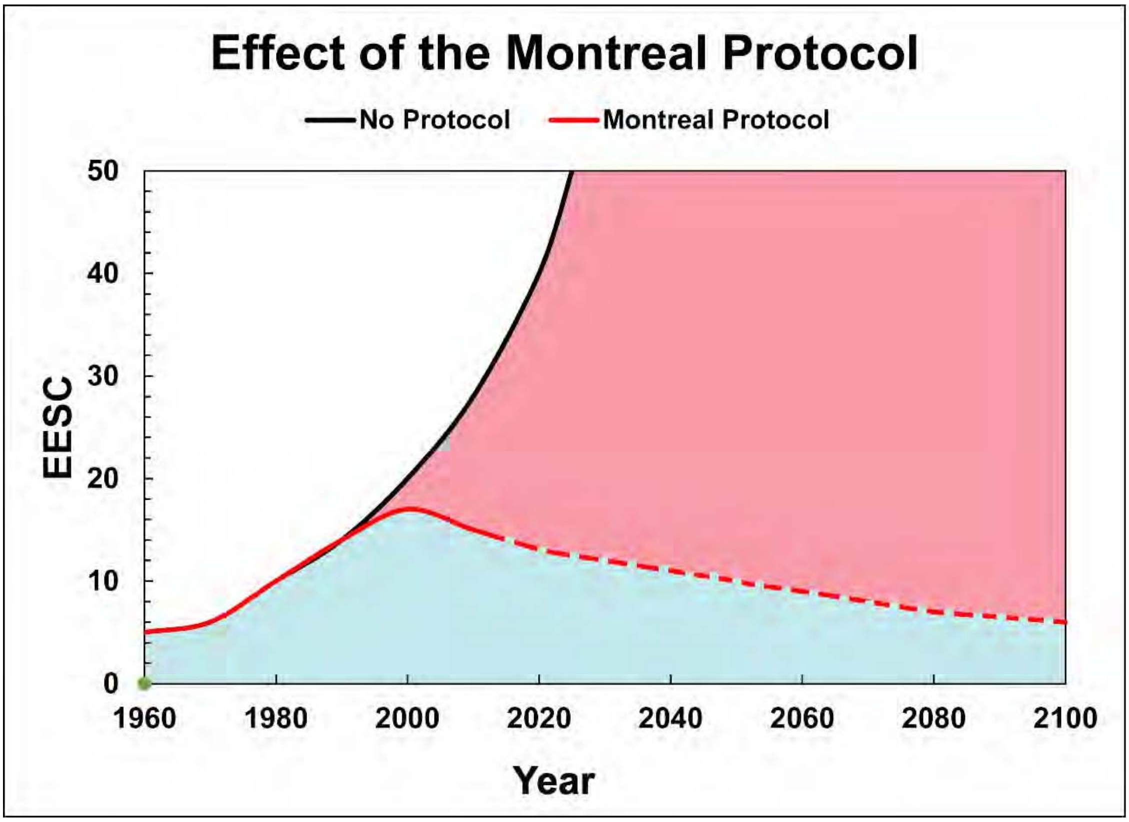

Figure 22.1: The observed (solid red line) and predicted (dashed red line) effects of the Montreal Protocol and its amendments and adjustments. The black line is a projection of the situation without the Montreal Protocol. (Figure provided by Dr P J Aucamp based on the 2014 report of the Scientific Assessment Report)

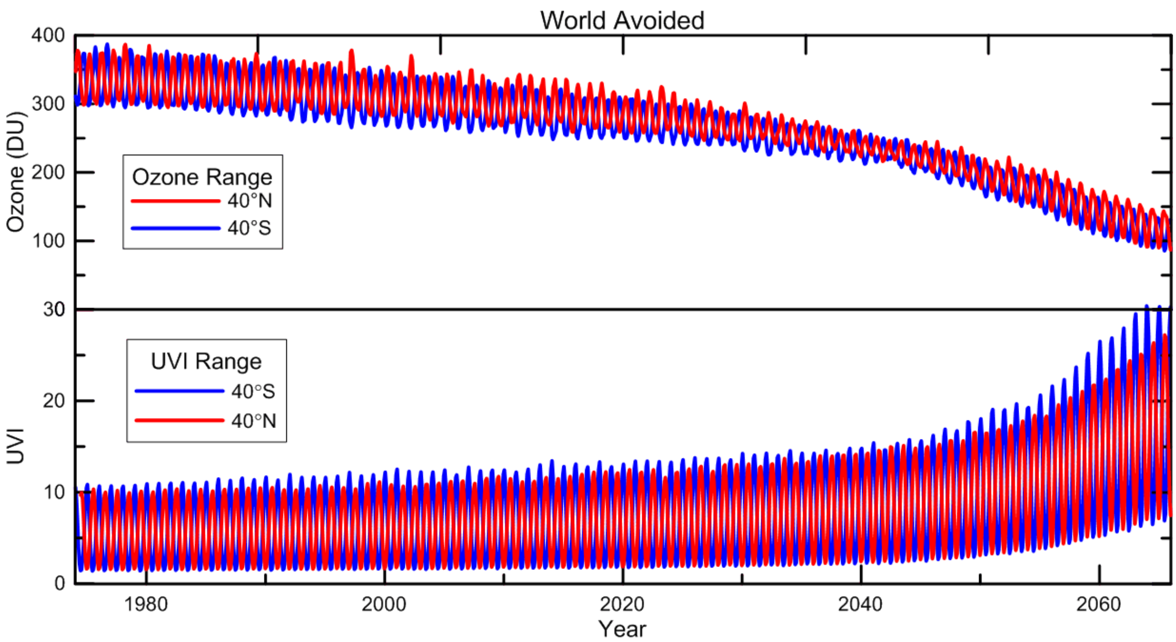

Figure 21.2: The observed (to 2014) and predicted effects of the Montreal Protocol and its amendments and adjustments. In 2065, the summer UVI would have increased to three times the 1975 values, and the wintertime UVI in 2065 would have been comparable to summertime UVI in 1975.

22. ARE THE CONTROL MEASURES IN THE MONTREAL PROTOCOL WORKING? WHAT IS THE WORLD WE AVOIDED?

a. Has the phase-out of ODSs changed levels of UV radiation?

The Montreal Protocol has been very successful.

The Montreal Protocol for the Protection of the Ozone Layer is the most successful environmental international agreement to date. It has been ratified by all of the 197 countries of the UN. All the CFCs have been phased out since January 2010. The phase-out of the HCFCs is on schedule and has been advanced.

The detail of the phase-out achieved and the predictions of future halocarbon concentrations in the stratosphere can be found in the Scientific Assessment Panel's 2014 report. Stratospheric ozone is no longer decreasing and is predicted to return to pre-1980 values before 2050 at mid-latitudes and a few years later at high latitudes. Concentrations of the ODSs have been decreasing for over ten years, and are expected to continue to decrease in the future (Figure 22.1 and 22.2).

A future scenario in which ODSs were not regulated and production grew at an annual rate of 3% was simulated in a study of the "world avoided" by the success of the Montreal Protocol. By 2020, 17% of the globally-averaged column ozone in 1980 would have been destroyed, with depletion increasing to more than 60% by 2060 (Figure 22.2). Decreases in stratospheric ozone due to increasing CFCs would have led to a marked increase in UV radiation, with the UV Index possibly trebling at mid-latitudes by 2065. In view of what is known about the effects of excess UV radiation exposure, this would have had serious environmental consequences. In Polar regions, substantial ozone depletion would have become year-round rather than seasonal, resulting in large increases in surface UV radiation, including during the summer months.

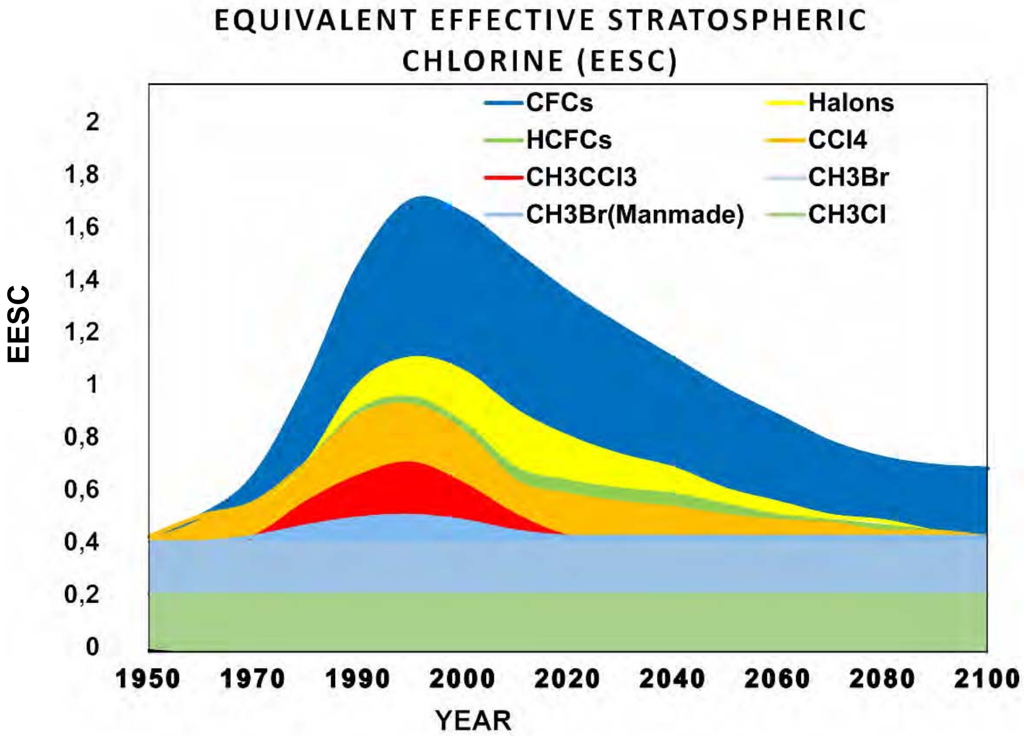

Figure 22.1: The past and predicted future concentrations of halocarbons in the stratosphere (Figure provided by Dr P J Aucamp based on the 2014 report of the Scientific Assessment Report)

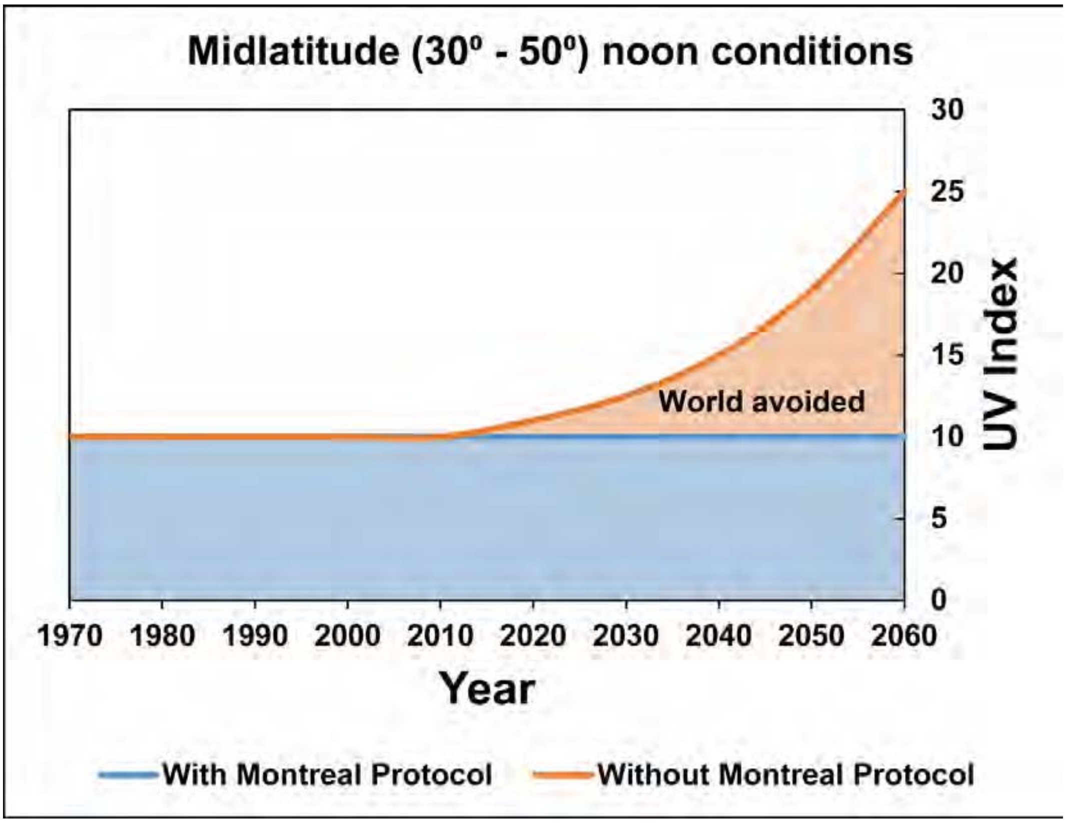

Figure 22.2: Prediction of the UVI indicating what could have happened in the absence of a Montreal Protocol (Adapted from Figure 5.11 Scientific Assessment of Ozone Depletion: 2010).

b. What effect has the phase-out of ODSs had on the climate?

As a result of the phase-out schedules of the Montreal Protocol, the global production and use of chlorofluorocarbons (CFCs) and halons has decreased significantly. However, the sustained growth in demand for refrigeration, air-conditioning and insulating foam products in developing countries has led to an increase in the consumption and emissions of hydrofluorocarbons (HFCs). Consequently the use of HCFCs and HFCs as replacements for CFCs and halons has increased. The HCFCs are low-ozone-depletion-potential substitutes for high-ozone-depletion-potential substances, particularly CFCs and halons, and were classified under the Protocol as "transitional substitutes" for the time it takes to commercialize new ozone-safe alternatives and replacements. Ultimately, HCFCs will be phased out globally under the Montreal Protocol leaving much of the application demand for refrigeration, air conditioning, heating and thermal-insulating foam production to be met by HFCs, HFOs and other replacement products. The demand for HCFCs and/or HFCs in many applications is expected to increase. HFCs do not deplete the ozone layer but, along with CFCs and HCFCs, are greenhouse gases that contribute to the radiative forcing of climate. Thus, the transition away from ozone depleting substances (ODSs) has implications for future climate. HFCs are in the "basket of gases" regulated under the 1997 Kyoto Protocol, a global treaty to reduce emissions of greenhouse gases by developed countries.

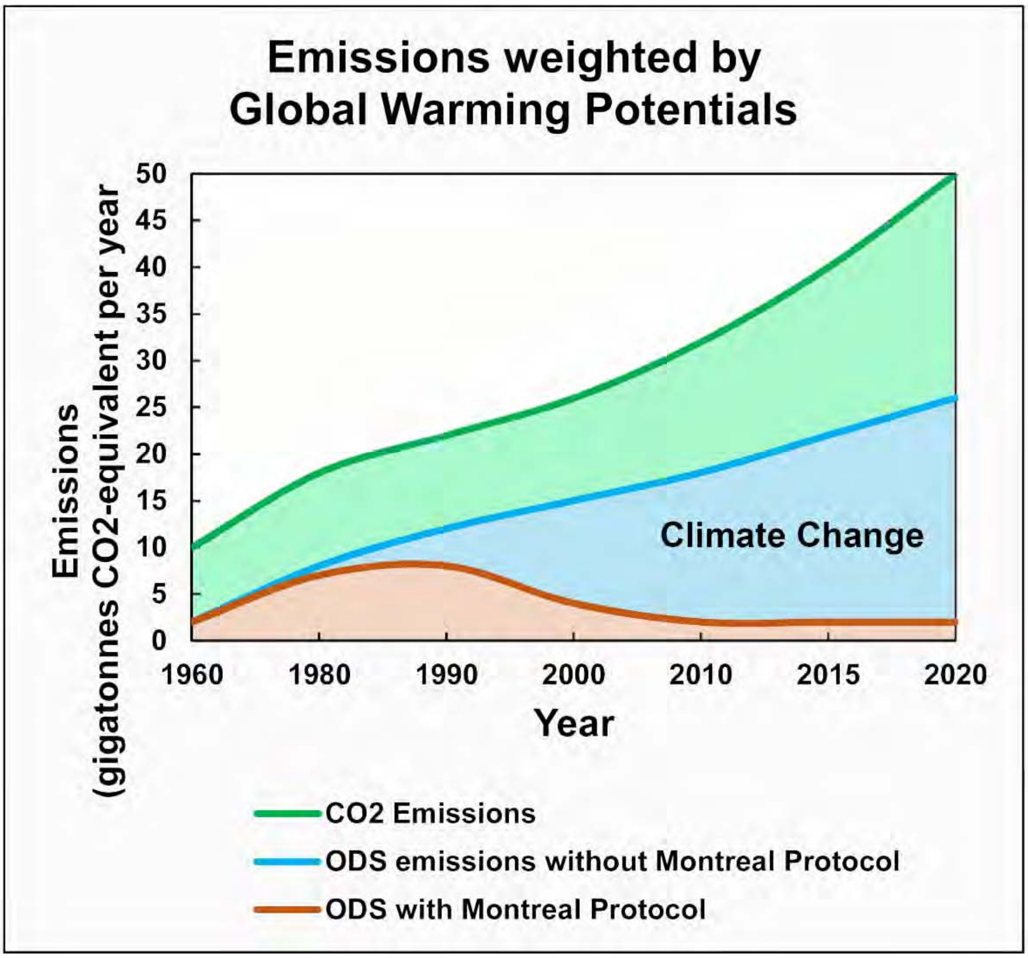

Figure 22.3: Montreal Protocol protection of ozone and climate (Based on: Twenty Questions and Answers about the Ozone Layer 2014 Update, Scientific Assessment of Ozone Depletion 2014, United Nations Environmental Programme, Nairobi.).

23. WHERE CAN I GET MORE INFORMATION ABOUT THE SCIENCE AND EFFECTS OF OZONE DEPLETION?

There are several websites that contain information on ozone, UV radiation, environmental effects and related topics. The sites mentioned below belong to dependable organizations and contain reliable information. Most of these sites contain links to other sources of information.

UNEP .... http://www.ozone.unep.org

WMO .... http://www.wmo.ch

WHO .... http://www.who.int

IPCC .... http://www.ipcc.ch

NOAA .... http://www.noaa.gov/climate.html

EPA .... http://www.epa.gov/ozone.html

NASA .... http://ozonewatch.gsfc.nasa.gov

NIWA .... http:// www.niwa.co.nz/UV-ozone

WOUDC .... http://www.woudc.org

Environment Canada .... http://www.ec.gc.ca