

2010

Environmental Effects of Ozone Depletion and its Interactions with Climate Change: 2010 Assessment

Sharon A. Robinson

University of Wollongong, sharonr@uow.edu.au

Stephen R. Wilson

University of Wollongong, swilson@uow.edu.au

Follow this and additional works at: <https://ro.uow.edu.au/scipapers>



Part of the [Life Sciences Commons](#), [Physical Sciences and Mathematics Commons](#), and the [Social and Behavioral Sciences Commons](#)

Recommended Citation

Robinson, Sharon A. and Wilson, Stephen R.: Environmental Effects of Ozone Depletion and its Interactions with Climate Change: 2010 Assessment 2010.
<https://ro.uow.edu.au/scipapers/456>

Environmental Effects of Ozone Depletion and its Interactions with Climate Change: 2010 Assessment

Abstract

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 2006, 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.

Keywords

GeoQUEST

Disciplines

Life Sciences | Physical Sciences and Mathematics | Social and Behavioral Sciences

Publication Details

This report was originally published as Andradý, AL, Aucamp, PJ, Austin, A, Bais, AF, Ballaré, CL, Björn, LO, Bornman JF, Caldwell, MM, Cullen, AP, de Groot, FR, Erickson III, DJ, Flint, SD, Häder, D-P, Hamid, H, Ilyas, S, M, Longstreth, J, Lucas, R, Madronich, S, McKenzie, RL, Norval, M, Paul ND, Robinson, SA, Shao, M, Solomon KR, Sulzberger, B, Takizawa, Y, Tang X, Torikai, A, van der Leun, JC, Williamson, CE, Wilson, SR, Worrest, RC & Zepp RG, Environmental Effects of Ozone Depletion: 2010 Assessment, United Nations Environment Programme, Kenya, 2010, 328 pages.

Original report available [here](#).

**UNITED NATIONS
ENVIRONMENT PROGRAMME**



UNEP

**ENVIRONMENTAL EFFECTS OF OZONE
DEPLETION AND ITS INTERACTIONS WITH
CLIMATE CHANGE:
2010 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
United Nations Environment Programme (UNEP)
P. O. Box 30552
Nairobi, Kenya

Published December 2010 by the Secretariat for The Vienna Convention for the Protection of the Ozone Layer and The Montreal Protocol on Substances that Deplete the Ozone Layer, United Nations Environment Programme (UNEP)

United Nations Environment Programme (UNEP), P. O. Box 30552, Nairobi, Kenya

UNEP, Environmental Effects of Ozone Depletion: 2010
Assessment, United Nations Environment Programme
ISBN 92-807-2312-X

Environmental effects of ozone depletion and its interactions with climate change: 2010 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 2006, 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 2010 Assessment will be published in the journal, *Photochemical & Photobiological Sciences*, **10**, 2011.

Janet F. Bornman
Nigel Paul,
Xiaoyan Tang

Co-Chairs of the Environmental Effects Assessment Panel



United Nations Environment Programme
PO Box 30552
Nairobi, Kenya
<http://www.unep.org/ozone>
<http://www.unep.ch/ozone>

Acknowledgments:

This assessment would not have been possible without the contributions of the following reviewers (in alphabetical order) all of whom made written and/or verbal comments on the content of the Chapters in this assessment. We thank them for their generous contribution of time and knowledge:

Dr Pedro J. Aphalo; Dr Amy T. Austin; Dr Germar Bernhard; Dr Marianne Berwick; Prof. Wolfgang Bilger; Dr Natalia Chubarova; Dr Thomas P. Coohill; Dr Sandra L. Cooke; Dr Susana Diaz; Prof. Brian Diffey; Prof. Nils Ekelund; Dr Auroop R. Ganguly; Dr Kunshan Gao; Dr W.D. Grant; Dr R. Elizabeth M. Griffin; Prof. Michaela Hegglin; Prof. Dag Hessen; Dr Rainer Hofmann; Dr Marcel A. K. Jansen; Prof. Jennifer Y. King; Dr Margaret Kripke; Prof. G. Kulandaivelu; Dr Shaoshan Li; Prof. Lawrence E. Licht; Mr. B. Liley; Dr Kevin K. Newsham; Dr Madan Pal; Dr Barrie M. Peake; Dr Norma D. Searle; Prof. Günther Seckmeyer; Dr Anna Maria Siani; Dr Rajeshwar Sinha; Dr Harry Slaper; Prof. Ruben Sommaruga; Dr J. Richard Soulen; Dr Johannes Stratmann; Dr Åke Strid; Prof. Hugh R. Taylor; Dr Anssi Vähätalo; Dr John Wargent; Dr Ann R. Webb; Prof. Huixiang Xie

Table of Contents

Abbreviations and Glossary	viii
Executive Summary	xv
Chapter 1. Ozone depletion and climate change: Impacts on UV radiation	1
Chapter 2. The human health effects of ozone depletion and in-teractions with climate change	30
Chapter 3. Effects of solar ultraviolet radiation on terrestrial ecosystems. Patterns, mechanisms, and interactions with climate change.....	83
Chapter 4. Effects of UV radiation on aquatic ecosystems and in-teractions with climate change.....	113
Chapter 5. Effects of solar UV radiation and climate change on biogeochemical cycling: Interactions and feedbacks.....	151
Chapter 6. Changes in air quality and tropospheric composition due to depletion of stratospheric ozone and interactions with climate.	187
Chapter 7. Effects of solar UV and climate change on materials.....	211
Members of the 2010 Environmental Effects Assessment Panel and UNEP representatives	229
Reviewers of the 2010 UNEP Environmental Effects Assessment Report	233
Appendix 2-1: Health risks associated with the use of substitutes for ozone depleting substances	A-1
Questions and Answers about the Environmental Effects of the Ozone Layer Depletion and Climate Change: 2010 Update.....	Q&A-1

Abbreviations and Glossary

Abbreviation	Complete term
1,25(OH) ₂ D	1,25-dihydroxyvitamin D
25(OH)D	25-hydroxyvitamin D
AK	Actinic keratosis
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)
BrO	Bromine monoxide
BSWF	Biological spectral weighting functions
BWF	Biological weighting function
CAS	Chemical Abstracts Service
CAT	Catalase
CC	Cortical cataract(s)
CCM	Chemistry-climate model (used to predict future changes in atmospheric composition)
CDFA	Chlorodifluoroacetic acid
CDK	Climatic droplet keratopathy
CDOC	Coloured dissolved organic carbon
CDOM	Coloured (or chromophoric) dissolved organic matter
CFC	Chlorofluorocarbon. Ozone depleting substance (e.g., CFC1 ₂ radical and dichlorodifluoromethane or Freon-12 (CCl ₂ F ₂)), now controlled under the Montreal Protocol
CH	Contact hypersensitivity
CH ₄	Methane (a greenhouse gas)

Abbreviation	Complete term
CIE	Commission Internationale de l'Eclairage (International Commission on Illumination)
Cl	Chlorine (an ozone depleting substance)
CM	Cutaneous melanoma
CO	Carbon monoxide
CO ₂	Carbon dioxide (a greenhouse gas)
COS	carbonyl sulfide
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))
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	US Environmental Protection Agency

Abbreviation	Complete term
EV	Epidermodysplasia verruciformis
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
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
Hg	Mercury (Hg _{0aq} and Hg(II) being different oxidation states)
HIV	Human immunodeficiency virus
HPV	Human papillomavirus
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
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
MAAs	Mycosporine-like amino acids
Mb	Megabase, equal to 1 million base pairs

Abbreviation	Complete term
MC1R	Melanocortin 1 receptor
MHC	Major histocompatibility complex
MS	Multiple sclerosis
N ₂ O	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
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
NOEC	No observed effect concentration
NO _x	Nitrogen oxides
O ₃	Ozone
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

Abbreviation	Complete term
P	Phosphorous
PAH	Polycyclic Aromatic Hydrocarbon(s)
PAM	Pulse amplitude modulated (fluorescence)
PAR	Photosynthetically Active Radiation, 400-700 nm waveband
PAUR II	Photochemical Activity and solar Ultraviolet Radiation campaign 2
pCO ₂	Partial pressure of carbon dioxide
PEC	Predicted environmental concentration
PER	Photoenzymatic repair
Pg	Peta gram (1x10 ¹² grams)
PHR1	The gene encoding CPD photolyase
PNEC	Predicted no effect concentration
POC	Particulate organic carbon
POM	Particulate organic matter
PR	Pathogenesis-related proteins
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
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 (Wm ⁻²) in the troposphere. 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)

Abbreviation	Complete term
ROS	Reactive oxygen species ($\cdot\text{OH}$ for example)
RT	Radiative transfer
SAGE	Stratospheric Aerosol and Gas Experiment, a satellite-based instrument
SCC	Squamous cell carcinoma
SH	Southern hemisphere
SOD	Superoxide dismutase
SZA	Solar zenith angle is the angle of the sun away from the vertical; at noon, it represents the highest point that the sun reaches.
TFA	Trifluoroacetic acid
Th1	T-helper 1
Th2	T-helper 2
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
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 _{Ery}	Erythemally-weighted UV irradiance, where the irradiance is weighted by the erythral 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 Wm^{-2} , then $\text{UVI} = 40 \times \text{UV-Ery}$
UVR8	UV-regulatory protein

Abbreviation	Complete term
VDR	Vitamin D receptor
VOC	Volatile organic compound (s)
WMO	World Meteorological Organization
WOUDC	World Ozone and UV Data Centre
XP	<i>Xeroderma pigmentosum</i>

Environmental Effects of Ozone Depletion: 2010 Assessment

Interactions of Ozone Depletion and Climate Change

Executive Summary

Ozone Depletion and Climate Change

- **There are strong interactions between ozone depletion and changes in climate induced by increasing greenhouse gases (GHGs).** Ozone depletion affects climate, and climate change affects ozone. The successful implementation of the Montreal Protocol has had a marked effect on climate change. Calculations show that the phase-out of chlorofluorocarbons (CFCs) reduced Earth's warming effect (i.e., radiative forcing) far more than the measures taken under the Kyoto protocol for the reduction of GHGs. The amount of stratospheric ozone can be affected by the increases in the concentration of GHGs, which lead to decreased temperatures in the stratosphere and accelerated circulation patterns, which tend to decrease total ozone in the tropics and increase total ozone at mid and high latitudes. Changes in circulation induced by changes in ozone can also affect patterns of surface wind and rainfall.
- **The Montreal Protocol is working, but it will take several decades for ozone to return to 1980 levels.** The concentrations of ozone depleting substances have been decreasing after reaching a peak in the 1990s, and ozone column amounts are no longer decreasing. Mid-latitude ozone is expected to return to 1980 levels before mid-century, which is earlier than predicted previously. However, the recovery rate will be slower at high latitudes. Springtime ozone depletion is expected to continue to occur at polar latitudes, especially in Antarctica in the next few decades.
- **Because of the success of the Montreal Protocol in controlling ozone depletion, increases in UV-B radiation have been small outside regions affected by the Antarctic ozone hole, and have been difficult to detect.** There is a large variability in UV-B radiation due to factors other than ozone, such as clouds and aerosols. There are few long-term measurements available to confirm the increases that would have occurred as a result of ozone depletion. At mid-latitudes, UV-B irradiances are currently up to 5% greater than in 1980, but increases have been substantial at high and polar latitudes where ozone depletion has been larger. Despite the low solar elevations in Antarctica, UV-B radiation doses in late spring during the ozone hole period can be sufficient to induce sunburn, and are about twice as great as those that would have occurred prior to the onset of ozone depletion. Unfortunately, no measurements were available prior to the onset of the ozone hole to confirm this change.
- **Without the Montreal Protocol, peak values of sunburning UV radiation could have tripled by 2065 at mid-northern latitudes.** This would have had serious consequences for

the environment and for human health. This contrasts sharply with the current situation, where clear-sky UV is only slightly greater than that prior to the onset of ozone depletion, and is expected to decrease in the decades ahead at mid- to high latitudes.

- **The projected changes in ozone and clouds may lead to large decreases in UV at high latitudes, where UV is already low; and to small increases at low latitudes, where it is already high. This could have important implications for health and ecosystems.** Compared to 1980, UV-B irradiance towards the end of the 21st century is projected to be lower at mid to high latitudes by between 5 and 20%, respectively, and higher by 2-3% in the low latitudes. However, these projections must be treated with caution because they also depend strongly on changes in cloud cover, air pollutants, and aerosols, all of which are influenced by climate change, and their future is uncertain. With these predicted changes in UV radiation it would become more difficult to achieve optimal exposure times for sufficient UV-B-induced vitamin D production at high latitudes, while the risk of skin damage would be increased at low latitudes.
- **Because the future UV climate remains uncertain, continued modelling and measurement efforts are needed.** Strong interactions between ozone depletion and climate change and uncertainties in the measurements and models limit our confidence in predicting future UV irradiance. It is therefore important to improve our understanding of the processes involved, and to continue monitoring ozone and surface UV spectral irradiances, both from the surface and from satellites. This capability will enable us to monitor and respond to unexpected changes in the future.

Human Health

- **Health risks of solar UV-B radiation can be assessed most confidently for cataracts and skin cancers. Although there is concern about an increased risk of infectious diseases, data to guide public health decisions are lacking.** The incidences of cataract and skin cancers continue to rise in many countries, with significant societal impacts and costs to health care systems. In some regions the incidence of melanoma in children and young people is no longer increasing, or increasing incidence is confined to less lethal forms. These changes probably reflect intensive public health information campaigns, based on sound research findings. For infectious diseases, equivalent research findings are not available except from animal studies. Use of replacements for ozone depleting substances may result in risks to health but these have not been quantified.
- **Health benefits of sun exposure are principally derived from vitamin D production in the skin following solar UV-B irradiation.** Optimal vitamin D status supports bone health and may decrease the risk of several internal cancers and autoimmune, infectious and cardiovascular diseases. It is not yet clear whether oral vitamin D supplementation provides all of the benefits of UV-induced vitamin D or whether higher vitamin D status is always beneficial. Appropriate sun exposure to balance risk and benefits depends on personal

characteristics such as genetic background (including skin colour and vitamin D receptor types) and external/environmental factors (including diet, season, time of day and latitude). This is an area of active current research, the results of which will provide guidance to the general public to better balance the benefits of sun exposure whilst minimizing risks.

- **Health effects associated with combined changes in solar UV radiation and climate are plausible; directed studies are required to guide health care decisions and future policies regarding health care.** Higher temperatures are likely to lead to more skin cancers for the same exposure to UV radiation. However, this is the most definitive statement that can be made to date about a combined effect, as more studies have not been done. Although higher temperatures may change sun exposure patterns, there is considerable uncertainty in modeling future human behaviour in response to climate change. There is enough information to suspect that combined effects could be serious, but the data to develop robust risk estimates are not available.

Terrestrial Ecosystems

- **In areas where substantial ozone depletion has occurred, results from a wide range of field studies suggest that increased UV-B radiation reduces terrestrial plant productivity by about 6%.** This reduction results from direct damage and increased diversion of plant resources towards protection and acclimation. Long-term effects of reduced plant growth could be important, particularly for potential carbon sequestration (capture).
- **Changes in UV radiation caused by global environmental change can have very important consequences for terrestrial ecosystems.** Region-specific changes in cloud cover and vegetative cover (in response to increased aridity or deforestation) predicted for the coming decades are likely to have large impacts on the levels of UV radiation received by terrestrial organisms. These variations in UV radiation (both UV-B and UV-A) will affect a large range of ecosystems.
- **Predicted changes in climate may modify plant and ecosystem responses to UV radiation.** For example, while moderate drought can decrease UV sensitivity in plants, further decreases in precipitation and increasing temperatures due to climate change are likely to restrict plant growth and compromise plants to re-distribute resources for protection from UV radiation and other climate factors. Thus even limited climate change could have consequences for survival, especially in harsh environments.
- **UV radiation promotes the breakdown of dead plant material and consequently carbon loss to the atmosphere.** Exposure of vegetation and soils to UV radiation may increase in the future at low to mid-latitudes due to reduced cloud cover or more intensive land use. The breakdown of dead plant material through the action of sunlight (photodegradation) is a very

important ecosystem process in many environments, especially for those components that decay only very slowly by microbial action.

- **Variations in UV-B radiation caused by climate change and ozone depletion can have large effects on plant interactions with pests, with important implications for food security and food quality.** Plant consumption by herbivores (e.g. insects) usually decreases under elevated UV-B radiation. Over the coming decades, rising atmospheric carbon dioxide and increased planting density may counteract this beneficial effect of UV-B radiation.
- **UV-B radiation may improve the quality of food, for example, through increased antioxidant activity, flavour and fibre content.** Knowledge gained in this area could be used in the design of agricultural systems that take advantage of these natural plant products to increase nutritional value.
- **Solar UV-B radiation changes microbial biodiversity with consequences for soil fertility and plant disease.** Changes in the composition of microbial communities on dead plant material can alter rates of decay (an important ecosystem process that contributes to soil fertility). On living plants, changes in species composition of microbes by UV-B radiation can affect susceptibility to fungal infections.

Aquatic Ecosystems

- **Detrimental effects of solar UV-B radiation have been demonstrated for many aquatic organisms.** In contrast, relatively little information is available regarding consequences on biodiversity and species composition, or on the interactions between trophic levels within natural ecosystems.
- **For several aquatic organisms, UV-B-induced negative effects are worsened by environmental pollution.** UV-B radiation has a greater impact on aquatic organisms in sites polluted by crude oil and heavy metals such as cadmium, selenium or copper.
- **Climate change will alter the exposure of aquatic organisms to solar UV radiation by influencing their depth distribution as well as the transparency of the water.** Increased temperature due to climate change tends to decrease the depth of the upper mixed layer, thus exposing organisms to higher irradiances. Dissolved organic matter (DOM) is the major factor influencing UV transparency in most inland waters and coastal areas. In some regions, DOM concentrations have nearly doubled in the past 20 years. Since some waterborne human pathogens are sensitive to solar UV radiation, changes in DOM may alter their exposure and inactivation.

- **Enhanced solar UV-B radiation in conjunction with rising global temperatures may negatively affect seaweeds that have ecologic and economic importance.** The vertical distribution of seaweeds in their ecosystem is strongly determined by solar UV radiation. Early developmental stages of brown and red algae are impaired by these environmental factors.
- **Climate-driven changes in environmental conditions may exceed the capacity of protective strategies of aquatic organisms to adapt to solar UV radiation.** Different species use different combinations of avoidance strategies, photoprotection and photorepair, which determine the limits of their ability to adapt to high solar UV radiation. While many cyanobacteria, which are major biomass producers in both marine and inland ecosystems, are sensitive to solar UV radiation, others can survive in habitats with extreme UV-B irradiances, frequent desiccation and extreme temperatures by using a combination of adaptive strategies.
- **The rise in atmospheric CO₂ concentrations increases the acidity of the water, making calcified organisms more vulnerable to solar UV-B radiation.** The continued acidification of marine waters impairs carbonate incorporation in calcified organisms, such as phytoplankton, seaweeds and corals.

Biogeochemical Cycles

- **There are interactions between the effects of solar UV radiation and climate change on the processes that drive the carbon cycle.** These interactions could accelerate the rate of atmospheric CO₂ increase and subsequent global warming beyond current predictions.
- **Projected shifts to warmer and drier conditions, such as in the Mediterranean and in western North America, will increase UV-induced carbon loss to the atmosphere.** UV-induced breakdown of dead plant material is likely to become a much more significant pathway for CO₂ emissions to the atmosphere.
- **In mid- and high-latitude oceanic areas, the capacity to take up atmospheric CO₂ is decreasing.** This decrease is mainly due to negative effects of climate change and solar UV radiation on photosynthesis and related CO₂ uptake processes in oceans.
- **Predicted climate-related increases in runoff from the Arctic and alpine regions to aquatic ecosystems will accelerate the UV-induced breakdown of soil organic carbon into atmospheric CO₂.** The runoff also reduces water clarity and thus UV exposure in freshwaters and the coastal ocean.

- **Feedbacks involving greenhouse gases other than CO₂ are increasing due to interactive effects of UV radiation and climate change.** For example, increases in oxygen-deficient regions of the ocean caused by climate change enhance emissions of nitrous oxide, an important greenhouse and ozone-depleting gas.
- **Further reductions in solar UV-B irradiance reaching the Earth's surface caused by recovery of the ozone layer may retard photochemical reactions of organic and inorganic pollutants.** This effect may increase the persistence and exposure concentrations of organic pollutants. On the other hand, in the case of metals, this may be beneficial, since UV-induced transformation of metals often increases their toxicity.

Air Quality

- **The impacts of air pollution on human health and the environment will be directly influenced by future changes in climate, emissions of pollutants, and stratospheric ozone.** Ultraviolet radiation is one of the controlling factors for the formation of photochemical smog which includes tropospheric ozone and aerosols; it also initiates the production of hydroxyl radicals, which control the amount of many climate- and ozone-relevant gases in the atmosphere. Uncertainties still exist in quantifying the chemical processes and wind-driven transport of pollutants. The net effects of future changes in UV radiation, meteorological conditions, and anthropogenic emissions may be large but will depend on local conditions, posing challenges for prediction and management of air quality.
- **Numerical models predict that future changes in UV radiation and climate will modify the trends and geographic distribution of hydroxyl radicals, thus affecting urban and regional photochemical smog formation, as well as the abundance of several greenhouse gases.** Concentrations of hydroxyl radicals are predicted to decrease globally by an average of 20% by 2100, with local concentrations varying by as much as a factor of two above and below current values. However, significant differences between modelled and measured values in a limited number of case studies show that we do not fully understand the chemistry of hydroxyl radicals in the atmosphere. Therefore, the consequences for human health and the environment are uncertain.
- **Photochemically produced tropospheric ozone is projected to increase over the next 20-40 years in certain regions of low and middle latitudes because of interactions of emissions, chemical processes, and climate change.** If emissions of anthropogenic air pollutants from combustion of fossil fuels, burning of biomass, and agricultural activities continue to increase, concentrations of tropospheric ozone will tend to increase. Climate-driven increases in temperature and humidity will also increase tropospheric ozone production in polluted regions, but reduce it in more pristine regions. Higher temperatures of some soils tend to increase emissions of nitrogen oxides (NO_x) and biogenic volatile organic compounds (VOCs), leading to greater background concentrations of ozone in the troposphere. For the future protection of human health and the environment, more effective

controls will need to be considered for emissions of NO_x and VOCs related to human activities.

- **Aerosols composed of organic substances have a major role for climate and air quality, and contribute a large uncertainty to the energy budget of the atmosphere.** Aerosols are mostly formed via the UV-initiated oxidation of volatile organic compounds from anthropogenic and biogenic sources, although the details of the chemistry are still poorly known and current models under-predict their abundance. A better understanding of their formation, chemical composition, and optical properties is required to assess their significance for air quality and to better quantify their direct and indirect radiative forcing of climate.
- **The decomposition of substitutes for ozone-depleting substances can lead to a range of chemical species, however with little relevance expected for human health and the environment.** The hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) used as substitutes for ozone-depleting CFCs can break down into trifluoroacetic acid (TFA), which is very stable and will accumulate in the oceans, salt lakes, and playas. However, based on historical use and projections of future uses, including new products entering the market such as the fluoro-olefins, increased loadings of TFA and monofluoroacetic acid (MFA) in these environmental sinks will be small. Even when added to existing amounts from natural sources, risks from TFA (and the more toxic MFA) to humans and organisms in the aquatic environment are judged to be negligible.

Materials

- **Increased ambient temperature accelerates the UV-induced degradation of plastics and wood, thus shortening their useful outdoor lifetimes.** Natural and man-made materials are widely used in outdoor construction, agriculture and other applications. The increased rate of degradation at the higher temperatures depends on the specific material, the UV radiation environment and the geographic location of exposure.
- **The presently available stabilisation technologies can mitigate the damage to some types of common polymers routinely exposed to solar UV radiation.** State of the art stabilisers, surface coatings and material substitution technologies, are likely to control the deleterious effects of environments that have enhanced UV radiation and temperature, but only for some types of common plastics.
- **Plastic nanocomposites and wood-plastic composites that are increasingly used in outdoor applications appear to have relatively higher solar UV radiation stability compared to conventional materials.** The use of nanofillers in composites is increasing as these deliver a superior performance compared to conventional composites. Wood-plastics

composites, although also UV-stable compared to the plastic alone, can still suffer reduced lifetimes at high humidity levels.

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

R. L. McKenzie^a, P. J. Aucamp^b, A. F. Bais^c, L.O. Björn^d, M. Ilyas^e, S. Madronich^f

^a *National Institute of Water and Atmospheric Research, NIWA Lauder, PB 50061 Otago, Central Otago, New Zealand.*

^b *Ptersa Environmental Management Consultants, PO Box 915751, Faerie Glen, 0043, South Africa.*

^c *Laboratory of Atmospheric Physics, Aristotle University of Thessaloniki, Campus Box 149, 54124 Thessaloniki, Greece.*

^d *Key Laboratory of Ecology and Environmental Science in Guangdong Higher Education, School of Life Science, South China Normal University, Guangzhou 510631, China, and Department of Biology, Lund University, Sölvegatan 35, SE-22362, Lund, Sweden.*

^e *Albiruni Environment and Science Development Centre, Gelugor, Malaysia*

^f *National Center for Atmospheric Research, Boulder, Colorado, USA*

Summary

The Montreal Protocol is working, but it will take several decades for ozone to return to 1980 levels. The atmospheric concentrations of ozone depleting substances are decreasing, and ozone column amounts are no longer decreasing. Mid-latitude ozone is expected to return to 1980 levels before mid-century, slightly earlier than predicted previously. However, the recovery rate will be slower at high latitudes. Springtime ozone depletion is expected to continue to occur at polar latitudes, especially in Antarctica in the next few decades. Because of the success of the Protocol, increases in UV-B radiation have been small outside regions affected by the Antarctic ozone hole, and have been difficult to detect. There is a large variability in UV-B radiation due to factors other than ozone, such as clouds and aerosols. There are few long-term measurements available to confirm the increases that would have occurred as a result of ozone depletion. At mid-latitudes UV-B irradiances are currently only slightly greater than in 1980 (increases less than ~5%), but increases have been substantial at high and polar latitudes where ozone depletion has been larger. Without the Montreal Protocol, peak values of sunburning UV radiation could have been tripled by 2065 at mid-northern latitudes. This would have had serious consequences for the environment and for human health.

There are strong interactions between ozone depletion and changes in climate induced by increasing greenhouse gases (GHGs). Ozone depletion affects climate, and climate change affects ozone. The successful implementation of the Montreal Protocol has had a marked effect on climate change. The calculated reduction in radiative forcing due to the phase-out of chlorofluorocarbons (CFCs) far exceeds that from the measures taken under the Kyoto protocol for the reduction of GHGs. Thus the phase-out of CFCs is currently tending to counteract the increases in surface temperature due to increased GHGs. The amount of stratospheric ozone can also be affected by the increases in the concentration of GHGs, which lead to decreased temperatures in the stratosphere and accelerated circulation patterns. These changes tend to decrease total ozone in the tropics and increase total ozone at mid and high latitudes. Changes in circulation induced by changes in ozone can also affect patterns of surface wind and rainfall.

The projected changes in ozone and clouds may lead to large decreases in UV at high latitudes, where UV is already low; and to small increases at low latitudes, where it is already

high. This could have important implications for health and ecosystems. Compared to 1980, UV-B irradiance towards the end of the 21st century is projected to be lower at mid to high latitudes by between 5 and 20% respectively, and higher by 2-3% in the low latitudes. However, these projections must be treated with caution because they also depend strongly on changes in cloud cover, air pollutants, and aerosols, all of which are influenced by climate change, and their future is uncertain.

Strong interactions between ozone depletion and climate change and uncertainties in the measurements and models limit our confidence in predicting the future UV radiation. It is therefore important to improve our understanding of the processes involved, and to continue monitoring ozone and surface UV spectral irradiances both from the surface and from satellites so we can respond to unexpected changes in the future.

Introduction

The amount of ultraviolet radiation (UV)^{*} received at Earth's surface has important implications for human health, terrestrial and aquatic ecosystems, biogeochemical cycles, air quality, and damage to materials, which are assessed in subsequent papers of this thematic issue. Research into these topics was stimulated by the realisation, more than 30 years ago, that the stratospheric ozone layer was at risk, and that there would be consequent increases in UV-B (280-315 nm) radiation. Increases in UV-B due to decreasing ozone amounts were observed during the 1980s and 1990s, particularly at high latitudes ($> \sim 60^\circ$), where ozone depletion was more pronounced. However, because of the success of the Montreal Protocol[†] in reducing the ozone depleting substances (ODSs), ozone is no longer decreasing and at unpolluted sites, unaffected by changes in cloud cover, the increases in UV have not continued in recent years. Based on our current understanding (which may be incomplete), a gradual recovery of ozone is expected in the decades ahead. Changes in other factors, such as clouds, air pollution (including aerosols), and surface albedo, are sometimes more important for changing UV radiation, and may also lead to future differences on urban and regional scales. For the forest and aquatic environments, respectively, the UV transmission of canopy foliage and water must also be considered.

By the end of the 21st century, amounts of ozone in most regions are expected to be greater than they were before ozone depletion began prior to 1980. Therefore, in the absence of changes in other factors, UV-B would be expected to decrease. However, at some locations it is possible that UV will remain elevated due to decreasing extinctions by clouds and aerosols, particularly if the combustion of fossil fuels is significantly reduced by that time. In some regions, such as at high latitudes, where increases in cloud cover and reduction of the area of snow or ice are projected as a consequence of climate change, decreases in UV at the surface may be expected.

It is well known that UV radiation can have harmful effects on human health (e.g., skin cancer and eye damage), terrestrial and aquatic ecosystems and materials. However, UV radiation also has beneficial effects, for example by stimulating the production of vitamin D in humans and other animals (adverse and beneficial effects are discussed in detail in Chapter 2. At mid- and high- latitudes, wintertime UV is very low, and human populations may be at risk from insufficient vitamin D, a risk which may increase further if ozone increases in the years ahead and if the current trend toward indoor living continues.

^{*} For ease of reading, we use "UV" as an abbreviation of "UV radiation" or "amount of UV radiation". The term "UV irradiance" means the measured quantity of UV radiation (usually in units of W m^{-2}) incident on a horizontal surface. See the glossary for further details, including definitions of UV-A, UV-B and UV-C.

[†] Here we take the Montreal Protocol to include its subsequent amendments and adjustments.

Here the past changes and projected future changes in UV are assessed, focussing on the effectiveness of the Montreal Protocol implementation and the effects of interactions between ozone depletion and climate change. Although brief progress reports¹³⁵⁻¹³⁷ have been published in the last three years, this paper summarises changes in our understanding of these factors in the period since the last full assessment report in 2007.¹³⁴ To put this work into context, we include a brief discussion of changes in stratospheric ozone, which is described in greater detail in the WMO Scientific Assessment of Ozone Depletion.¹⁵⁰

Past changes in UV

Despite the paucity of corroborative long-term measurements of UV radiation, studies and theory have established a clear inverse relationship between column ozone and UV-B radiation reaching the surface of Earth. It is therefore generally accepted^{134, 149} that during the period of declining column ozone starting prior to 1980 and continuing through the 1990s, UV would have increased by a few percent at mid-latitudes (~ i.e., latitudes 30°-60° in both hemispheres), so that the UV experienced there since the late 1990s probably exceeds that at any time in the last century. However, this assumes that changes in cloud cover and aerosols have been small – an assumption which at many locations is not valid. Further, over timescales of hundreds of years or longer, it is unknown whether the current UV levels are particularly severe. Better proxy methods are needed to estimate these effects reliably and to better understand the severity of the present situation in a longer historical context.

Estimates of UV from periods prior to modern instruments

Changes in UV over timescales of centuries have been estimated from records of sunspot number – an index of solar activity. Increased solar activity leads to increased UV-C (100-280 nm) radiation in the upper atmosphere, which in turn enhances the photochemical formation of ozone and hence the absorption of UV-B radiation. Therefore an inverse relationship between solar activity and UV-B irradiance at the surface is expected. For example, the 11-year solar activity cycle is responsible for increases in UV-C irradiance of a few percent between minimum and maximum. These increases lead to enhanced production of stratospheric ozone, which in turn reduces UV-B transmitted to Earth's surface by a few percent between solar minima and solar maxima in recent solar cycles. It has been further suggested that long-term changes in UV-C exceed these variations by a factor of two, and that during quieter periods (low number of sunspots), such as the Maunder minimum in the 17th century, surface UV-B irradiance may have been significantly higher than in the modern epoch.¹⁰⁶

Over much longer timescales, before the appearance of man, UV irradiances may have been much greater than at present, due to differences in the composition of the atmosphere. For example, a recent modelling study estimated that about 4 billion years ago, UV-B radiation may have been several orders of magnitude higher than at present.²⁶ Another modelling study suggested that about 250 million years ago the UV-B levels may also have been elevated, mainly at higher latitudes.⁴⁸ Historic changes in UV-B, their causes, and methods to probe them have recently been reviewed.¹⁶

For the more recent past, on timescales of a century or so, attempts have been made to estimate UV irradiances using information about daily sunshine duration. For example, daily totals of solar UV radiation back to 1893 were reconstructed for Central Europe.³⁸ The estimated annually averaged erythemal irradiances (UV-Ery)[‡] in this region were found to be only weakly depend-

‡ Erythemally weighted UV (i.e., “sunburning” irradiance, UV-Ery) is the irradiance weighted by the erythema action spectrum (see Fig. 1-6). This is often reported to the public in terms of the UV Index (UVI) where UVI =

ent on ozone amounts. Thus, assuming that any ozone changes prior to 1980 were no larger than those since 1980,²¹ this new information extends our knowledge of historical changes in UV irradiance to the period before direct measurements were available. However the uncertainty in the reconstruction is typically 10-20% for annual means.

Satellite estimates of UV

Estimates of surface UV irradiance are available from satellite measurements for the period since the late 1970s. Changes in UV at different spectral bands over the period 1979 to 2008 for the entire globe have been derived from a series of polar orbiting satellite instruments, as summarised for UV-Ery in Fig. 1-1.⁵² Although satellite observations are available to higher latitudes, the latitude range in this study is limited to 55°S to 55°N to avoid large solar zenith angle effects and seasonal bias caused by missing data during polar nights. The reduced latitude range also helps to reduce the effects of uncertainties in the retrieval associated with distinguishing reflections from clouds or snow.^{24, 39} Over this time period, UV increased significantly at all latitudes except the equatorial zone. Over the shorter period from 1979 to 1998, the increase was caused by decreases in ozone amount, but after 1998, ozone amounts and UV irradiance in the northern mid-latitudes have been approximately constant. The annual average UV increase due to ozone changes is partially offset by an increase in clouds and aerosols which led to a decrease in transmission of UV to the surface (i.e., a “dimming”), especially at higher latitudes in the southern hemisphere. For clear skies, the largest increases in estimated UV-Ery were in the southern hemisphere (about 8% at 50°S for clear-sky conditions compared to 5% at 50°N). At lower latitudes, the increases were smaller. It should be noted that the effects of absorbing aerosols have not been included in this analysis because the satellite sensors do not adequately probe the lowermost regions of the atmosphere. Thus, the estimates are insensitive to changes in pollution in the boundary layer (approximately the lower-most kilometre) of the atmosphere. This means that, while the results are applicable for zonal averages, they may not be applicable in regions where there are heavy concentrations of absorbing aerosols and air pollutants that change with time. Furthermore, in some regions there can be large longitudinal variabilities in ozone trends,⁹⁸ which would in turn affect the longitudinal variability in UV trends. Consequently, the changes in Fig. 1-1 may not apply in specific regions, particularly urban areas.

In the above study, as in most other studies of this type, estimates of UV irradiance are based on data from polar orbiting satellites, which typically have only one overpass per day. As a result, no

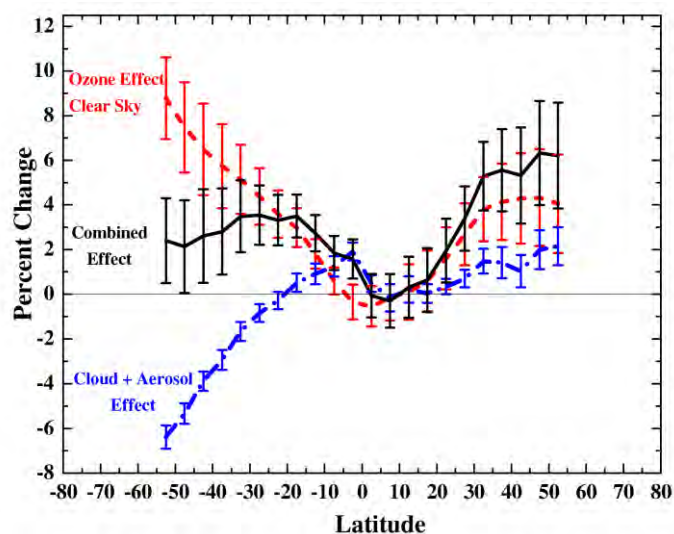


Fig. 1-1 Change in erythemal irradiance as a function of latitude between 55°S and 55°N (negative values of latitude for southern hemisphere) over the 30-year period from 1979 to 2008, estimated from satellite data. The red line (dashed) represents the change in clear-sky irradiance due to decreases in ozone; the blue line represents the change due to changes in clouds and non-absorbing aerosols, and the black line represents the combined effect. Adapted from ref⁵².

40. UV-Ery (W m^{-2}). For clear skies it can be approximately estimated⁷⁴ from $\text{UVI} = 12.5 (\cos(\text{SZA}))^{2.42} (\text{O}_3/300)^{-1.23}$, where O_3 is the total ozone column amount in DU and SZA is the solar zenith angle.

information on diurnal variability is provided, and there are significant uncertainties in the estimated daily doses (integrated UV irradiance during a day). Following earlier attempts to use data from geostationary satellites to estimate effects of clouds in Europe,¹⁴¹ a new algorithm has been developed to estimate diurnally-varying spectral irradiance of UV at the surface over North America based on information (e.g., cloud, surface albedo and aerosol data) from such satellites.⁴⁴ The results show reasonable agreement between the satellite data and ground-based observations from the US Department of Agriculture UV-monitoring network (bias within $\pm 3.5\%$ and root mean square differences of between 14 and 25%). The use of detailed information on cloud cover from geostationary satellites will improve the estimation of daily doses of UV, which are more relevant for effects that depend on accumulated UV.

Ground-based studies

There were few long-term records of UV radiation from ground-based instruments prior to the era of satellite measurements. The first co-ordinated ground-based networks were established in the 1970s,¹³ but their geographical coverage was limited during the period of most-rapid depletion of ozone prior to the 1990s. Furthermore, in some cases, the wavelength response of the instruments was such that they were not particularly sensitive to changes in the amount of ozone, and the UV irradiances were more strongly affected by changes in other factors, such as clouds and aerosols. Consequently, the expected increase in UV radiation attributable to ozone depletion was not well established by direct measurements of surface UV radiation. Significant increases in UV irradiance have been observed from the United States National Science Foundation's UV spectroradiometer network in Antarctica,¹⁵ where ozone depletion has been substantial. However, because ozone depletion had started well before the deployment of these instruments, the full extent of the changes in UV-B could not be fully documented. Model calculations suggest that in some cases, the peak UV-B irradiances would have doubled since the pre-1980 era, and current values in spring are approximately twice as large as corresponding values in the Arctic where ozone depletion has been less severe.^{14, 150}

Long-term changes in observed UV irradiance at the surface vary geographically, and are not always in response to ozone changes alone. In some locations, the response of UV radiation to the beginning of an ozone recovery is apparent, but in other places UV radiation is still increasing. Since the mid-1990s, mean annual changes in UV-Ery within the United States Department of Agriculture's UV Network ranged from -0.5% to $+0.2\%$ per year,⁵⁴ although in most of these cases the trends for individual months were not statistically significant. Over the measurement period of about one decade, there was a general increase in ozone, suggesting that changing cloud, aerosol, air pollution and snow conditions were also important determinants of variability in surface radiation in addition to ozone changes. At Belsk, Poland, although an increase in column ozone occurred between 1995 and 2006, UV-B did not decrease, but instead tended to level off.¹⁸ Such variations could arise from differences in the changes in clouds and aerosols among the measurement sites, as discussed further below. The results of UV measurements and reconstructions have been compared in a comprehensive study in Europe. Eight sites were involved, and the study included an attribution of the changes in UV to ozone and clouds.³² At some sites, records of UV were reconstructed from the 1960s to the present. Upward trends in UV were observed from 1980 to mid-1990s for most sites. However, UV irradiances in the 1980s, before ozone depletion became apparent at these sites, were also low compared with the long-term average. Year-to-year variability was also large, but there was a strong commonality in the long-term changes between the sites, indicating that widespread regional effects are important. Attribution of the observed changes between ozone and cloud effects shows that the low irradiances in the 1980s were primarily a cloud/aerosol effect. The largest effects from ozone generally occurred in the 1990s (see Fig. 1-2). The eruption of Mt Pinatubo in 1991 had an important contribution to the changes in the mid-1990s, through reducing the ozone amounts (tending to increase UV) and increasing aerosol ex-

tinctions (tending to decrease UV). As discussed further below, these results for Europe cannot be extrapolated to other regions, as there are strong regional differences in the patterns in long-term changes in cloud cover.⁶⁹

Biological proxies to measure UV

In the absence of direct measurements over longer periods, attempts have been made to use biological proxies to estimate past changes in UV radiation. For example, changes in the concentration of compounds in plant spore walls have been used to estimate changes in UV at several sites over a wide range of latitudes since 1960,⁷³ and studies are in progress to determine whether similar changes in fossilized plants and in pollen can be used to estimate past UV.¹⁷ However, the ratio between two UV protective substances, as a proxy for UV-B, showed no correlation with either sunspot activity or volcanic eruptions.¹⁰⁵ In another study, the concentrations of a different UV-protective substance in herbarium samples of a liverwort (a moss-like plant) were investigated as a proxy for UV-B. However, no trend was found over the years 1850-2006.⁹⁵

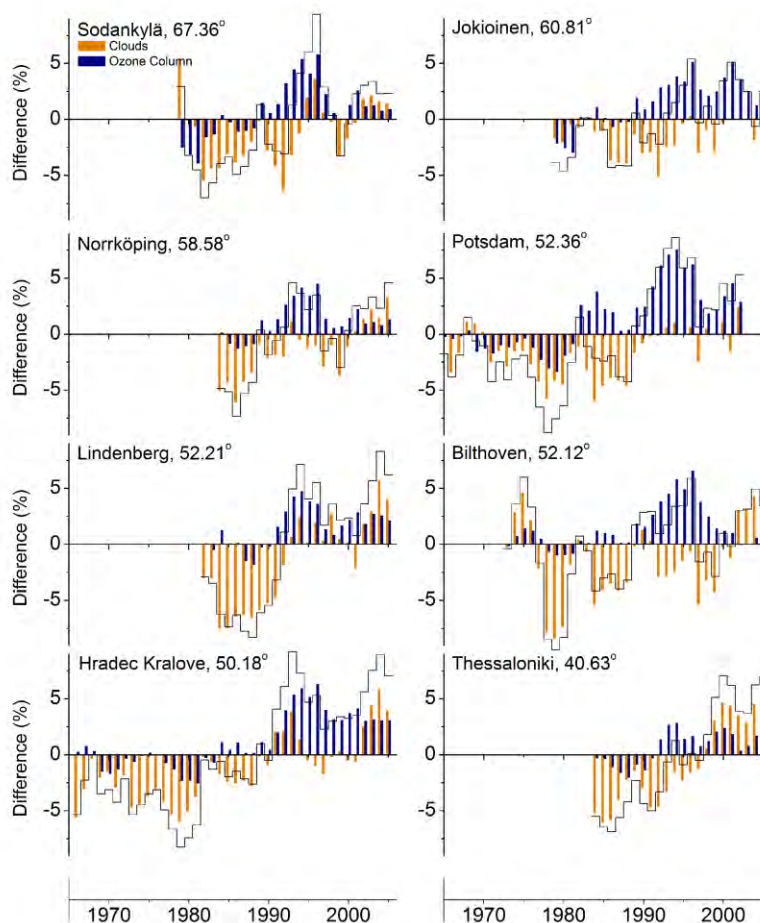


Fig.1-2. The long-term impacts of ozone and clouds (including aerosols) on UV-Ery have been estimated separately at eight European sites by comparing the UV-Ery derived from measurements at each site with that derived from model calculations using the climatological ozone record. The step lines show the combined effect of clouds and ozone on UV-Ery. All estimates, expressed as differences from the long-term mean over the period of observations at each site, have been smoothed first by a 3-year running average. Adapted from ref ³².

Further studies have been carried out to investigate the association between UV radiation and the concentration of protective compounds (flavonoids) in Antarctic mosses.¹⁰⁷ Measurements taken since the 1970s, spanning periods before and after the onset of Antarctic ozone depletion, reveal significant negative correlations between measured ozone amounts and the concentration of flavonoids, suggesting that these herbarium specimens may reveal historical UV-B radiation. However, factors other than ozone, such as changes in cloud cover and distribution in the locations of samples, may have had a significant influence on the UV exposures received.

A spore dosimetry method has been used to investigate relationships and trends of biologically effective doses of solar UV radiation in Asia, Europe and South America from 1999 to

2007.⁸⁷ However, the changes in UV deduced using these dosimeters is much larger than expected from changes in ozone over the same period, suggesting that there may be other factors that are not yet accounted for properly.

Effects on UV of air pollution, aerosols and clouds

Regional effects

Cloud cover and transmission can vary appreciably as a function of geography and topography, leading to significant differences in UV for sites at similar latitudes.

Large reductions in surface UV irradiance have been observed at polluted locations compared to pristine locations, caused by aerosols in the boundary layer, by differences in the profile of ozone, and by interactions between ozone and aerosols in the lower atmosphere.^{60, 79, 126} Naturally-occurring aerosols (e.g., Saharan dust, aerosols from wild fires or emissions of volatile organic compounds) have been shown to cause substantial reductions in UV-B radiation, far from their source regions.¹¹⁹

In urban areas, the effects of pollution on UV can be large. A recent study quantified the contributions to differences in UV irradiances between a site with pristine conditions (Lauder, New Zealand) and a megacity (Tokyo, Japan).⁷⁹ For a given solar elevation, irradiances were much greater at the pristine site, particularly in the summer months. Parts of the differences are attributable to well-known effects, including seasonal differences in Sun-Earth separation, and differences in stratospheric ozone. Blocking of solar radiation by buildings was also significant in the city, as was, on some occasions, absorption of UV-A by NO₂ and of UV-B by SO₂. Significant reductions in UV radiation by NO₂ have also been observed in Moscow.²⁵ Co-located measurements of UV-B irradiance and aerosol optical characteristics in a relatively polluted environment, in Pune, western India, revealed a reduction in UV-B by ~50% per unit increase in the aerosol optical depth§ measured at 0.4 µm.⁹⁷

These effects on UV radiation of aerosols and pollutants in the boundary layer air can seriously compromise the accuracy of retrievals of surface UV radiation from satellite-based measurements, which generally use back-scattered solar ultraviolet radiation. A large part of the radiation that is back-scattered near the surface and contains information on absorption from aerosols, cannot reach the satellite sensor. These instruments therefore tend to overestimate the UV irradiance at the surface under polluted conditions.^{56, 59, 126} A new approach for correction of satellite-derived UV irradiance estimates, using climatological fields of aerosol absorption optical depth from a global ground-based network and a model, has recently been reported.¹⁰ Although the corrected values are in better agreement with measurements, a significant bias remains.

Global dimming and brightening effects

In addition to local pollution effects, UV irradiances are affected at regional or even global scales by effects such as “global dimming and brightening”. Widespread deployment of instruments to measure broad-band global irradiance began in the mid-20th century, and has resulted in valuable data on decadal changes in solar radiation. Recent analysis has made it clear that many regions experienced reductions in global irradiance up to the 1980s, followed by a reversal thereafter.^{72, 147} The causes of these changes may vary from region to region and may include long-term changes

§ The optical depth of aerosols (AOD) is a measure of the reduction in direct beam irradiance due to the presence of the aerosols, and depends on the wavelength. If the AOD at a given wavelength is unity (1), then the direct beam is attenuated by the factor $1/e = 0.368$.

in extinctions from aerosols (from anthropogenic pollution^{3, 153}), volcanic eruptions,⁹² or cloud cover.⁷² Changes in clouds and aerosols may themselves be influenced by climate change, as discussed further below.

In the northern hemisphere, apart from some regions in Asia,^{67, 153} there has been widespread brightening in recent decades, due to reductions in air pollutants, aerosols and clouds, but this tendency has been less pronounced since 2000. Analysis of satellite data over Europe also shows an increase in transmittance of solar radiation between 1987 and 2002.⁹⁰

The effects of both dimming and brightening are likely to be larger at UV wavelengths. Long-term increases in the concentrations of aerosols since pre-industrial times probably contributed to reductions in UV radiation at the surface in more densely populated regions (e.g., Europe) from well before the time when UV measurements were routinely available. It has been estimated that the aerosol optical depth, at wavelength 550 nm, has increased by about 20% since preindustrial times,¹³³ which could have led to significant decreases of UV-B radiation. Another study has estimated that there may have been a reduction in annual mean UV of up to 20% since 1750 in some industrialized regions.⁶⁸

Changes in UV radiation due to changes in aerosol optical depth observed in Thessaloniki, Greece, over the period 1997–2005, have been consistent with the broad trends.⁶¹ A recent update⁸¹ reported a decrease of ~7% per decade in aerosol optical depth and an increase of ~9% per decade in UV-B irradiance over the period 1991–2006. At another site (Moscow) the weak spectral dependence observed in the changes of UV irradiance implies that they are due to changes in clouds and aerosols rather than ozone.²³ If those recent trends in atmospheric transmittance continue, that would imply that the UV radiation in these regions may not yet have reached its peak.

The longer term reductions in UV from anthropogenic pollution prior to the 1980s are probably larger than any increases due to the more recent depletion of stratospheric ozone. Effects from aerosols in the future are uncertain. Significant increases in the background optical depth of stratospheric aerosols have been observed over the past two decades from Mauna Loa Observatory in the remote Pacific.⁵⁵ These have been ascribed to increased pollution originating in Asia, but the changes in aerosol extinctions have not yet had a significant impact on UV irradiances at that site.

Important differences in cloud effects between northern hemisphere and southern hemisphere sites have been identified from measurements of UV spectral irradiance. For example, it has been shown, using data from multiple sites, that the effects of cloud cover on UV are smaller in New Zealand than at corresponding latitudes in Europe.¹¹⁰ However, based on global satellite data (including the oceans) the southern hemisphere appears to be generally cloudier overall, with a reduced frequency of clear-sky occurrences, than corresponding northern hemisphere locations.³⁶

The Montreal Protocol

Past successes and expectations for the future

The Montreal Protocol continues to be effective in protecting the stratospheric ozone layer. However, the timing of the return to pre-1980 ozone and UV values cannot yet be predicted precisely. The concentrations of ODSs are decreasing, and the concentrations of replacement chemicals are increasing.^{51, 102} Stratospheric ozone is no longer decreasing and in some cases there is evidence for an increase. A European study⁴⁹ showed that at mid-latitudes in the northern hemisphere and in the Arctic there was an almost monotonic negative trend in ozone from the late 1970s to the mid-1990s followed by an increase, as expected from the changes in ODSs, which peaked in 1997. Improved models that include better estimates of atmospheric circulation predict a slightly faster ozone layer recovery at mid-latitudes, and a slightly slower recovery at high latitudes compared

with results from earlier models.⁸⁸ Unfortunately, few high-quality long-term measurements are available to monitor the effectiveness of the Montreal Protocol in terms of UV radiation received at Earth's surface.

Attribution of changes in ozone to the Montreal Protocol

In the past it has been argued that at least part of the recently-observed reductions in the decline of ozone may in fact be the result of changes in atmospheric circulation,⁴⁹ rather than the result of reductions in the concentrations of ODSs due to the Montreal Protocol. Although the slowdown of ozone depletion may be statistically significant at northern mid-latitudes, it was argued that the attribution of the levelling off of ozone column amounts due to reductions of chlorine and bromine in the stratosphere has not yet been verified.¹²⁵ However, it has recently been shown, using ground-based measurements of ozone vertical profiles, that the increases in ozone detected at higher regions in the stratosphere (above 40 km) – where chemical effects outweigh dynamical effects – are consistent with changes in ODSs resulting from the Montreal Protocol.¹²³

In most regions, any recovery in total ozone column amounts is not yet statistically significant. The recovery should be detectable earlier at southern middle- and high-subpolar latitudes where changes are larger, and the natural ozone variability is smaller.¹⁴² A study of ozone variabilities in the Antarctic vortex region, where ozone is affected by both chemical and dynamical processes,¹⁵² reported that, in this region at least, decreases in the concentrations of stratospheric halogens are the primary cause of the recent reduction in the rate of decline of ozone amounts.

In the northern temperate zone, the long-term globally averaged trends in total ozone derived from 50–60 stations range from about -2% per decade in the late 1980s to around +1% per decade by the start of the 21st century.⁸ Analysis of height-resolved data showed that nearly half of the increase in total ozone is due to increases in the lower stratosphere, with the troposphere contributing only about 5% of the decadal change, which is consistent with expectations based on the Montreal Protocol.

Full attribution of changes in total ozone or in ozone profiles to changes in ODS abundances resulting from the Montreal Protocol remains problematic due to observational uncertainty and natural variability as discussed in the Science Assessment.¹⁵⁰

Effect on global warming

In addition to its effectiveness in the reduction of ODSs, the Montreal Protocol has also reduced global warming. This arises because the Global Warming Potential (GWP = 1 for CO₂) of the replacements is less than that of the original CFCs. For example, the GWPs of CFC-11 and CFC-12 are 3800 and 8100, respectively, while the GWP for HCFC-22 (a major replacement), is 1500.⁵⁷ Model calculations indicate that the climate protection already achieved through the Montreal Protocol alone is larger than the reduction target of the first commitment period of the Kyoto Protocol (ending 2012).¹³⁹ In fact, without the Montreal Protocol, the radiative forcing due to increasing chlorofluorocarbons (CFCs) over the period 1990 to 2020 would have been comparable with that due to increasing GHGs. The reduction in radiative forcing from the phase-out of CFCs far exceeds that from the measures taken under the Kyoto protocol for the reduction of emissions of GHGs. It has been estimated that the cooling effect at Earth's surface due to the phase-out of ODSs is approximately equal to the warming effect due to increasing GHGs at least through the first two decades of the 21st century.¹³⁹ Thus, the Montreal Protocol has succeeded not only in reducing the content of chlorine in the atmosphere, but has also reduced global warming. The replacement halocarbons now in use are also GHGs, so they continue to add to global warming but to a lesser extent than the ODSs they replaced.¹²² At polar latitudes in both hemispheres, climate feedback effects from ozone depletion could have led to a warmer surface by up to ~1°C in some locations,⁸⁶ but a cooler surface in others.¹²⁹ Within the atmosphere substantial regional differences

would have occurred at different altitudes due to changes in circulation: some regions would have warmed up to 3°C (middle stratosphere over Antarctica), while others would have cooled up to 6°C (upper stratosphere over mid-latitudes).⁸⁶

The world avoided

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.⁸⁹ By 2020, 17% of the globally-averaged column ozone in 1980 would have been destroyed, with depletion increasing to more than 60% by 2060 (Table 1-1). Decreases in stratospheric ozone due to increasing CFCs would have led to a marked increase in UV irradiance, with the UV index (UVI, see glossary) at northern mid-latitude summer tripling by 2065 (see Fig. 1-3). 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, including in the summer months. However, this simulation did not include tropospheric chemical processes and, in case of the large ozone depletions predicted, the increased penetration of UV into the troposphere could have resulted in an increase in ozone in that region (i.e., the so-called “self-healing” effect), which could have ameliorated some of these projected decreases.

Table 1-1. Estimated ODS concentrations (EESC, defined in glossary), annual global mean column ozone, and the peak UV index at 40°N that would have occurred in 1980, 2020, 2040 and 2065 if the Montreal Protocol had not been implemented.⁸⁹

	1980	2020	2040	2065
EESC (ppbv)	2	11.5	20	40
O ₃ (DU)	310	250	220	100
UVI _{max}	10	12.5	15	30

Future uncertainties

The largest uncertainties in estimating future ozone result from interactions with climate change, as discussed in more detail below. Other uncertainties include the continued political will to comply with the Montreal Protocol, unexpected volcanic eruptions, and unexpected developments in our understanding of the atmospheric processes involved.

The precise quantitative contribution of very short-lived bromine compounds to lower stratospheric ozone depletion also remains uncertain.¹¹⁸ Furthermore, larger amounts of ODSs than previously estimated are now thought to be contained in existing storage banks (i.e., repositories for CFCs), and a large proportion of these ODSs may eventually be released into the atmosphere, where they will continue to destroy ozone.³⁰

Ozone depletion from anthropogenic oxides of nitrogen is also likely to be more important in the future as the concentrations of atmospheric chlorine decline.⁶⁶ The ozone depletion potential of N₂O, a greenhouse gas that is emitted from soils, was recently estimated. It was shown that by the middle of the 21st century, N₂O will be the major ozone depleting gas.¹⁰¹

Thus, although the Montreal Protocol has succeeded in controlling most of the ODSs, remaining uncertainties in threats to the ozone layer and climate change mean that potential changes in surface UV radiation are still a matter of concern.

Interactions with climate change

Scientifically, and at political and policy levels, there are strong links between the depletion of ozone and climate change. The Kyoto Protocol on climate change has similarities with the successful Montreal Protocol. However, addressing climate change is much more complicated than the phase-out of ODSs.⁵⁷

There has been an increased focus on understanding physical interactions between ozone depletion and climate change. These are more complex than previously thought (see also Chapters 3-6). They can work in both directions: changes in ozone can induce changes in climate, and *vice versa*. Changes in climate can also induce changes in UV radiation without affecting ozone. Thus, the return of ozone (or UV) to its value at any particular date in the past should not necessarily be interpreted as a recovery from the effects of ODSs.¹⁴⁴

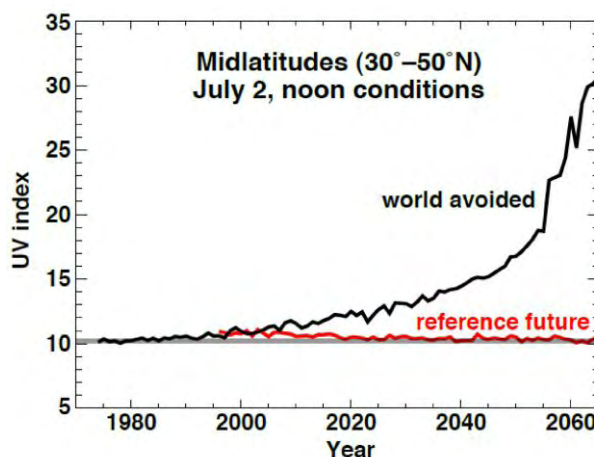


Fig. 1-3. UV index for clear skies predicted by a climate-chemistry model versus year for two future scenarios: (black curve) the “world avoided” by implementing the Montreal Protocol, and (red curve) a “reference future”, calculated using the observed and currently predicted chlorine concentrations. The UV index is calculated using the July 30° – 50° N zonal-mean ozone, and for local noon on 2 July. The horizontal grey line shows the 1975–1985 average from the fixed chlorine simulation. Adapted from ref⁸⁹.

Impacts of ozone depletion on climate change

As noted earlier,¹³⁹ the Montreal Protocol has helped to mitigate effects caused by the increases in the main GHGs (i.e., CO₂, CH₄ and N₂O). However, on the negative side, future reductions in GHGs arising from this Montreal Protocol “windfall” will be slower, leading to more rapidly increasing climate impacts from the main GHGs in the future. Further, the concentrations of hydrofluorocarbons (HFCs), which are replacements for CFCs and are also GHGs, are increasing rapidly. By 2050, the increased climate forcing from these HFCs will exceed the reduction in climate forcing due to the phase-out of CFCs.¹⁴⁰ It has been suggested that rapid action to curb further emissions of HFCs may be among the most effective means of limiting climate change in the next few decades.⁸⁵

In recent decades, increases in Antarctic temperatures may have been suppressed by changes in stratospheric ozone affecting wind patterns even at locations in the northern hemisphere,¹⁰⁴ so that melting of the west Antarctic ice sheet may proceed faster in future decades, as stratospheric ozone recovers.¹¹⁵ The effects of changes in stratospheric chemistry and circulation associated with ozone recovery have not been included in all models used in previous assessments of climate change,¹¹ although these effects have been investigated together in the most recent Scientific Assessment of Ozone Depletion.¹⁵⁰ Improved predictions of climate change should be achieved by extending the upper boundary of climate models to include the stratosphere.

For accurate prediction of future changes in climate, all forcing agents must be included, rather than the principal GHGs alone. These forcing agents should include changes in ozone with altitude⁴³ and longitude,²⁸ changes in the mixtures and concentrations of ODSs,¹¹³ and changes in aerosols.¹¹⁴ For example, climate models that include stratospheric chemistry predict that the observed increase in westerly winds at southern high latitudes will not continue, as previously thought, but will decrease in the next few decades as ozone recovers.¹²⁰

Impacts of climate change on stratospheric ozone and UV radiation

Changes in different components of the earth-atmosphere system due to global warming may affect ozone and UV radiation. The changes in UV may be a direct consequence of the changes in ozone, or they may be due to changes in other factors such as changes in aerosols, clouds, or surface reflectance. The extent of sea-ice in the Arctic is decreasing rapidly due to global warming and models suggest that ice cover in summer will disappear within the next few decades.^{27, 96} The reduced surface albedo may have important implications for future climate by increasing the fraction of solar energy that is absorbed at Earth's surface. Furthermore, organisms that were once living below the ice will be exposed to increased doses of UV, but organisms living above the surface will receive lower doses of UV due to the reduced reflectivity. It has been postulated that reductions in Arctic sea-ice resulting from climate change could also lead to significant reductions in ozone and associated increases in UV due to changes in atmospheric circulation.¹⁰⁹

As discussed further elsewhere,¹⁵⁰ increases in GHGs are expected to influence future changes in ozone. For example, as noted previously,¹³⁴ outside polar regions, decreased stratospheric temperatures that result from climate change are expected to slow down the rate of chemical destruction of ozone, and so aid ozone recovery. However, in polar regions the decreased stratospheric temperatures can lead to increased areas of polar stratospheric clouds, which provide surfaces for rapid ozone loss, and therefore inhibit ozone recovery.¹⁰³ Most models also predict that by the end of the 21st century, ozone amounts will be significantly greater than they were in 1980, before the onset of anthropogenic depletion of ozone.^{71, 144} However, changes in atmospheric circulation resulting from climate change can induce regional differences in ozone, leading to increases in UV in some regions and reductions in other regions.⁵⁰

It has been suggested that global warming could be counteracted by injection of sulphur compounds directly into the stratosphere to produce aerosols that reflect incoming solar radiation back to space. A secondary effect of this strategy would be the direct reduction of UV radiation reaching the surface due to extinction by these aerosols. However, this geo-engineering strategy would increase Arctic ozone depletion during the 21st century and delay Antarctic ozone recovery by 30 to 70 years.¹³⁰ Other geo-engineering schemes have also been suggested. However, because the atmosphere is a complex system, any deliberate interventions should be treated with great care as they may have unanticipated adverse effects.

Future changes in UV

Changes in UV radiation in the future are estimated by model simulations that are based on the projected changes in ozone and clouds, which are the most important factors that are known to influence UV. Because of the complex interactions between ozone depletion and climate change, particularly with regard to future changes in clouds and aerosols, continued monitoring of ozone and UV radiation will remain important. In particular, it will be necessary to maintain an extensive ground-based UV measurement capability to enable us to confirm whether the measures taken under the Montreal Protocol continue to be effective, and whether the model predictions for the future are consistent with observations.

Projected changes in clear-sky UV

New simulations have been carried out using coupled Chemistry-Climate Models (CCM), incorporating projected changes in total ozone columns and vertical profiles of ozone and temperature. One such study⁶³ reported that clear-sky surface erythemal irradiance would decrease over mid-latitudes by 5 to 15% over the 21st century, while at southern high latitudes the decrease would be twice as much. Surface erythemal irradiance was projected to decrease globally at somewhat higher rates in the first half of the 21st century and more slowly later on. This decreasing tendency

would be more pronounced over latitudes where stratospheric ozone depletion was largest.¹³¹ Another simulation⁶³ for the period 1980-2080 found that a reduction of UV to values similar to those in 1980 would be achieved before the mid-century at most latitudes, but because of the continued increase of ozone thereafter, UV would continue to decrease. By 2080, erythemally weighted irradiances would be on average 25% lower at high latitudes and 10% lower at mid-latitudes. These estimates have appreciable uncertainties, ranging from about 3% at mid latitudes to about 5% at high latitudes. For some weighting functions (e.g., DNA-damage) the changes are larger.

Fig. 1-4 shows the projected annually averaged changes in clear-sky UV-Ery from 1960 to 2100 relative to 1980,^{121, 150} based on projected changes in ozone from 15 models. These new simulations show that UV-Ery is projected to return to its 1980 values in the early 2020s at northern latitudes, with a slower return in the southern hemisphere, especially over Antarctica. These return dates are significantly earlier than reported in the previous assessment. UV-Ery is projected to continue to decrease thereafter, except at low latitudes where a small increase is projected. However,

there is a wide range in return dates between the models. These studies do not take into account the potentially important changes in cloudiness, surface reflectivity, and tropospheric aerosol loading due to or additional to climate change. The projected return date for annual mean UV to 1980 levels occurs a few years earlier than for ozone, which is projected to return to its 1980 levels earlier for the summer months when UV high, than for the winter months when UV is low.

Another atmospheric chemistry-climate model has been used to isolate the effects of climate change from those of ozone depletion and recovery on clear-sky UV-Ery.⁵⁰ Under the “moderate” emissions scenario (designated AB1) of the Intergovernmental Panel on Climate Change,⁵⁷ tropospheric ozone increases markedly between 1965 and 2095 as a result of changes in atmospheric circulation induced by climate change. The overall change varies with location and season. The predicted decrease in UV-Ery of 9% in northern high latitudes is a much larger effect than that due to stratospheric ozone recovery alone. In the tropics, clear-sky UV-Ery is predicted to increase by 4%; and in southern high latitudes in late spring and early summer by up to 20%. The latter increase is equivalent to nearly half of that generated by the Antarctic “ozone hole”. The results suggest that climate change will alter the tropospheric ozone budget and UV radiation at the surface, with consequences for tropospheric temperatures, air quality, and human and ecosystem health.

Projected effects of cloud changes on UV

Although clouds have large effects on UV, there has been only limited progress in forecasting future cloud prevalence or characteristics, or in calculating the detailed radiative effects of realistic cloud situations. It is uncertain whether the radiative effects of clouds in the future will be greater or less than at present. A recent modelling study suggests that, in response to climate change, cloud cover will increase at high latitudes by up to 5% but will decrease at low latitudes (< ~30°) by up to 3%.¹³² If this prediction is correct, there could be important implications for human

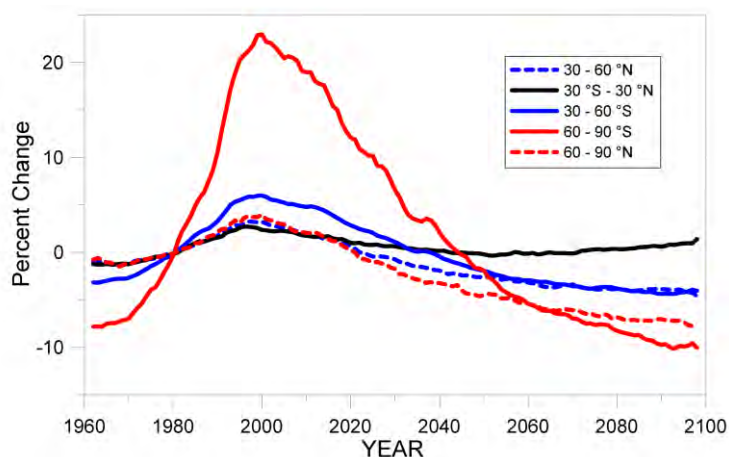


Fig. 1- 4. Time series of projected changes in annual mean of noon-time clear-sky erythemally weighted UV over the period 1960 to 2100, relative to 1980, smoothed with a 5-year running mean. Results are zonal means for several latitude belts. Updated from ref.^{5, 96}

health, the local ecosystems, biogeochemical cycles and air quality, since UV radiation would increase at low latitudes where it is already high, but decrease at high latitudes where it is already low. The already large latitudinal gradients in UV radiation will become even larger. However, these modelled cloud effects have not yet been verified against observed effects, and large uncertainties remain.

New simulations with 15 different CCMs have provided more robust predictions of ozone, and 4 of these models also provided estimates of future surface solar irradiance both under clear-skies and for cloud-affected conditions.³⁷

When the effects of projected changes in clouds are included, a further reduction in UV-Ery of about 2% is calculated for mid-latitudes. In the tropics, UV is projected not to return to its levels in 1980. Although UV is projected to decrease at all latitudes during the 21st century, in the tropics this decrease is smaller and lasts only until the middle of the century. Thereafter low latitude UV-Ery increases in response to the projected decreases in ozone due to the acceleration of the large scale atmospheric transport (specifically, the “Brewer-Dobson” circulation).¹¹³ Although the magnitude of this increase due to ozone is small (on average 2%) compared to the changes projected for the higher latitudes, the inclusion of clouds in the calculations results in an additional increase in UV-Ery of between 3 and 6% at low latitudes (see Fig. 1-5). This additional increase in a region where UV-Ery is already high would increase the risk of adverse effects on ecosystems and human health.

At high latitudes, especially in the Arctic spring, increasing cloudiness is expected to further reduce the UV irradiance at the surface. While changes in ozone are responsible for a reduction in UV-Ery of up to ~10%, the increases in cloud cover predicted by the models produce a further reduction in UV-Ery of ~10%. Reduced surface albedo due to decreases in the extent of sea ice during the 21st century will further amplify these reductions in UV at the surface (but increase UV below the sea surface that was formerly covered by ice). We note that the differences in the estimates among models are large, reducing confidence in these results. More work is needed to simulate future cloud changes with confidence.

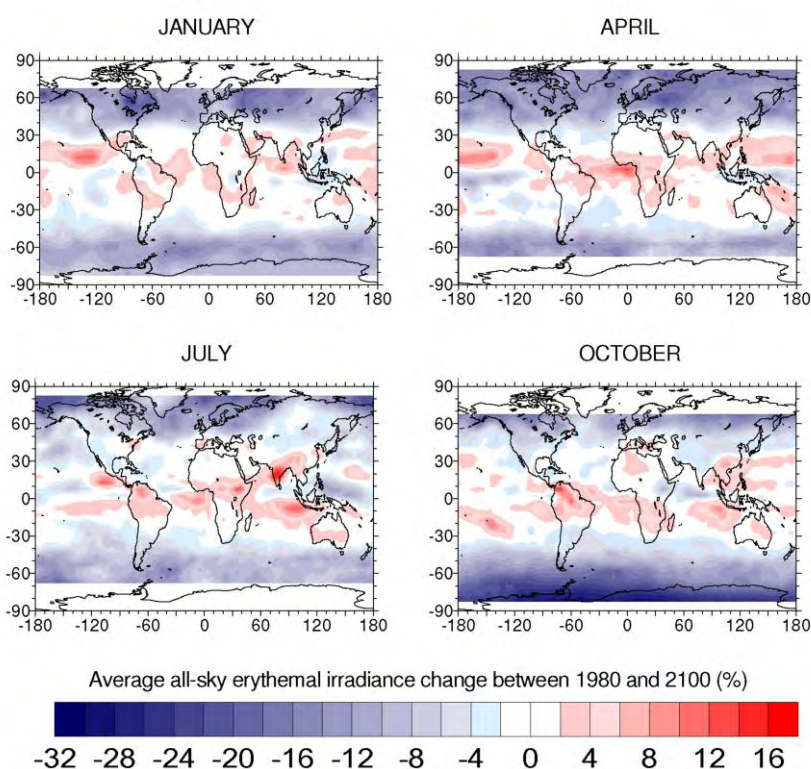


Fig. 1-5. Multi-model average changes in surface erythemal irradiance from 1980 (1975-1985) to 2100 (2089-2099) under all-sky conditions for four months, calculated with a radiative transfer model using projections of ozone, cloudiness, temperature and solar radiation from 15 different CCM runs. Updated from refs.^{121, 131} Note the seasonally-dependent bands of missing data at high latitudes.

The changes described in Figs 4 and 5 are for erythemally-weighted UV irradiances. For other environmental effects, the influence of ozone differs, as described further below. However, the influences of changing cloud cover are similar for most environmental effects.

Biological relevance of ozone changes

Sensitivity of UV radiation to ozone changes

The damaging or beneficial effects of UV radiation often have a strong wavelength-dependence, the effect being generally larger at shorter wavelengths. These effects are quantified using weighting functions, also called “action spectra”, which typically increase towards shorter wavelengths in the UV-B region. Examples of action spectra, illustrating their huge diversity, are shown in Fig. 1-6. Action spectra express the relative response at different wavelengths. To calculate physical effects, they are combined with a response in relevant units at the normalisation wavelength.

The relationship between change in total column ozone (O_3) and change in biologically effective UV irradiance (E) can be quantified in terms of the “Radiation Amplification Factor” (RAF). For *small* changes in ozone, the RAF is defined as the relative fractional change in effective UV irradiance with fractional change in total column ozone:

$$RAF = - (\Delta E/E) / (\Delta O_3/O_3)$$

where ΔE and ΔO_3 are the respective changes of UV irradiance (E) and ozone (O_3). For example, $RAF=1.5$ means that a 1% decrease in ozone will lead to a 1.5% increase in effective UV. Processes with steeper action spectra are more sensitive to changes in ozone, and have larger RAFs (see Fig. 1-6). An earlier assessment⁷⁵ included a comprehensive list of RAFs for various action spectra available at that time. Since then, several new action spectra have become available. An updated list of RAFs for these, and for some commonly-used older action spectra, is tabulated below (Table 1-2). Note that uncertainties in the weighting functions can be large and these uncertainties propagate through to these RAFs. Therefore, differences in the RAFs, shown in Table 1-2, should not be over-interpreted.

As the effect of ozone on UV is non-linear, for larger changes in ozone, the power form should be used⁸²:

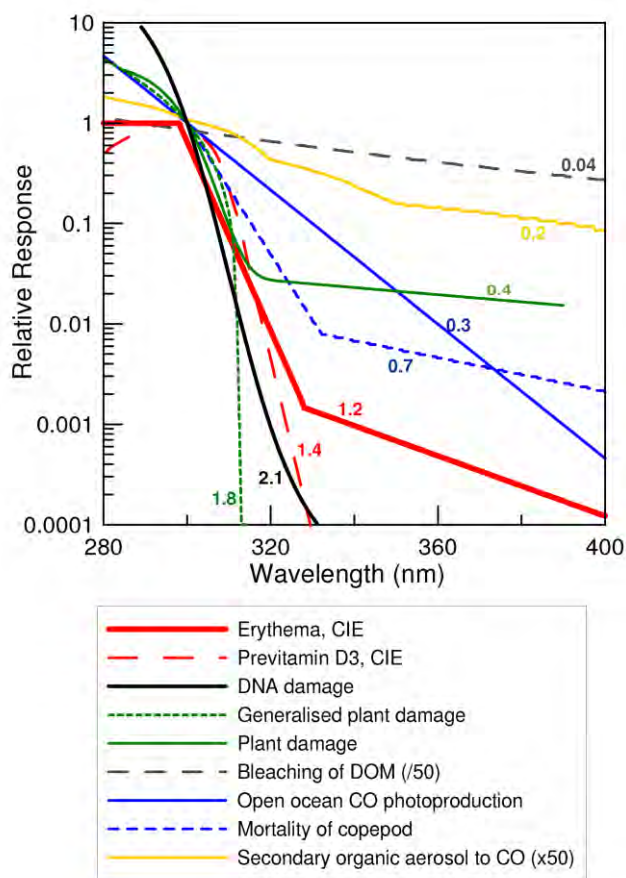


Fig. 1-6. Weighting functions for several of the UV-induced effects listed in Table 2. Curves are labelled by their summertime RAF and colour-coded according to the nature of the effect (e.g., health effects in red). Note that the action spectra for bleaching of dissolved organic matter (DOM) and secondary organic aerosols have been scaled by 1/50 and 50, respectively, to bring their normalisation at 300 nm close to unity.

$$E^+/E^- = (O_3^-/O_3^+)^{RAF}$$

where the superscripts (+ and -) refer to the cases with higher or lower ozone amounts, respectively.

Table 1-2. RAFs for action spectra calculated on the basis of daily integrals for latitude 30°N. This is an update of Table 1.1 in ref.⁷⁵

Effect	RAF Jan (290 DU)	RAF July (305 DU)	Refer- ence
Exponential decay (14 nm/decade)	1.00	1.01	-
UV-B (280-315 nm)	1.25	0.99	-
UV-A (315-400 nm)	0.03	0.02	-
Erythema (CIE, standard reference)	1.1	1.2	⁸⁰
Erythema (from tuneable laser)	1.6	1.5	⁴
Squamous skin cancer in humans (SCUP)	1.2	1.2	³¹
US Industrial Safety Standard (ACGIH)	1.4	1.5	¹
Cataract using whole pig lens	1.3	1.1	⁹³
Visual sensitivity in insect	0.1	0.1	⁷⁷
Previtamin D3 (CIE)	1.7	1.4	²⁰
DNA damage (Setlow)	2.2	2.1	¹¹²
DNA damage in alfalfa	0.5	0.6	¹⁰⁰
Generalised plant damage (Caldwell, truncated at 313 nm)	2.2	1.8	²²
Plant damage (extended to 390 nm)	0.3	0.4	⁴²
Phytoplankton <i>Phaeodactylum</i>	0.3	0.3	²⁹
Phytoplankton <i>Prorocentrum</i>	0.4	0.4	²⁹
Phytoplankton	0.8	0.8	¹⁹
Inhibition of photosynthesis in phytoplankton	0.3	0.3	¹²
Damage to freshwater cladoceran (<i>Daphnia</i>)	0.72	0.74	¹⁴⁸
Bleaching of dissolved organic matter (DOM)	0.04	0.04	⁹⁴
Baltic Sea - photoammonification	0.2	0.2	¹³⁸
Photoproduction of CO from tropical savanna litter	0.3	0.3	¹⁰⁸
Coastal ocean biologically labile photoproduction	0.2	0.2	⁸⁴
Open ocean CO photoproduction	0.3	0.3	¹⁵⁴
Mortality of copepod <i>Boeckella gracilipes</i>	0.6	0.7	¹²⁷
DNA damage in embryos of sea urchin	0.1-0.2	0.1-0.2	⁷⁰
Inhibition of hypocotyl growth in <i>Arabidopsis</i>	1.6	1.3	⁴⁵
Inhibition of photosynthesis in kelp (depth dependent)	0.1-0.4	0.1-0.4	⁸³
Secondary organic aerosol to carbon monoxide	0.2	0.2	⁷⁶
Secondary organic aerosol to formic acid	0.2	0.2	¹⁴³

Effect	RAF Jan (290 DU)	RAF July (305 DU)	Refer- ence
Material: PVC, 2.5% TiO ₂ , approx as $\exp(-0.058*\lambda)$	0.3	0.3	⁵
Material: Rigid Sheets, approx as $\exp(-0.082*\lambda)$	0.4	0.4	⁶
Material: Mechanical pulp, approx as $\exp(-0.110*\lambda)$	0.08	0.08	⁷
$O_3 \rightarrow O_2 + O(^1D)$	1.5	1.4	⁵⁸
$H_2O_2 \rightarrow 2 OH$	0.3	0.3	⁵⁸
$NO_2 \rightarrow NO + O(^3P)$	0.02	0.02	⁵⁸
$HNO_3 \rightarrow OH + NO_2$	0.8	0.8	⁵⁸
$NO_3^-(aq) \rightarrow NO_2(aq) + O^-$	0.6	0.5	⁵⁸
$CH_2O \rightarrow H + HCO$	0.5	0.4	⁵⁸
$CH_2O \rightarrow H_2 + CO$	0.2	0.1	⁵⁸
$CH_3COCH_3 \rightarrow CH_3CO + CH_3$	1.5	1.5	⁵⁸

While the concept of RAF is a good approximation, it cannot generally be applied as a single value under all circumstances. It depends on all factors that may alter the shape of the irradiance spectrum, the solar zenith angle (SZA) and the ozone column amount being particularly important. This dependency for the erythral action spectrum is illustrated in Fig. 1-7. For SZAs between 0° and 50°, the RAF is 1.1 ± 0.1 , but for larger than 50° SZA and large total ozone column amounts, resulting in strong absorption of radiation, the RAF for erythema gradually decreases. Limitations of the RAF and its application to other action spectra have been discussed in more detail elsewhere.⁸²

Attempts to quantify the risks and benefits of UV radiation

Assessments prior to 2006¹³⁴ emphasized the risks of increased UV radiation, and gave little attention to benefits. However, in recent years there has been increased awareness of possible benefits. Therefore, future reductions in UV irradiance as the ozone layer recovers may not necessarily be beneficial in some regions, particularly if ozone returns to higher levels than prior to the 1980s. Significant reductions in UV could have implications for human health, and possibly other environmental effects. For human health, the main beneficial effect of UV radiation is through inducing the synthesis of vitamin D in the skin. Balancing the risks and benefits of solar UV radiation has become a challenge for policymakers and health advisors.

The most important determinant of UV radiation at Earth's surface is the path length of the radiation through the atmosphere. Consequently, differences in sun angle are

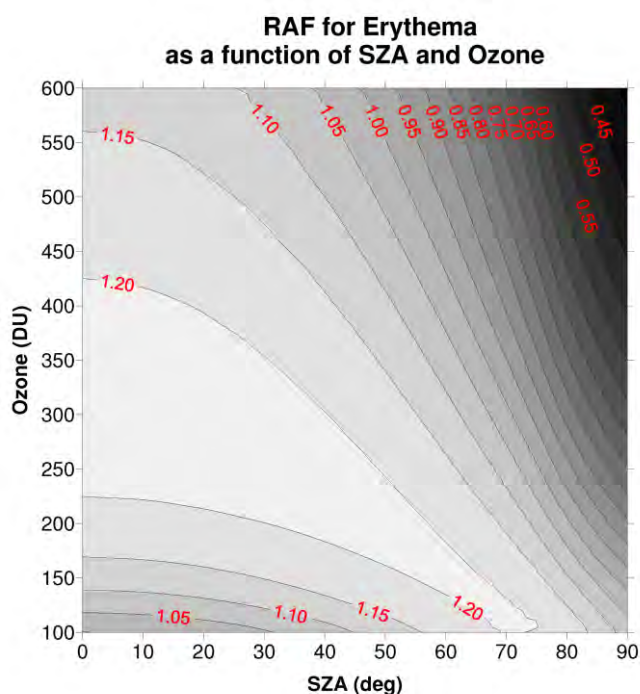


Fig. 1-7. The RAF for erythema,⁸⁰ calculated as a function of solar zenith angle and total ozone column amount.

responsible for large latitudinal and seasonal variations in both beneficial and harmful UV. These changes differ in magnitude, depending on the relevant weighting functions. Compared with the action spectrum for erythema⁸⁰ which is used to calculate the UVI, the action spectrum for vitamin D production²⁰ is confined more to the UV-B region (see erythema and pre-vitamin D curves in Fig. 1-6). This affects the seasonal and diurnal variability. Thus at mid latitudes, the UVI at noon in winter is typically 1, which is only about 10% of its summer value. On the other hand, vitamin D-weighted UV radiation shows a summer/winter contrast that is approximately twice as large as that for UVI. In each case, the weighted irradiances decrease at higher latitudes, and the ratio between summer and winter values increases rapidly. Daily doses show more marked seasonal variations than peak noon values due to the longer daylight periods in summer and shorter daylight periods in winter.

Because of the success of the Montreal Protocol, increases in UV-B radiation due to ozone depletion have been modest in most populated regions of the world (i.e., outside the regions affected by the Antarctic ozone hole). Thus wintertime deficiencies in vitamin D production in mid and high latitude regions are unlikely to have been ameliorated (See Chapter 2). Monthly climatological maps of the mean vitamin D-weighted UV radiation incident on a horizontal surface, and various other biological weightings, are now available,⁶⁹ and methods have been devised to estimate vitamin D-weighted UV from measurements of erythema irradiance.^{40, 99} In many cases the biologically-relevant dose may differ appreciably from that on a horizontal surface. For non-horizontal surfaces the winter dose is increased significantly compared to horizontal surfaces, particularly under conditions of high surface albedo.⁶⁵ It should also be noted that the action spectra for the production of vitamin D and erythema published to date have large uncertainties, and may require revision in the future.⁹¹ Both of these weighting functions include an arbitrary normalisation, so their magnitudes should not be interpreted in terms of direct health consequences.

The effective dose of vitamin D-weighted UV over 60 min around local noon has been calculated from spectral measurements at three European stations.⁶² Seasonal and latitudinal differences between sites are very large (see Fig. 1-8). In summer, these noon doses at the lower latitude sites can be up to 250 times higher than in winter at higher latitudes. For some skin types, optimal vitamin D production is impractical for some months, especially at the high latitude sites. We emphasise that there is large uncertainty in determining the thresholds shown in Fig. 1-8 (shaded area). These uncertainties will likely be resolved as results from new studies become available.

Measurements of spectral irradiance have been used to estimate the exposure times to optimize beneficial effects of UV while minimizing risks (Fig 1-9).⁷⁸ These calculations are for radiation falling on a horizontal surface. For more realistic surface geometries, the exposure times would tend to be longer at high UVI values (when the sun is high in the sky), and shorter at lower UVI values (when the sun is lower in the sky). Generally, there is a

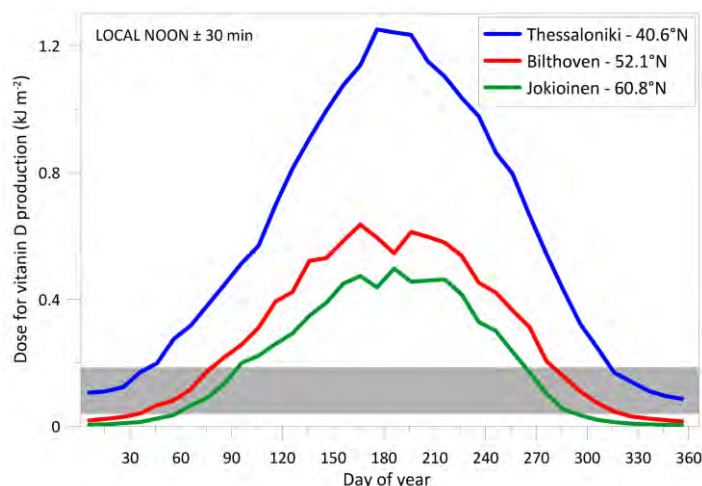


Fig. 1-8. Average vitamin D weighted UV dose received on a horizontal surface exposed for 60 min centred at local noon at three sites. The shaded area represents the range of thresholds equivalent to 1000 IU vitamin D production for 25% of skin exposed according to¹⁴⁵ for the full range of Fitzpatrick skin types (I-VI).⁴¹ Adapted from ref⁶².

wide margin between UV insufficiency and damage; however, this is not the case for low UVI when little skin is exposed. Based on these calculations, for the present wintertime UV irradiances at mid-latitudes ($\sim 45^\circ\text{N}$ or S), sufficient vitamin D should be produced in less than 1 hour of full body exposure. However, this result is inconsistent with earlier findings that no vitamin D is produced at mid-latitudes in winter¹⁴⁶ and therefore suggests that there may be a problem with the currently accepted action spectrum for the production of vitamin D. The sensitivity of the vitamin D assay method for the earlier study¹⁴⁶ was rather low compared with modern techniques and more work is needed to resolve these inconsistencies. See Chapter 2 for further discussion on the vitamin D issue.

Personal exposure to UV radiation

The exposure of an individual to UV (personal exposure) can far exceed the thresholds recommended by health agencies, especially during summer vacation periods when the available daily dose received at mid-latitudes on a horizontal surface can exceed 70 standard erythemal doses (SED).² Even in Antarctica, where the sun elevation is smaller than at lower latitudes, UV exposures can approach that value. This is partly because of low ozone amounts and partly because of the long length of day and high surface albedo. A study of UV exposures of expeditioners on Antarctic resupply voyages was performed using polysulphone dosimetry over the summer, including the period of the springtime Antarctic “ozone hole”. The median measured daily exposure was 3.2 SED and about 80% of the workers received more than the occupational exposure limits. At one of the sites (Casey, 66°S), peak UVI values sometimes exceeded 12. Some workers also reported mild erythema.⁴⁶

The UV radiation received by an individual may be expressed in terms of the exposure ratio (ER) of erythemally-weighted dose received by a given part of the body and the available ambient dose incident on a horizontal surface. These ratios are usually expressed as percentages:

$$\text{ER} = 100\% \times \text{ED}_p / \text{ED}_a$$

where ED_a is the ambient erythemal dose, in SED, received on a horizontal surface ($1 \text{ SED} = 1 \text{ Standard Erythemal Dose} = 100 \text{ J m}^{-2}$ of erythemally weighted irradiance),³⁵ and ED_p is the personal dose received by an individual, based on a measurement at a representative anatomical site. While this is a valid quantity for assessing skin damaging effects such as erythema, in other cases (e.g., for assessing vitamin D production), a further scaling would be necessary to account for the proportion of uncovered skin.

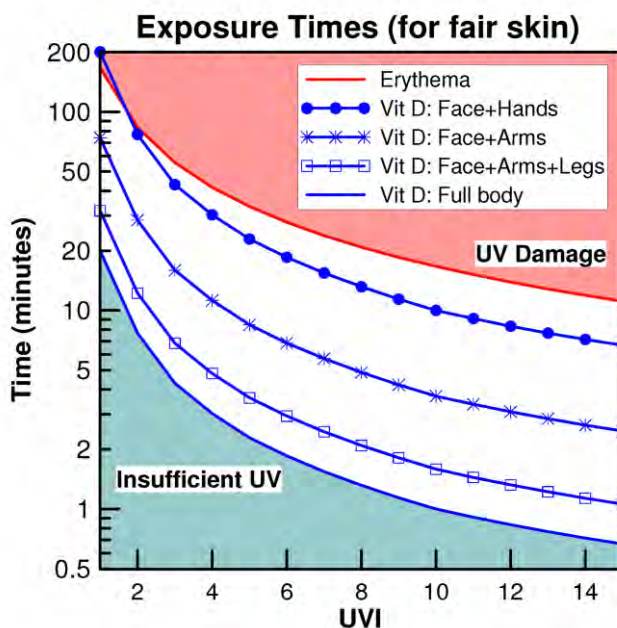


Fig. 1-9. Indicative exposure times for skin damage or for sufficient vitamin D production as functions of UVI, where “sufficient” vitamin D production is taken as the time required to receive a dose equivalent to 1000 IU. The latter times depend on the area of skin exposed and both depend on the skin type. The curves are for fair skin (for which it has been assumed that 1 Minimum Erythemal Dose (MED) = 250 J m^{-2}). For highly susceptible individuals, the times for erythema could be shorter, while for darker skins these times could be up to ~ 5 -times longer. Adapted from ref.⁷⁸.

Exposure ratios depend on lifestyle, but are usually very small. This may be beneficial for preventing skin damage, but may be detrimental for maintaining optimal vitamin D status.

A comprehensive study in Germany using polysulfone UV dosimeter badges concluded that the ER varies greatly between the anatomical body sites tested, but is typically ~2%.⁶⁴ In two studies in New Zealand using electronic dosimeters, an ER of ~5% was measured for primary school children,¹⁵¹ and only reached ~20% for the population subset of outdoor workers.⁴⁷ Another study in Denmark using electronic personal UV dosimeters,⁵³ appears to refute the widespread belief that most of our lifetime cumulative UV dose is received during childhood.¹²⁸

However, in some population groups, exposure ratios can be much larger. A recent study, using polysulfone UV dosimeter badges, reported no significant differences in solar UV exposure on a specific anatomical site (chest) among three groups of Italian sunbathers: (1) healthy suntanned people, (2) healthy non-suntanned people and (3) people affected by abnormally high sensitivity to solar exposure.¹¹⁷ The mean ER reported in the study was ~20%, and ranged from ~10 to ~40%. Another study, by the same group, on skiers at a high albedo alpine site found even higher ER values on the forehead, with a median ER of 60%, and sometimes even exceeding 100%.¹¹⁶ However, large ER values are the exception rather than the rule for the wider population.

Prior to the industrial revolution, and especially before the widespread introduction of glass windows, these exposure ratios would have been much larger. For the glass material used in typical windows, the transmission falls below 10% for wavelengths less than 310 nm. Consequently, only 5-10% of sun-burning UV radiation and an even smaller fraction of vitamin D-weighted UV radiation are typically transmitted. However, the resulting reductions in UV exposure may have been negated by changes in clothing habits and the fashion to be tanned. In recent years, there has been a further trend towards more indoor vocational and recreational activities in everyday life, punctuated with only occasional exposures to high UV irradiances, for example during vacations.³⁴ To circumvent the difficulties in monitoring UV exposures, attempts have been made to develop behavioural models for estimating exposure to UV radiation for different population types.³³

Gaps in our knowledge

At the present time, there are few reliable satellite-based measurements of atmospheric ozone, which are needed to estimate global patterns and variability in UV radiation. A continuation of reliable measurements - without gaps - is vitally important. Most current satellite sensors for estimating surface UV radiation do not adequately probe the lower troposphere (altitudes below ~5km), so the method for deriving surface UV radiation is rather insensitive to changes in pollution in the boundary layer of the atmosphere.

Despite the few attempts to reconstruct past UV records, there is a large gap in our knowledge of past changes in UV on a global scale, and in particular, the changes resulting from decreasing ozone over the latter part of the 20th century, especially prior to the satellite era.

Projections of future changes in UV radiation are uncertain, due mainly to the complexity in the projections of cloud and aerosol changes. It is therefore important to maintain a geographically wide-spread network of high-quality ground-based UV spectral measurements to determine whether the measures taken under the Montreal Protocol are effective in moderating UV radiation, and whether future model predictions are consistent with observations. Our ability to predict future changes in UV is limited by our inability to accurately predict future changes in clouds and pollution. Even if we were confident about changes in cloud cover, we are still limited in our ability to model their effects realistically. The inclusion of stratospheric processes (chemistry and circulation) in climate models would lead to more accurate predictions.

Knowledge about the ranges of both beneficial and detrimental effects of UV radiation is still incomplete. For many biological processes, including skin cancer or vitamin D production in humans, our ability to assess biological impacts is limited by incomplete knowledge of the relevant action spectra and the geometric conditions of exposure. Even the widely-used action spectrum for erythema is an idealization which may be inappropriate in many cases.

Finally, although the main focus of this assessment is on the long term effects of ozone depletion, it is noted that ozone can also change over much shorter time scales,^{9, 111, 124} and the biological impacts of the corresponding changes in UV may also be important. It is not known whether the frequency and severity of these events will change in future as a result of climate change. In many cases (including erythema and vitamin D production), threshold effects, recovery times, repair mechanisms, and linearities of the effects are not well established. Knowledge of reciprocity of effects is incomplete. For example, is the effect from an exposure to UV for a given period always equivalent to that from a UV source of one tenth the strength with an exposure period 10 times as long?

References

- 1 ACGIH, 1992, Threshold limit values for chemical substances and physical agents, 1992-1993, in *American Conference of Governmental Industrial Hygienists*, **Vol. 31**, Cincinnati, OH, USA.
- 2 Allen M and McKenzie R, 2005, Enhanced UV exposure on a ski-field compared with exposures at sea level, *Photochem. Photobiol. Sci.*, **4**, 429-437.
- 3 Alpert P and Kishcha P, 2008, Quantification of the effect of urbanization on solar dimming, *Geophys. Res. Lett.*, **35**, L08801.
- 4 Anders A, Altheide HJ, Känlmann M and Tronnier H, 1995, Action spectrum for erythema in humans investigated with dye lasers, *Photochem. Photobiol.*, **61**, 200-205.
- 5 Andradý AL, Fueki K and Torikai A, 1989, Photodegradation of rigid PVC formulations. I. Wavelength sensitivity of light induced yellowing by monochromatic light, *J. Appl. Polymer. Sci.*, **37**, 935-946.
- 6 Andradý AL, Fueki K and Torikai A, 1991, Spectral sensitivity of polycarbonate to light-induced yellowing, *J. Appl. Polymer. Sci.*, **42**, 2105-2107.
- 7 Andradý AL, Song Y, Parthasarathy V.R., Fueki K and Torikai A, 1991, Photoyellowing of mechanical pulp. Part I: Examining the wavelength sensitivity of light-induced yellowing using monochromatic radiation, *TAPPI Journal*, **74**, 162-168.
- 8 Angell JK and Free M, 2009, Ground-based observations of the slowdown in ozone decline and onset of ozone increase, *J. Geophys. Res.*, **114**, D07303.
- 9 Anton M, Cancillo ML, Serrano A, Vaquero JM and Garcia JA, 2007, Ozone mini-hole over southwestern Spain during January 2004: Influence over ultraviolet radiation, *Geophys. Res. Lett.*, **34**, L10808.
- 10 Arola A, Kazadzis S, Lindfors A, Krotkov N, Kujanpää J, Tamminen J, Bais A, di Sarra A, 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 and Kinne S, 2009, A new approach to correct for absorbing aerosols in OMI UV, *Geophys. Res. Lett.*, **36**, L22805.
- 11 Baldwin MP, Dameris M and Shepherd TG, 2007, How Will the Stratosphere Affect Climate Change?, *Science*, **316**, 1576-1577.
- 12 Banaszak AT and Neale PT, 2001, Ultraviolet radiation sensitivity of photosynthesis in phytoplankton from an estuarine environment, *Limnol. Oceanogr.*, **46**, 592-603.

- 13 Berger DS and Urbach F, 1982, A climatology of sunburning ultraviolet radiation *Photochem. Photobiol.*, **35**, 187-192.
- 14 Bernhard G, Booth CR and Ebrahimian JC, 2008, Comparison of UV irradiance measurements at Summit, Greenland; Barrow, Alaska; and South Pole, Antarctica, *Atmos. Chem. Phys.*, **8**, 799–810.
- 15 Bernhard G, Booth CR and Ebrahimian JC, 2010, Climatology of ultraviolet radiation at high latitudes derived from measurements of the national Science Foundation's spectral irradiance monitoring network, in *UV Radiation in Global Change: Measurements, Modeling and Effects on Ecosystems* eds.: Gao W, Schmoldt DL and Slusser JR, Tsinghua University Press, Beijing and Springer, New York, p. 544.
- 16 Björn LO and McKenzie RL, 2007, Attempts to probe the ozone layer and the UV-B levels of the past, *Ambio*, **36**, 366-371.
- 17 Blokker P, Boelen P, Broekman RA and Rozema J, 2006, The occurrence of p-coumaric acid and ferulic acid in fossil plant materials and their use as UV-proxy, *Plant Ecol.*, **41**, 197-208.
- 18 Borkowski JL, 2008, Modelling of UV radiation variations at different time scales, *Ann. Geophys.*, **26**, 441–446.
- 19 Boucher NP and Prezelin BB, 1996, An in situ biological weighting function for UV inhibition of phytoplankton carbon fixation in the Southern Ocean, *Marine Ecology-Progress Series*, **144**, 223-236.
- 20 Bouillon R, Eisman J, Garabedian M, Holick M, Kleinschmidt J, Suda T, Terenetskaya I and Webb A, 2006, Action spectrum for the production of previtamin D3 in human skin, Commission Internationale de L'Eclairage Report No. CIE 174:2006, Vienna, Austria, p. 16
- 21 Brönnimann S, Vogler C, Staehelin J, Stolarski R and Hansen G, 2008, Total ozone observations during the past 80 years, in *Climate Variability and Extremes during the Past 100 Years* eds.: Brönnimann S, Luterbacher J, Ewen T, Diaz HF, Stolarski RS and Neu U, Springer, Netherlands, pp. 129-140.
- 22 Caldwell MM, 1971, Solar UV irradiation and the growth and development of higher plants, in *Current Topics in Photobiology and Photochemistry, Photophysiology*, **Vol. VI** ed.: Giese AC, Academic Press, New York, U.S.A., pp. 131-177.
- 23 Chubarova N, 2008, UV variability in Moscow according to long-term UV measurements and reconstruction model, *Atmos. Chem. Phys.*, **8**, 3025–3031.
- 24 Chubarova N, Nezval YI, Verdebout J, Krotkov N and Herman J, 2005, Long-term UV irradiance changes over Moscow and comparisons with UV estimates from TOMS and METEOSAT, in *Ultraviolet Ground- and Space-based Measurements, Models, and Effects* (Eds.: Bernhard G, Slusser JR, Herman JR and Gao W), San Diego, pp. 63-73.
- 25 Chubarova NY, Larin IK, Lebedev VV, V.S.Partola, Lezina YA and Rublev AN, 2008, Experimental and Model Study of Changes in Spectral Solar Irradiance in the Atmosphere of Large City due to Tropospheric NO₂ Content, in *Current Problems in Atmospheric Radiation, International Radiation Symposium*, **Vol. 1** (Eds.: Nakajima T and Yamasoe MA), American Institute of Physics, Iguazu, Brazil, pp. 459-462.
- 26 Cnossen I, Sanz-Forcada J, Favata F, Witasse O, Zegers T and Arnold NF, 2007, Habitat of early life: Solar X-ray and UV radiation at Earth's surface 4–3.5 billion years ago, *J. Geophys. Res.*, **112**, E02008.
- 27 Comiso JC, Parkinson CL, Gersten R and Stock L, 2008, Accelerated decline in the Arctic sea ice cover, *Geophys. Res. Lett.*, **35**, L01703.
- 28 Crook JA, Gillett NP and Keeley SPE, 2008, Sensitivity of Southern Hemisphere climate to zonal asymmetry in ozone, *Geophys. Res. Lett.*, **35**, L07806.

- 29 Cullen JJ, Neale PJ and Lesser MP, 1992, Biological weighting function for the inhibition of phytoplankton photosynthesis by ultraviolet radiation, *Science.*, **258**, 646-650.
- 30 Daniel JS, Velders GJM, Solomon S, McFarland M and Montzka SA, 2007, Present and future sources and emissions of halocarbons: Toward new constraints., *J. Geophys. Res.*, **112**, D02301.
- 31 De Gruijl FR and Van der Leun JC, 1994, Estimate of the wavelength dependency of ultraviolet carcinogenesis in humans and its relevance to the risk assessment of stratospheric ozone depletion, *Health. Phys.*, **67**, 319-325.
- 32 den Outer P, Slaper H, Kaurola J, Lindfors A, Kazantzidis A, Bais A, Feister U, Junk J, Janouch M and Josefsson W, 2010, Reconstructing of erythemal ultraviolet radiation levels in Europe for the past 4 decades, *J. Geophys. Res.*, **115**, D10102.
- 33 Diffey B, 2008, A behavioral model for estimating population exposure to solar ultraviolet radiation, *Photochem. Photobiol.*, **84**, 371–375.
- 34 Diffey BL, 2002, Human exposure to solar ultraviolet radiation, *J. Cosmet. Dermatol.*, **1**, 124-130.
- 35 Diffey BL, Jansén CT, Urbach F and Wulf HC, 1997, The Standard Erythema Dose: a new photobiological concept, *Photodermatol. Photoimmunol. Photomed.*, **13**, 64-66.
- 36 Eguchi N and Yokota T, 2008, Investigation of clear-sky occurrence rate estimated from CALIOP and MODIS observations, *Geophys. Res. Lett.*, **35**, L23816.
- 37 Eyring V, Chipperfield MP, Giorgetta MA, Kinnison DE, Manzini E, Matthes K, Newman PA, Pawson S, Shepherd TG and . DWW, 2008, Overview of the New CCMVal Reference and Sensitivity Simulations in Support of Upcoming Ozone and Climate Assessments and the Planned SPARC CCMVal Report, *SPARC Newsletter*, **30**, 20-26.
- 38 Feister U, Junk J, Woldt M, Bais A, Helbig A, Janouch M, Josefsson W, Kazantzidis A, Lindfors A, den Outer PN and Slaper H, 2008, Long-term solar UV radiation reconstructed by ANN modelling with emphasis on spatial characteristics of input data, *Atmos. Chem. Phys.*, **8**, 3107-3118.
- 39 Fioletov V, Kimlin M, Krotkov N, McArthur B, Kerr J, Wardle D, Herman J, Meltzer R, Mathews T and Kaurola J, 2004, UV index climatology over North America from ground-based and satellite estimates, *J. Geophys. Res.*, **109**.
- 40 Fioletov VE, McArthur LJB, Mathews TW and Marrett L, 2009, On the relationship between erythemal and vitamin D action spectrum weighted ultraviolet radiation, *J. Photochem. Photobiol. B.*, **95**, 9-16.
- 41 Fitzpatrick TB, 1988, The validity and practicality of Sun-reactive skin types I through VI, *Arch. Dermatol.*, **124**, 869-871.
- 42 Flint SD and Caldwell MM, 2003, A biological spectral weighting function for ozone depletion research with higher plants, *Physiol. Plant.*, **117**, 137-144.
- 43 Forster PM, Bodeker GE, Schofield R, Solomon S and Thompson DWJ, 2007, Effects of ozone cooling in the tropical lower stratosphere and upper troposphere, *Geophys. Res. Lett.*, **34**, L23813.
- 44 Gadhavi H, Pinker RT and Laszlo I, 2008, Estimates of surface ultraviolet radiation over north America using Geostationary Operational Environmental Satellites observations, *J. Geophys. Res.*, **113**, D21205.
- 45 Gardner G, Lin C, Tobin EM, Loehrer H and Brinkman D, 2009, Photobiological properties of the inhibition of etiolated *Arabidopsis* seedling growth by ultraviolet-B irradiation, *Plant Cell Environ.*, **32**, 1573-1583.

- 46 Gies P, Watz R, Javorniczky J, Roy C, Henderson S, Ayton J and Kingston M, 2009, Measurements of the UVR exposures of expeditioners on Antarctic resupply voyages, *Photochem. Photobiol.*, **85**, 1485-1490.
- 47 Hammond V, Reeder A and Gray A, 2009, Patterns of real-time occupational ultraviolet radiation exposure among a sample of outdoor workers in New Zealand, *Pub. Hlth.*, **123**, 182-187.
- 48 Harfoot MJB, Beerling DJ, Lomax BH and Pyle JA, 2007, A two-dimensional atmospheric chemistry modeling investigation of Earth's Phanerozoic O₃ and near-surface ultraviolet radiation history, *J. Geophys. Res.*, **112**, D07308.
- 49 Harris NRP, Kyrö E, Staehelin J, Brunner D, Andersen S-B, Godin-Beekmann S, Dhomse S, Hadjinicolaou P, Hansen G, Isaksen I, Jörrä A, Karpetchko A, Kivi R, Knudsen B, Krizan P, Lastovicka J, Maeder J, Orsolini Y, Pyle JA, Rex M, Vanicek K, Weber M, Wohltmann I, Zanis P and Zerefos C, 2008, Ozone trends at northern mid- and high latitudes – a European perspective, *Ann. Geophys.*, **26**, 1207-1220.
- 50 Hegglin MI and Shepherd TG, 2009, Large climate-induced changes in ultraviolet index and stratosphere-to-troposphere ozone flux, *Nat. Geosci.*, **2**, 687-691.
- 51 Hendrick F, Johnston PV, De Mazière M, Fayt C, Hermans C, Kreher K, Theys N, Thomas A and Van Roozendael M, 2008, One-decade trend analysis of stratospheric BrO over Harestua (60°N) and Lauder (45°S) reveals a decline, *Geophys. Res. Lett.*, **35**, L14801.
- 52 Herman J, 2010, Global increase in UV irradiance during the past 30 years (1979 to 2008) estimated from satellite data, *J. Geophys. Res.*, **115**, D04203.
- 53 Heydenreich J and Wulf HC, 2005, Miniature personal electronic UVR dosimeter with erythema response and time-stamped readings in a wristwatch, *Photochem Photobiol.*, **81**, 1138-1144.
- 54 Hicke JA, Slusser J, Lantz K and Pascual FG, 2008, Trends and interannual variability in surface UVB radiation over 8 to 11 years observed across the United States, *J. Geophys. Res.*, **113**, D21302.
- 55 Hofmann DJ and Montzka SA, 2009, Recovery of the ozone layer: the ozone depleting gas index, *Eos (Transactions of the American Geophysical Union)*, **90**, 1-2.
- 56 Ialongo I, Casale GR and Siani AM, 2008, Comparison of total ozone and erythema UV data from OMI with ground-based measurements at Rome station, *Atmos. Chem. Phys.*, **8**, 3283-3289.
- 57 IPCC, 2007, IPCC Fourth Assessment Reports (AR4): Working Group I Report: The Physical Basis, WMO/UNEP Report No. <http://www.ipcc.ch/>
- 58 JPL, 2009, *Chemical Kinetics and Photochemical Data for Atmospheric Studies Evaluation Number 16*, Vol. **09-31**, NASA Panel for Data Evaluation, Jet Propulsion Laboratory, Los Angeles.
- 59 Kazadzis S, Bais A, Arola A, Krotkov N, Kouremeti N and Meleti C, 2009, Ozone Monitoring Instrument spectral UV irradiance products: comparison with ground based measurements at an urban environment, *Atmos. Chem. Phys.*, **9**, 585-594.
- 60 Kazadzis S, Bais A, Balis D, Kouremeti N, Zempila M, Arola A, Giannakaki E, Kazantzidis A and Amiridis V, 2009, Spatial and temporal UV irradiance and aerosol variability within the area of an OMI satellite pixel, *Atmos. Chem. Phys.*, **9**, 4593-4601.
- 61 Kazadzis S, Bais AF, Amiridis V, Balis D, Meleti C, Kouremeti N, Zerefos CS, Rapsomanikis S, Petrakakis M, Kelesis A, Tzoumaka P and Kelektoglou K, 2007, Nine years of UV aerosol optical depth measurements at Thessaloniki, Greece, *Atmos Chem. Phys.*, **7**, 2091-2101.

- 62 Kazantzidis A, Bais AF, Zempila MM, Kazadzis S, Outer PNd, Koskela T and Slaper H, 2009, Calculations of the human Vitamin D exposure from UV spectral measurements at three European stations, *Photochem. Photobiol. Sci.*, **45**, 45-51.
- 63 Kazantzidis A, Tourpali K and Bais AF, 2009, Variability of cloud-free ultraviolet dose rates on global scale due to modeled scenarios of future ozone recovery, *Photochem. Photobiol.*, **86**, 117-122.
- 64 Knuschke P, Unverricht I, Ott G and Jansen M, 2007, Personenbezogene messung der UV-Exposition von Arbeitnehmern im freien, Bundesanstalt für Arbeitsschutz und Arbeitsmedizin (BAUA) Report No., Dortmund/Berlin/Dresden, p. 195.
<http://www.baua.de/cae/servlet/contentblob/699494/publicationFile/46848/F1777.pdf>
- 65 Koepke P and Mech. M, 2005, UV radiation on arbitrarily oriented surfaces: Variation with atmospheric and ground properties, *Theor. Appl. Climatol.*, **81**, 25-32.
- 66 Konopka P, Engel A, Funke B, Müller R, Grooß J-U, Günther G, Wetter T, Stiller G, Clarmann Tv, Glatthor N, Oelhaf H, Wetzell G, López-Puertas M, Pirre M, Huret N and Riese M, 2007, Ozone loss driven by nitrogen oxides and triggered by stratospheric warmings can outweigh the effect of halogens., *J. Geophys. Res.*, **112**, D05105.
- 67 Kumari BP, Londhe AL, Daniel S and Jadhav DB, 2007, Observational evidence of solar dimming: Offsetting surface warming over India, *Geophys. Res. Lett.*, **34**, L21810.
- 68 Kvalevag MM, Myhre G and Lund Myhre CE, 2009, Extensive reduction of surface UV radiation since 1750 in world's populated regions, *Atmos. Chem Phys. Disc.*, **9**, 10457-10486.
- 69 Lee-Taylor J and Madronich S, 2007, Climatology of UV-A, UV-B, and erythemal radiation at the Earth's surface, 1979-2000, NCAR Report No., Boulder, July, p. 52.
[\(http://cprm.acd.ucar.edu/Models/TUV/\)](http://cprm.acd.ucar.edu/Models/TUV/)
- 70 Lesser MP, Barry TM, Lamare MD and Barker MF, 2006, Biological weighting functions for DNA damage in sea urchin embryos exposed to ultraviolet radiation, *J. Exp. Mar. Biol. Ecol.*, **328**, 10-21.
- 71 Li F, Stolarski RS and Newman PA, 2009, Stratospheric ozone in the post-CFC era, *Atmos. Chem. Phys.*, **9**, 2207–2213.
- 72 Liley JB, 2009, New Zealand dimming and brightening, *J. Geophys. Res.*, **114**, D00D10.
- 73 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, *Nat. Geosci.*, **1**, 592-596.
- 74 Madronich S, 2007, Analytic formula for the clear-sky UV index, *Photochem. Photobiol.*, **83**, 1537-1538.
- 75 Madronich S, McKenzie RL, Björn LO and Caldwell MM, 1998, Changes in biologically active ultraviolet radiation reaching the Earth's surface, *J. Photochem. Photobiol. B.*, **46**, 5-19.
- 76 Mang SA, Henriksen DK, Adam P. Bateman, Andersen MPS, Blake DR and Nizkorodov SA, 2008, Contribution of carbonyl photochemistry to aging of atmospheric secondary organic aerosol, *J. Phys. Chem. A*, **112**, 8337-8344.
- 77 Mazza CA, Izaguirre MM, Curiale J and Ballare CL, 2009, A look into the invisible: ultraviolet-B sensitivity in an insect (*Caliothrips phaseoli*) revealed through a behavioural action spectrum, *Proc. R. Soc. Lond. B. Biol. Sci.*, **277**, 367-373.
- 78 McKenzie RL, Liley JB and Björn LO, 2009, UV Radiation: Balancing Risks and Benefits, *Photochem. Photobiol.*, **85**, 88–98.

- 79 McKenzie RL, Weinreis C, Johnston PV, Liley B, Shiona H, Kotkamp M, Smale D, Takegawa N and Kondo Y, 2008, Effects of urban pollution on UV spectral irradiances, *Atmos. Chem. Phys.*, **8**, 5683–5697.
- 80 McKinlay AF and Diffey BL, 1987, A reference action spectrum for ultra-violet induced erythema in human skin, in *Human Exposure to Ultraviolet Radiation: Risks and Regulations* eds.: Passchier WF and Bosnjakovic BFM, Elsevier, Amsterdam, pp. 83-87.
- 81 Meleti C, Bais A, Kazadzis S, Kouremeti N, Garane K and Zerefos C, 2009, Factors affecting solar ultraviolet irradiance measured since 1990 at Thessaloniki, Greece, *Int. J. Remote Sens.*, **30**, 4167-4179.
- 82 Micheletti MI, Piacentini RD and Madronich S, 2003, Sensitivity of biologically active UV radiation to stratospheric ozone changes: effect of action spectrum shape and wavelength range, *Photochem. Photobiol.*, **78**, 456-461.
- 83 Miller H, L. III, Neale PJ and Dunton KH, 2009, Biological weighting functions for UV inhibition of photosynthesis in the kelp *Laminaria hyperborea* (phaeophyceae), *J. Phycol.*, **45**, 571-584.
- 84 Miller WL, Moran MA, Sheldon WM, Zepp RG and Opsahl SP, 2002, Determination of apparent quantum yield spectra for the formation of biologically labile photoproducts, *Limnol. Oceanogr.*, **47**, 343-352.
- 85 Molina M, Zaelke D, Sarma KM, Andersen SO, Ramanathan V and Kaniaru D, 2009, Reducing abrupt climate change risk using the Montreal Protocol and other regulatory actions to complement cuts in CO₂ emissions, *Proc. Nat. Acad. Sci. USA.*, **106**, 20616-20621.
- 86 Morgenstern O, Braesicke P, Hurwitz MM, O'Connor FM, Bushell AC, Johnson CE and Pyle JA, 2008, The world avoided by the Montreal Protocol, *Geophys. Res. Lett.*, **35**, L16811.
- 87 Munakata N, Kazadzis S, Bolseé D, Schuch N, Koskela T, Karpetchko A, Meleti C, Casiccia C, Rosa MBd, Saida T, Nishigori C, Ogata K, Imafuku K, Liu C-M, Lestari S, Kanoko M, Cornain S, Mulyadi K and Hieda K, 2009, Variations and trends of biologically effective doses of solar ultraviolet radiation in Asia, Europe and South America from 1999 to 2007, *Photochem. Photobiol. Sci.*, **8**, 1117-1124.
- 88 Newman PA, Daniel JS, Waugh DW and Nash ER, 2007, A new formulation of equivalent effective stratospheric chlorine (EESC), *Atmos. Chem. Phys.*, **7**, 4537–4552.
- 89 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 and Velders GJM, 2009, What would have happened to the ozone layer if chlorofluorocarbons (CFCs) had not been regulated?, *Atmos. Chem. Phys.*, **9**, 2113-2128.
- 90 Norris JR and Wild M, 2007, Trends in aerosol radiative effects over Europe inferred from observed cloud cover, solar “dimming,” and solar “brightening”, *J. Geophys. Res.*, **112**, D08214.
- 91 Norval M, Björn LO and Gruijl FRd, 2010, Is the action spectrum for the UV-induced production of previtamin D₃ in human skin correct?, *Photochem. Photobiol. Sci.*, **9**, 11-17.
- 92 Ohvri H, Teral H, Neiman L, Kannel M, Uustare M, Tee M, Russak V, Okulov O, Joeveer A, Kallis A, Ohvri T, Terez EI, Terez GA, Gushchin GK, Abakumova GM, Gorbarenko EV, Tsvetkov AV and Laulainen N, 2009, Global dimming and brightening versus atmospheric column transparency, Europe, 1906-2007, *J. Geophys. Res.*, **114**, D00D12.

- 93 Oriowo OM, Cullen AP, Chou BR and Sivak JG, 2001, Action spectrum and recovery for in vitro UV-induced cataract using whole lenses, *Invest. Ophthalmol. Vis. Sci.*, **42**, 2596-2602.
- 94 Osburn CL, Zagarese HE, Morris DP, Hargreaves BR and Cravero WE, 2001, Calculation of spectral weighting functions for the solar photobleaching of chromophoric dissolved organic matter in temperate lakes, *Limnol. Oceanogr.*, **46**, 1455-1467.
- 95 Otero S, Núñez-Olivera E, Martínez-Abaigar J, Tomás R and Huttunen S, 2009, Retrospective bioindication of stratospheric ozone and ultraviolet radiation using hydroxycinnamic acid derivatives of herbarium samples of an aquatic liverwort, *Environ. Pollut.*, **157**, 2335-2344.
- 96 Overland J, Turner J, Jennifer Francis, Gillett N, Marshall G and Tjernström M, 2008, The Arctic and Antarctic: Two Faces of Climate Change, *Eos (Transactions of the American Geophysical Union)*, **89**, 177-178.
- 97 Panicker AS, Pandithurai G, Takamura T and Pinker RT, 2009, Aerosol effects in the UV-B spectral region over Pune, an urban site in India, *Geophys. Res. Lett.*, **36**, L10802.
- 98 Peters DHW, Gabriel A and Entzian G, 2008, Longitude-dependent decadal ozone changes and ozone trends in boreal winter months during 1960-2000, *Ann. Geophys.*, **26**, 1275-1286.
- 99 Pope SJ, Holick MF, Mackin S and Godar DE, 2008, Action spectrum conversion factors to change erythemally weighted to previtamin D3-weighted UV doses, *Photochem. Photobiol.*, **84**, 1277-1283.
- 100 Quaite FE, Sutherland BM and Sutherland JC, 1992, Action spectrum for DNA damage in alfalfa lowers predicted impact of ozone depletion, *Nature*, **358**, 576-578.
- 101 Ravishankara AR, Daniel JS and Portmann RW, 2009, Nitrous oxide (N₂O): The dominant ozone-depleting substance emitted in the 21st century, *Science*, **326**, 123-125.
- 102 Reimann S, Vollmer MK, Folini D, Steinbacher M, Hill M, Buchmann B, Zander R and Mahieu E, 2008, Observations of long-lived anthropogenic halocarbons at the high-Alpine site of Jungfraujoch (Switzerland) for assessment of trends and European sources, *Sci. Tot. Environ.*, **391**, 224-231.
- 103 Rex M, Salawitch RJ, Deckelmann H, Gathen Pvd, Harris NRP, Chipperfield MP, Naujokat B, Reimer E, Allaart M, Andersen SB, Bevilacqua R, Braathen GO, Claude H, Davies J, Backer HD, Dier H, Dorokhov V, Fast H, Gerding M, Godin-Beekmann S, Hoppel K, Johnson B, Kyro E, Litynska Z, Moore D, Nakane H, Parrondo MC, Jr. ADR, Skrivankova P, Stubi R, Yushkov PV and Zerefos C, 2006, Arctic winter 2005: Implications for stratospheric ozone loss and climate change, *Geophys. Res. Lett.*, **33**, L23808.
- 104 Rind D, Jonas J, Stammerjohn S and Lonergan P, 2009, The Antarctic ozone hole and the Northern Annular Mode: A stratospheric interhemispheric connection, *Geophys. Res. Lett.*, **36**, L09818.
- 105 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.
- 106 Rozema J, van Geel B, Björn LO, Lean J and Madronich S, 2002, Toward solving the UV puzzle, *Science*, **296**, 1621-1622.

- 107 Ryan KG, Burne A and Seppelt RD, 2009, Historical ozone concentrations and flavonoid levels in herbarium specimens of the Antarctic moss *Bryum argenteum*, *Glob. Change Biol.*, **15**, 1694-1702.
- 108 Schade GW, Hofmann RM and Crutzen PJ, 1999, CO emissions from degrading plant matter (I). Measurements, *Tellus*, **51**, 889-908.
- 109 Scinocca JF, Reader MC, Plummer DA, Sigmond M, Kushner PJ, Shepherd TG and Ravishankara AR, 2009, Impact of sudden Arctic sea-ice loss on stratospheric polar ozone recovery, *Geophys. Res. Lett.*, **36**.
- 110 Seckmeyer G, Glandorf M, Wichers C, McKenzie RL, Henriques D, Carvalho F, Webb AR, Siani AM, Bais A, Kjeldstad B, Brogniez C, Werle P, Koskela T, Lakkala K, Lenoble J, Groebner J, Slaper H, den Outer PN and Feister U, 2008, Europe's darker atmosphere in the UV-B, *Photochem. Photobiol. Sci.*, **7**, 925-930.
- 111 Seckmeyer G, Mayer B, Bernhard G, Erb R, Albold A, Jäger H and Stockwell WR, 1997, New maximum UV irradiance levels observed in Central Europe, *Atmos. Environ.*, **31**, 2971-2976.
- 112 Setlow RB, 1974, The wavelengths in sunlight effective in producing skin cancer: A theoretical analysis, *Proc. Nat. Acad. Sci. USA.*, **71**, 3363-3366.
- 113 Shepherd TG and Jonsson AI, 2008, On the attribution of stratospheric ozone and temperature changes to changes in ozone-depleting substances and well-mixed greenhouse gases, *Atmos. Chem. Phys.*, **8**, 1435-1444.
- 114 Shindell D, 2008, Climate Change: Cool ozone, *Nat. Geosci.*, **1**, 85-86.
- 115 Shindell DT and Schmidt GA, 2004, Southern Hemisphere climate response to ozone changes and greenhouse gas increases, *Geophys. Res. Lett.*, **31**, L18209.
- 116 Siani AM, Casale GR, Diémoz H, G. Agnesod, Kimlin MG, Lang CA and Colosimo A, 2008, Personal UV exposure on a ski-field at an alpine site, *Atmos. Chem. Phys.*, **8**, 3749-3760.
- 117 Siani AM, Casale GR, Sisto R, Borra M, Kimlin MG, Lang CA and Colosimo A, 2009, Short-term UV exposure of sunbathers at a Mediterranean Sea site, *Photochem. Photobiol.*, **85**, 171-177.
- 118 Sinnhuber B-M, Sheode N, Sinnhuber M, Chipperfield MP and Feng W, 2009, The contribution of anthropogenic bromine emissions to past stratospheric ozone trends: a modelling study, *Atmos. Chem. Phys.*, **9**, 2863-2871.
- 119 Sola Y, Lorente J, Campmany E, Cabo Xd, Bech J, Redano A, Martinez-Lozano JA, Utrillas MP, Alados-Arboledas L, Olmo FJ, Diaz JP, Exposito FJ, Cachorro V, Sorribas M, Labajo A, Vilaplana JM, Silva AM and Badosa J, 2008, Altitude effect in UV radiation during the Evaluation of the Effects of Elevation and Aerosols on the Ultraviolet Radiation 2002 (VELETA-2002) field campaign, *J. Geophys. Res.*, **113**, D23202.
- 120 Son S-W, Polvani LM, Waugh DW, Akiyoshi H, Garcia R, Kinnison D, Pawson S, Rozanov E, Shepherd TG and Shibata K, 2008, The impact of stratospheric ozone recovery on the Southern Hemisphere westerly jet, *Science.*, **320**, 1486-1489.
- 121 SPARC CCMVal, 2010, *SPARC Report on the Evaluation of Chemistry-Climate Models*, V. Eyring, T. G. Shepherd, D. W. Waugh (Eds.), SPARC Report No. 5, WCRP-132, WMO/TD-No. 1526, <http://www.atmosphysics.utoronto.ca/SPARC>
- 122 Steinbacher M, Vollmer MK, Buchmann B and Reimann S, 2008, An evaluation of the current radiative forcing benefit of the Montreal Protocol at the high-Alpine site Jungfraujoch, *Sci. Tot. Environ.*, **391**, 217-223.
- 123 Steinbrecht W, Claude H, Schönenborn F, McDermid IS, Leblanc T, Godin-Beekman S, Keckhut P, Hauchecorne A, van Gijzel JAE, Swart DPJ, Bodeker GE, Parrish A, Boyd IS, Kämpfer N, Hocke K, Stolarski R, Frith SM, Thomason LW, Remsberg EE,

- von Savigny C, Rozanov A and Burrows JP, 2009, Ozone and temperature trends in the upper stratosphere at five stations of the Network for the Detection of Atmospheric Composition Change, *Int. J. Remote Sens.*, **30**, 3875 - 3886
- 124 Stick C, Krüger K, Schade NH, Sandmann H and Macke A, 2006, Episode of unusual high solar ultraviolet radiation over central Europe due to dynamical reduced total ozone in May 2005, *Atmos. Chem. Phys.*, **6**, 1771-1776.
- 125 Stolarski RS and Frith SM, 2006, Search for evidence of trend slow-down in the long-term TOMS/SBUV total ozone data record: the importance of instrument drift uncertainty, *Atmos. Chem. Phys.*, **6**, 4057-4065.
- 126 Tanskanen A, Lindfors A, Maatta A, Krotkov N, Herman J, Kaurola J, Koskela T, Lakkala K, Filolettov V, Bernhard G, McKenzie RL, Kondo Y, O'Neill M, Slaper H, denOuter PN, Bais A and Tamminen J, 2007, Validation of the daily erythemal UV doses from Ozone Monitoring Instrument with ground-based UV measurement data, *J. Geophys. Res.*, **112**, D24S44.
- 127 Tartarotti B, Cravero W and Zagarese HE, 2000, Biological weighting function for the mortality of *Boeckella gracilipes* (Copepoda, Crustacea) derived from experiments with natural solar radiation, *Photochem. Photobiol.*, **72**, 314-319.
- 128 Thieden E, 2008, Sun exposure behaviour among subgroups of the Danish population, *Dan Med Bull.*, **55**, 47-68.
- 129 Thompson DWJ and Solomon S, 2002, Interpretation of recent Southern Hemisphere climate change, *Science.*, **296**, 895-899.
- 130 Tilmes S, Müller R and Salawitch R, 2008, The sensitivity of polar ozone depletion to proposed geoengineering schemes, *Science.*, **320**, 1201-1204.
- 131 Tourpali K, Bais AF, Kazantzidis A, Zerefos CS, Akiyoshi H, Austin J, Brühl C, Butchart N, Chipperfield MP, Dameris M, Deushi M, Eyring V, Giorgetta MA, Kinnison DE, Mancini E, Marsh DR, Nagashima T, Pitari G, Plummer DA, Rozanov E, Shibata K and Tian W, 2009, Clear sky UV simulations for the 21st century based on ozone and temperature projections from chemistry-climate models, *Atmos. Chem. Phys.*, **9**, 1165-1172.
- 132 Trenberth KE and Fasullo JT, 2009, Global warming due to increasing absorbed solar radiation, *Geophys. Res. Lett.*, **36**, L07706.
- 133 Tsigaridis K, Krol M, Dentener FJ, Balkanski Y, Lathière J, Metzger S, Hauglustaine DA and Kanakidou M, 2006, Change in global aerosol composition since preindustrial times, *Atmos. Chem. Phys.*, **6**, 5143-5162.
- 134 UNEP, 2007, Environmental effects of ozone depletion and its interactions with climate change: 2006 assessment, *Photochem. Photobiol. Sci.*, **6**, 201-332.
- 135 UNEP, 2008, Environmental effects of ozone depletion and its interactions with climate change: Progress report, 2007, *Photochem. Photobiol. Sci.*, **7**, 15-27.
- 136 UNEP, 2009, Environmental effects of ozone depletion and its interactions with climate change: Progress report, 2008, *Photochem. Photobiol. Sci.*, **8**, 13-22.
- 137 UNEP, 2010, Environmental effects of ozone depletion and its interactions with climate change: Progress report, 2009, *Photochem. Photobiol. Sci.*, **9**, 275-294.
- 138 Vähätalo A and Zepp RG, 2005, Photochemical mineralization of dissolved organic nitrogen to ammonium in the Baltic Sea, *Environ. Sci. Technol.*, **39**, 6985-6992.
- 139 Velders GJM, Andersen SO, Daniel JS, Fahey DW and McFarland M, 2007, The importance of the Montreal Protocol in protecting climate, *Proc. Nat. Acad. Sci. USA.*, **104**, 4814-4819.
- 140 Velders GJM, Fahey DW, Daniel JS, McFarland M and Andersen SO, 2009, The large contribution of projected HFC emissions to future climate forcing, *Proc. Nat. Acad. Sci. USA.*, **106**, 10949-10954

- 141 Verdebout J, 2000, A method to generate surface UV radiation maps over Europe using GOME, Meteosat, and ancillary geophysical data, *J. Geophys. Res.*, **105**, 5049-5058.
- 142 Vyushin D, Fioletov VE and Shepherd TG, 2007, Impact of long-range correlations on trend detection in total ozone, *J. Geophys. Res.*, **112**, D14307.
- 143 Walser ML, Park J, Gomez AL, Russell AR and Nizkorodov SA, 2007, Photochemical aging of secondary organic aerosol particles generated from the oxidation of d-Limonene, *J. Phys. Chem. A*, **111**, 1907-1913.
- 144 Waugh DW, Oman L, Kawa SR, Stolarski RS, Pawson S, Douglass AR, Newman PA and Nielsen JE, 2009, Impacts of climate change on stratospheric ozone recovery, *Geophys. Res. Lett.*, **36**, L03805.
- 145 Webb AR and Engelsen O, 2006, Calculated ultraviolet exposure levels for a healthy vitamin D status, *Photochem. Photobiol.*, **82**, 1697-1703.
- 146 Webb AR, Kline L and Holick MF, 1988, Influence of season and latitude on the cutaneous synthesis of vitamin D3: Exposure to winter sunlight in Boston and Edmonton will not promote vitamin D3 synthesis in human skin, *J. Clin. Endocrinol. Metab.*, **67**, 373-378.
- 147 Wild M, 2009, Global dimming and brightening: A review, *J. Geophys. Res.*, **114**, D00D16.
- 148 Williamson CE, Neale PJ, Grad G, Lange HJd and Hargreaves BR, 2001, Beneficial and detrimental effects of uv on aquatic organisms: implications of spectral variation, *Ecol. Appl.*, **11**, 1843-1857.
- 149 WMO, 2007, Scientific Assessment of Ozone Depletion: 2006, World Meteorological Organisation Report No. 50, Geneva.
http://www.wmo.int/pages/prog/arep/gaw/ozone_2006/ozone_asst_report.html
- 150 WMO, 2011, Scientific Assessment of Ozone Depletion: 2010, World Meteorological Organisation Report No. 52, Geneva, Switzerland, p. In Press
- 151 Wright CY, Reeder AI, Bodeker GE, Gray A and Cox B, 2007, Solar UVR exposure, concurrent activities and sun-protective practices among primary schoolchildren, *Photochem. Photobiol.*, **83**, 749-758.
- 152 Yang ES, Cunnold DM, Newchurch MJ, Salawitch RJ, McCormick MP, J.M. Russell I, Zawodny JM and Oltmans SJ, 2008, First stage of Antarctic ozone recovery, *J. Geophys. Res.*, **113**, D20308.
- 153 Zerefos C, Eleftheratos K, Meleti C, Kazadtzis S, Romanou A, Ichoku C, Tselioudis G and Bais A, 2009, Solar dimming and brightening over Thessaloniki, Greece, and Beijing, China, *Tellus*, **69**, 657-665.
- 154 Ziolkowski LA and Miller WA, 2007, Variability of the apparent quantum efficiency of CO photoproduction in the Gulf of Maine and Northwest Atlantic, *Mar. Chem.*, **105**, 258-270.

Chapter 2. The human health effects of ozone depletion and interactions with climate change

M. Norval,^a R.M. Lucas,^b A.P. Cullen,^c F.R. de Gruijl,^d J. Longstreth,^e Y. Takizawa^f and J.C. van der Leun^g

^a*Biomedical Sciences, University of Edinburgh Medical School, Edinburgh EH8 9AG, Scotland*

^b*National Centre for Epidemiology and Population Health, The Australian National University, Canberra 0200, Australia*

^c*School of Optometry, University of Waterloo, Waterloo, Ontario N2L 5T6, Canada*

^d*Department of Dermatology, Leiden University Medical Centre, P.O. Box 9600, NL-2300 RC Leiden, The Netherlands*

^e*The Institute for Global Risk Research, Bethesda, MD 20817, USA*

^f*National Institute for Minamata Diseases, 4058 Hama, Minamata City, Kumamoto 867-0008, Japan*

^g*Ecofys, Kanaalweg 16G, NL-3526 KL Utrecht, The Netherlands*

Summary

Depletion of the stratospheric ozone layer has led to increased solar UV-B radiation (280-315 nm) at the surface of the Earth. This change is likely to have had an impact on human exposure to UV-B radiation with consequential detrimental and beneficial effects on health, although behavioural changes in society over the past 60 years or so with regard to sun exposure are of considerable importance. The present report concentrates on information published since our previous report in 2007.

The adverse effects of UV radiation are primarily on the eye and the skin. While solar UV radiation is a recognised risk factor for some types of cataract and for pterygium, the evidence is less strong, although increasing, for ocular melanoma, and is equivocal at present for age-related macular degeneration. For the skin, the most common harmful outcome is skin cancer, including melanoma and the non-melanoma skin cancers, basal cell carcinoma and squamous cell carcinoma. The incidence of all three of these tumours has risen significantly over the past five decades, particularly in people with fair-skin, and is projected to continue to increase, thus posing a significant world-wide health burden. Overexposure to the sun is the major identified environmental risk factor in skin cancer, in association with various genetic risk factors and immune effects. Suppression of some aspects of immunity follows exposure to UV radiation and the consequences of this modulation for the immune control of infectious diseases, for vaccination and for tumours, are additional concerns. In a common sun allergy (polymorphic light eruption), there is an imbalance in the immune response to UV radiation, resulting in a sun-evoked rash.

The major health benefit of exposure to solar UV-B radiation is the production of vitamin D. Vitamin D plays a crucial role in bone metabolism and is also implicated in protection against a wide range of diseases. Although there is some evidence supporting protective effects for a range of internal cancers, this is not yet conclusive, but strongest for colorectal cancer, at present. A role for vitamin D in protection against several autoimmune diseases has been studied, with the most convincing results to date for multiple sclerosis. Vitamin D is starting to be assessed for its protective properties against several infectious and coronary diseases.

Current methods for protecting the eye and the skin from the adverse effects of solar UV radiation are evaluated, including seeking shade, wearing protective clothing and sunglasses, and using sunscreens. Newer possibilities are considered such as creams that repair UV-induced DNA damage, and substances applied topically to the skin or eaten in the diet that protect against some of the detrimental effects of sun exposure. It is difficult to provide easily understandable public health messages regarding “safe” sun exposure, so that the positive effects of vitamin D production are balanced against the negative effects of excessive exposure.

The international response to ozone depletion has included the development and deployment of replacement technologies and chemicals. To date limited evidence suggests that substitutes for the ozone depleting substances do not have significant effects on human health.

In addition to stratospheric ozone depletion, climate change is predicted to affect human health, and potential interactions between these two parameters are considered. These include altering the risk of developing skin tumours, infectious diseases and various skin diseases, in addition to altering the efficiency by which pathogenic microorganisms are inactivated in the environment.

Introduction

Depletion of the ozone layer has led to an increase in solar UV-B radiation reaching the Earth’s surface, with many consequences for human health. These can be beneficial, such as promoting the synthesis of vitamin D, or detrimental, such as inducing skin cancer and cataract. It should be noted here that changes in human behaviour with regard to sun exposure over the past 60 years or so have probably contributed much more significantly to alterations in health risks than ozone depletion. Such changes, leading to an increase in exposure to solar UV radiation, include the widespread perception that a tanned skin is desirable and an indicator of good health, the huge rise in the popularity of sunshine holidays (and thus exposures to different UV radiation environments) encouraged by inexpensive air travel, and the wearing of minimal clothing and swimwear when air temperatures rise. Other changes have led to a decrease in exposure to solar UV radiation, including fewer outdoor occupations and more urban living. Climate change may also increase the vulnerability of the population to UV radiation.

The present assessment focuses on the four year period from 2006 to the present, except where some background information is included for clarity. It follows a similar format to our previous report published in 2007.²³⁵ First the harmful effects of solar UV radiation on the eye, the skin and the immune system are considered. Secondly the positive aspects of UV-mediated endogenous production of vitamin D in protecting against several diseases are discussed. A third section considers ways in which individuals can protect their eyes and skin from solar UV radiation, and provides some cost-benefit analyses. The impact of toxicity and air pollution resulting from new substitutes for the ozone depleting substances is discussed (with detail presented in an online supplement to this paper). A final section assesses the sparse information available to date on the possible health effects of the interactions between climate change and ozone depletion. Changes in lower atmospheric air quality as a result of UV radiation and climate change may also have health consequences, and this is considered elsewhere (see Chapter 6).

The effects of solar UV radiation on the eye

There is convincing evidence that UV radiation exposure is a risk factor for some types of cataract, pterygium, pinguecula (conjunctival degeneration) and squamous cell carcinoma of the cornea and conjunctiva. In addition, acute photokeratitis and photoconjunctivitis are clearly UV-induced, and retinal burns can result from high intensity exposure, such as looking directly at the sun. For other disorders including ocular melanoma and age-related macular degeneration, the evidence of a role for UV radiation is scanty and/or contradictory. Previous reports have reviewed the mechanics of UV-B irradiation of target tissues in the eye,²³⁵ and the two major effects of chronic UV radiation, pterygium and cataract,^{81, 235} as well as effects on the cornea and conjunctiva.¹⁹⁸ Here we update that evidence and focus further on diseases where there remains uncertainty for an association with exposure to UV radiation, particularly UV-B radiation.

Pterygium

Pterygium is an inflammatory, proliferative and invasive growth on the conjunctiva and cornea of the human eye that can impair vision.²³⁵ Recent studies support an association between higher levels of sun exposure and development of both primary and recurrent (after surgery) pterygium,²⁸⁴ but provide no information regarding the relative importance of UV-A or UV-B radiation.

Previous work has implicated both dust and UV radiation in the pathogenesis of pterygium.⁸⁵ Support for the latter is indicated by the high prevalence in fishermen and sailors, who are not exposed to dust, but to UV radiation that is scattered and highly reflected from the sea, which can be up to 20% of the incident UV radiation.⁸⁸ Furthermore, exposure to scattered, rather than direct, UV radiation is more likely to irradiate the region of the eye where pterygium is generally found. Indeed it has been suggested that scattered light may expose the basal stem cells at the junction of the white of the eye and the cornea to increased amounts of UV radiation, leading to mutations in tumour suppressor genes and the generation of damaging reactive oxygen radicals.⁸⁵ UV-B irradiation may also cause the release of pro-inflammatory cytokines into tears bathing the mucosal surface, with resulting chronic inflammation and fibrovascular proliferation leading to pterygium formation.³⁷⁵

Cataract

In the previous report²³⁵ we assessed the epidemiological evidence for an association between exposure to UV-B radiation and the three main types of age-related cataract: cortical, nuclear and posterior subcapsular. There is considerable evidence that UV irradiation is a risk factor for the development of cortical cataract, with less evidence to support a relationship with nuclear cataract, although the timing of exposure may be particularly important for the latter. The evidence for an association with posterior subcapsular cataract remains weak. There has been little progress in this area. One study established an action spectrum for cataractogenesis using cultured whole porcine crystalline lens,²⁴¹ which was in good agreement with previously published action spectra for isolated lens epithelial cells and *in vivo* models. The peak effectiveness for the production of lens anterior subcapsular lesions occurred in the UV-B waveband, around 290 nm (see Chapter 1, Table 1-2). More recent research has focused largely on animal studies, examining mechanisms of UV-induced development of cataract. A wide range of animals has been used, including mice and rats,^{19, 96, 211} rabbits^{112, 113} and guinea pigs,²¹⁴ but none provides an ideal model for the human lens, and whether UV-A or UV-B wavelengths are more important for cataract formation varies from species to species.

Ocular melanoma

Limited evidence indicates that there may be a link between solar UV-B radiation and the development of ocular melanoma. Such tumours include both external, involving the eyelid and conjunctiva, and intraocular tumours, involving the iris, ciliary body and choroid (collectively known as the uvea). The latter comprise the majority of ocular melanomas and are the most common primary eye cancer in adults with a reported annual incidence per million of 6 in fair-skinned and 0.3 in dark-skinned individuals.¹⁵⁷ Examples are shown in Fig. 2-1.

Although there is substantial lenticular transmission of UV-B radiation in childhood, this decreases with age so that, in adulthood, uveal melanocytes are exposed to only a small amount of UV-B radiation.²³⁵ This suggests that exposure of external and uveal melanocytes to UV-B radiation, at least in adulthood, is different. One study showed that higher exposure to UV radiation in the first 20 years of life is a risk factor for ocular melanoma,³²⁷ while others have demonstrated an increased risk in relation to light-coloured irides, previous photokeratitis (due to welding or snow blindness), exposure to sunlamps, and wearing sunglasses or hats (interpreted as indicating photosensitivity).^{155, 278, 282, 348}

Such evidence supports exposure to UV radiation as a causative factor in ocular melanomas, but epidemiological data suggest that the effects may be confined to external tumours.²⁸⁷ For example, the age-standardised incidence of conjunctival melanoma increased more than 7-fold in Swedish men and women between 1960 and 2005, with the increase confined to tumours of UV-exposed conjunctiva (rather than the tarsal conjunctiva lining the eyelid). In contrast, the incidence of uveal melanoma is stable or even declining.^{277, 319} In the non-Hispanic white population in the USA (1992-2002), there was an inverse latitudinal gradient in the incidence of conjunctival melanoma (2.5-fold increase from 47-48° to 20-22° latitude, i.e. increasing incidence with higher ambient UV radiation), but decreasing risk of uveal melanoma with decreasing latitude (higher ambient UV radiation).³⁷²

Age-related macular degeneration

Age-related macular degeneration (AMD), also called age-related maculopathy, is the most frequent cause of loss of vision in humans living in developed countries. This retinal disease is most commonly the non-exudative (dry/atrophic) form, but the more severe exudative (wet/neovascular) form can also occur (see Fig. 2-2). The aetiology of AMD is unclear but is thought to involve both genetic and external factors, such as solar UV radiation. In animal studies, reactive oxygen species generated as a result of UV-induced changes can damage the retinal pigment epithelium, leading to degeneration of photoreceptors of the neural retina and the development of AMD.¹⁵⁶

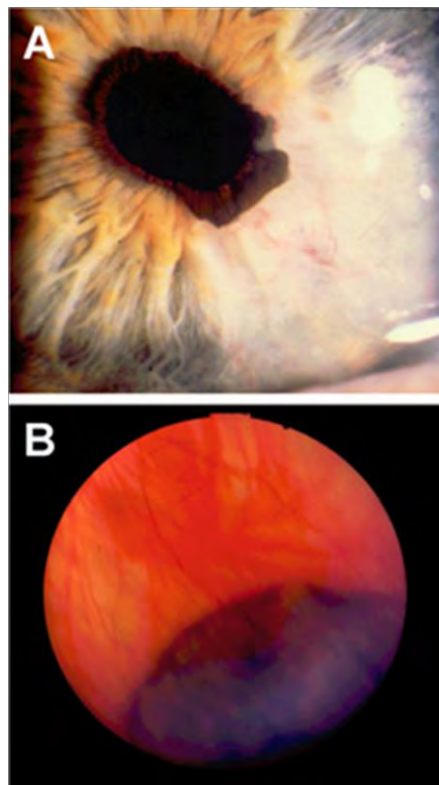


Fig. 2-1. Intraocular malignant melanoma: (A) an amelanotic iris melanoma with nutrient blood vessels, causing a rolling out (ectropion) of the pigment layer and distortion of the pupil, and (B) a dome-shaped choroidal melanoma with mottled appearance (photographs supplied by Dr A. Cullen, University of Waterloo, Canada).

AMD is significantly more common in higher ambient UV radiation settings or in population groups having greater exposure to UV radiation, such as farmers and fishermen.^{27, 335} Higher sun exposure, assessed either by questionnaire^{27, 108} or by facial wrinkling,¹⁵⁰ is associated with an increased risk of AMD, particularly the exudative form. Furthermore, in an Australian study, participants who had a history of sun-sensitive skin (burning rather than tanning) had a decreased risk of exudative AMD compared with subjects who had average sun-sensitivity,²⁵⁰ an observation that could be explained by the former subjects having had lower lifetime sun exposure. These findings form a consistent picture of support for UV radiation being a risk factor, at least in exudative AMD. However, other studies reveal no association between ambient UV radiation or past sun exposure and AMD,²⁰⁴ and no evidence to support dependence on a specific wavelength range. It is possible that any correlation between UV radiation and AMD may be confounded by other factors such as variable genetic susceptibility or even blue light which is capable of generating reactive oxygen species.

The effects of solar UV radiation on the skin

Melanoma

Epidemiology of melanoma. The annual incidence of cutaneous malignant melanoma (CMM) varies geographically from between 5 and 24 per 100,000 in Europe and the USA^{71, 195, 265} to over 70 per 100,000 in higher ambient UV radiation regions of Australia and New Zealand.^{68, 263, 272} Even in locations with lower incidence, there are specific high-risk groups such as non-Hispanic white men older than 65 years in the USA, where the incidence is greater than 125 cases per 100,000.¹⁹⁵ In Australia, melanoma is currently the third most commonly reported cancer in men and women overall, and the commonest in women aged 17-33 years.³ CMM is uncommon in individuals under the age of 20, although an increase of 2.9% per year between 1973 and 2003 in the USA has been reported in a recent review.¹⁸⁷

Many studies in various countries indicate that the incidence of CMM has increased by 1-3% per year over the past half century.^{36, 69, 192, 220, 248} In a few instances it has stabilised over recent years,^{68, 255} particularly in people younger than 40 years. For example, in Sweden, the previously rapid increase in the incidence of CMM in teenagers from 1973 levelled off between 1983 and 1992, and since then has decreased.¹⁷² This situation has been attributed to intensive public health campaigns over the past 30 years or so advocating avoidance of sunburn and seeking medical care promptly if pigmented skin lesions arise.^{92, 93, 289, 298, 354} The increasing incidence pertains particularly to thin (early) melanomas, with the incidence of thick (late) melanomas relatively unchanged.^{36, 192, 220, 248} Whether this is real or an artefact of screening and diagnostic drift (*in situ* lesions not diagnosed previously as CMM now being included) remains controversial.

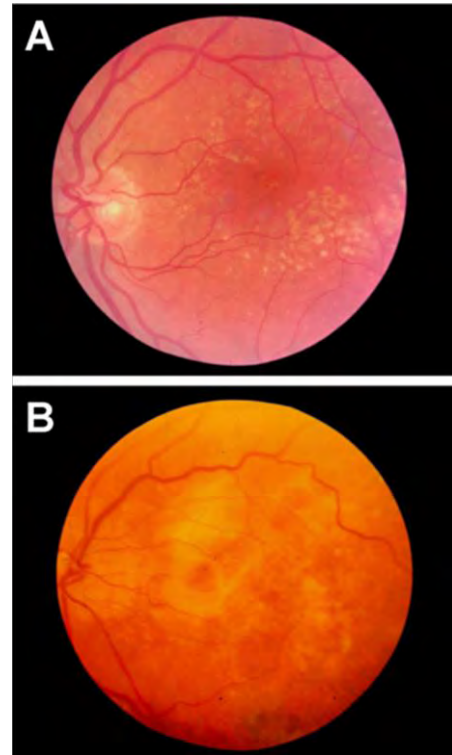


Fig. 2-2. Age-related macular degeneration: (A) early dry form showing discrete yellow spots (drusen) at the posterior pole and mild retinal pigment epithelial changes, and (B) sudden onset wet form with extensive macular oedema (fluid in and behind the retina), suggesting underlying abnormal blood vessels (photographs supplied by Dr A. Cullen, University of Waterloo, Canada).

Mortality rates due to CMM, which increased in most European countries as well as in North America, Australia and New Zealand in the 1980s, peaked around 1990 and, since then have tended to be stable, for example in the USA,¹⁹⁵ or to decrease, for example in women in Northern Ireland.²²⁰ Any such reduction in the next few years will probably be due to early detection and treatment rather than to primary prevention and changes in ambient UV radiation.

The distribution of CMM varies by age and sex, probably related to different patterns of exposure to the sun. Head and neck tumours are found particularly in elderly populations,^{70, 71, 355} and are thought to be correlated with chronic sun exposure, as indicated by their association with solar keratoses,^{55, 336} considered as a marker of repeated solar UV irradiation. In younger age groups, the highest rates of CMM occur on the trunk in males and on the extremities in females.^{272, 355} Intermittent sun exposure and sunburn^{70, 239, 355} in childhood^{84, 189, 230} and throughout adulthood^{84, 189} are major risk factors.

In high ambient UV radiation locations, the development of pigmented moles (acquired melanocytic nevi, AMN) in young children is very common,^{146, 364} particularly where there is a combination of fair skin type with higher sun exposure and episodes of sunburning. For example, only 8.3% of Brazilian children aged 2-8 years had no AMN.³⁶⁴ Waterside vacations in the USA were associated with a 5% increase in the number of small moles in children examined at age 7 years, with a lag in the development of new moles of one year after the vacation.²⁴⁹

An important question for CMM in relation to stratospheric ozone depletion concerns the wavelength dependency of initiation and development. Although an early study in the *Xiphophorus* hybrid fish suggested a role for UV-A radiation,²⁸⁶ this has not been supported by more recent work in the same model²¹² or in mammalian models, including the South American opossum²⁶⁶ and several genetically modified mouse strains [for example ⁷⁷]. The weight of evidence now supports UV-B radiation as critical to the initiation of melanoma, although a contributory role for chronic exposure to UV-A radiation in the progression of melanoma, through free radical formation or direct effects on DNA, is possible.³⁴⁵

Genetic damage and risk of melanoma. Cancer is thought to result from mutations in genes that control cell proliferation and migration/invasion into surrounding tissue. Mutations in key genes in CMM have been identified; but there is a lack of characteristic UV-related mutations in these genes and it is not clear whether and how they might be affected by UV radiation.

In human CMM, the pathway involving Ras proteins is frequently activated, with stimulation of cell growth, while the protein p16Ink4a, which acts as a tumour suppressor, is frequently down-regulated. In parallel with epidemiological findings on risk from early life exposures, and in contrast to an earlier study,³³⁴ a single exposure to UV radiation of newborn mice deficient in *p16Ink4a* induced melanomas in the adult animals, and a defect in DNA repair (deficient XPC protein) further enhanced the formation of melanomas.³⁶³

Recently, the entire genetic sequences of a cell line from a CMM metastasis and a lymphoblast cell line derived from normal blood cells of the same person have been compared. There was an astonishingly large number of mutations in the CMM cells (33,345 somatic base substitutions), the majority of which were typical of changes that accompany exposure to UV radiation.²⁵² This titanic analysis unambiguously established that UV radiation was the major cause of the mutations, at least in this CMM.

Non-melanoma skin cancer

Epidemiology of non-melanoma skin cancer. Individuals in many countries continue to experience significant annual increases in the incidences of the non-melanoma skin cancers (NMSCs): basal cell carcinoma (BCC) and squamous cell carcinoma (SCC).^{40, 333} For example, the incidence of BCC increased by 3% per year from 1996-2003 in the UK,²¹ and the incidence of SCC increased four-fold from 1960-2004 in Sweden.⁷⁰ The incidence of NMSC in Australia in 2002 was five times greater than the incidence of all other cancers combined.³⁰¹ In subtropical Australia, the incidence rate for people affected by a primary BCC was almost the same as for those with multiple lesions, indicating that the disease burden may be higher than is apparent from the usually cited incidence rates that rely on number of people affected rather than number of tumours.²⁶⁴ In some regions or subpopulations, the increases in the incidence rates have slowed,^{21, 196} particularly in younger cohorts (<60 years for BCC and <50 years for SCC),³⁰¹ possibly related to the introduction of public health educational programmes. In some locations there is a change in the distribution of NMSC on the body with an increase occurring on the trunk and upper arms. This has been attributed to the fashion for intentional body tanning in recent years.⁷⁰ One study in the Netherlands found that, between 1990 and 2004, an increasing proportion of BCC patients were in the high socio-economic status group, as defined by income and value of housing (with a concomitant decrease in the proportion in the lower socioeconomic status group).³³³

In most populations, SCC is about 2.2-fold and BCC about 1.6-fold more common in men than women.¹⁹⁰ This is possibly due to higher sun exposure in males who tend to have more outdoor occupations and recreational activities, a larger area of skin exposed than women, and are less likely to use sunscreens.^{80, 238} However, recent animal studies also suggest that there may be a biological gender bias in risk, possibly through protective effects of local synthesis of estrogens that protect females against UV-induced photocarcinogenesis.^{80, 238, 356}

Exposure to solar UV-B radiation is well-recognised as the predominant environmental risk factor for both SCC and BCC.^{9, 374} For SCC, cumulative life-time exposure, particularly occupational sun exposure, is key.²⁵⁷ For BCC, the relationship is thought to be more complex: in one study the risk of BCC on the head was especially increased in sun-sensitive individuals, whereas BCCs on the trunk were more related to the number of reported sunburns rather than to general sun-sensitivity.²²⁷ One common location for BCC is the inner canthus of the eye where the upper and lower eyelids meet. This is relatively sun-protected by the nose, eyebrow ridge, orbit and the cheek bone, but UV radiation may be reflected from the tear film, resulting in high dose exposure near the tear duct.³⁰

Genetic damage and risk of non-melanoma skin cancer. Several UV-B-specific mutations are recognised in BCCs and SCCs,²³⁵ such as in the *p53* gene and also in the *PTCH* gene of BCCs.¹⁴⁹ A number of other UV-related genetic factors may also be important in NMSC risk, but are less well-described. These include mutations in genes related to repair of DNA damage^{8, 78, 200, 283, 305, 342} and alterations in DNA methylation, where the latter is known to promote UV-induced DNA damage and affect genes involved in the regulation of the cell cycle and cell adhesion.^{276, 315, 332, 339} Variants of the melanocortin 1 receptor (*MC1R*) gene that determines skin pigmentation and phototype, and variants in other pigment genes, have been associated with BCC risk^{37, 41, 141} and various polymorphisms in genes related to UV-induced immunosuppression and tolerance can affect the risk of BCC and SCC.^{4, 225, 350, 351} Finally, variants in the gene coding for the vitamin D receptor (see “Immune and other effects of vitamin D” section below) increase the risk of NMSC¹¹⁸ and of solar keratosis,⁵¹ the precursor lesion to NMSC.

Effects of solar UV radiation on the immune system

Mechanisms of UV-induced immunosuppression

Immune responses fall into two broad categories – innate and acquired/adaptive. The former responses are non-specific and act rapidly as the initial response to microbial challenge. The latter responses are specific to each microorganism, and require, in many cases, that the antigens are taken up by antigen presenting cells (often dendritic cells), processed and then presented to the particular T lymphocytes that recognise the antigen fragments. As a consequence, these T cells are activated to proliferate and to secrete immune mediators. It was recognised many years ago that exposure of mice to UV radiation can suppress adaptive immune responses,¹⁸⁰ and that antigen-specific tolerance is induced, so that a further application of the same antigen at a later date still does not lead to the generation of an immune response.³¹⁴ More recently, it has been demonstrated that UV radiation can downregulate already established (memory) immune responses.^{72, 226, 341} Furthermore, exposure to multiple suberythral doses of UV radiation from solar simulated lamps, to mimic what might occur during the summer months, does not lead to any protection against the immunosuppression developing, despite most people responding to such chronic irradiation by tanning and epidermal thickening.²³⁶

The mechanisms involved are complex and are summarised in Fig. 2-3. Details can be found in recent reviews.^{23, 25, 79, 280} The main points are that DNA and *trans*-urocanic acid in the epidermis act as important chromophores to initiate the immunosuppressive pathway and that a particular subset of T cells, called T regulatory cells, are induced at the end. On stimulation, these produce the immunosuppressive cytokine, interleukin (IL)-10, and develop and maintain immune tolerance. They also suppress the activation, cytokine production and proliferation of other types of T cells which are involved in immunostimulatory functions. Various aspects of UV-induced immunosuppression that affect human health are outlined below, starting with viral and bacterial infections and vaccination, followed by the skin cancers, and ending with the “sun-allergy” disease, polymorphic light eruption (PLE).

The effect of UV-induced immunosuppression on infectious diseases

Although there are about twenty models of infection in rodents that indicate a significant down-regulation in acquired immune responses to the microbe in question following UV radiation, robust evidence of such an outcome in human subjects is limited at present to two viruses, namely herpes simplex

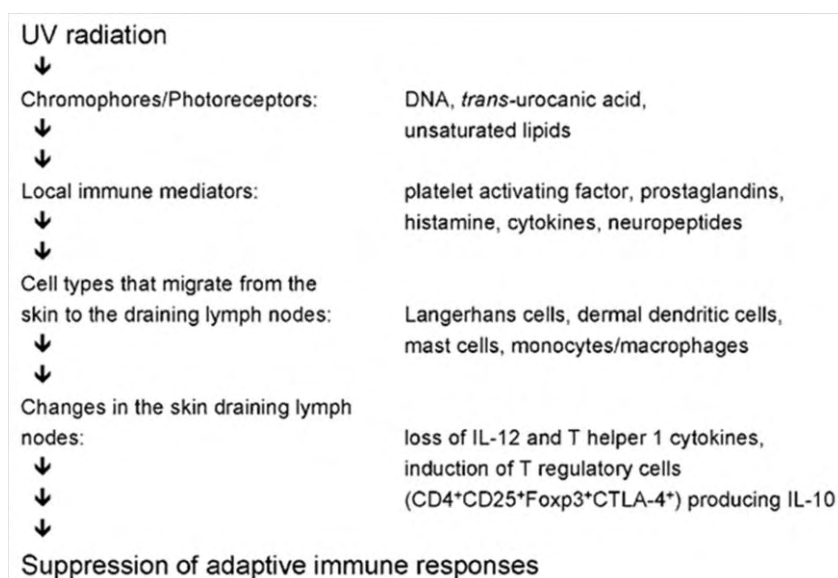


Fig.2-3. Summary of steps leading to suppression of cell-mediated immunity following UV irradiation.

virus (HSV), which causes cold sores, and human papillomavirus (HPV), which commonly causes warts. It is possible that other human infections may be affected but have not been investigated as yet.

Viral infections. Aspects of the reactivation of HSV from latency following exposure to solar UV radiation were outlined in our previous report.²³⁵ In brief, the viral genome is maintained in nerve tissue following the primary infection, and UV radiation is a common stimulus for its reactivation, release from the nerve tissue, and subsequent replication in the epidermis. There is probably a direct interaction between the latent HSV and UV radiation, possibly via damage to nerve endings, which leads to the activation of promoters within the viral genome. In addition, temporary UV-induced immunosuppression in the local skin site will occur, allowing replication of the virus and development of the „cold sore“ before immune control is regained.

For HPV, two interactions between solar UV-B radiation and the virus will be discussed here. First, the most common *de novo* malignancy arising in organ transplant recipients (OTR) is skin cancer: SCC occurs 65-250 times, BCC 10 times and CMM 6-8 times more frequently than in the general population. In OTR, persistent warts caused by HPV infection, cutaneous SCCs and their precursor lesions (actinic keratoses) arise mainly on sun-exposed body sites, leading to the conclusion that solar UV radiation is the major environmental risk factor for SCC in such patients. Up to 90% of SCCs from OTR contain HPV DNA.^{26, 147} HPV, UV radiation and the immunosuppressive drugs interact to promote the tumourigenesis. For example, UV irradiation of the skin not only induces local immune suppression by the mechanisms outlined in Fig. 2-3, but certain HPV types can express proteins that interfere with the normal response of the cell to UV irradiation, such as the repair of DNA damage and the removal by apoptosis of cells with DNA damage.^{163, 256, 304, 324} Cyclosporin A, until recently the most commonly used immunosuppressive drug in OTR, also interferes with the mechanisms involved in the repair and removal by apoptosis of cells with UV-induced damage to DNA.³⁰⁶ Hence, the end result is the selection and accumulation of cells with altered phenotype, leading to skin cancer. Conversely, other newer immunosuppressive drugs such as sirolimus may reduce the risk of skin cancer.¹⁰⁵

Secondly, HPV infection appears to be involved in SCCs in healthy (immunocompetent) subjects. As in the OTR, the SCCs arise on areas of the body exposed most frequently to sunlight, such as the face and backs of the hands. A higher prevalence of DNA of certain HPV types (beta-HPV species 2) is found in SCCs than in uninvolved skin from the same subjects or in controls.¹¹ The same HPV types are associated with SCCs located on body sites most exposed to the sun.¹⁰⁹ A population survey of workers in Australia with and without a history of frequent sun exposure found that the prevalence of the DNA of cutaneous HPV was significantly higher in the forehead skin in individuals who spent more time outdoors and in those with a history of skin cancer.⁵⁷ Indeed, the risk of cutaneous HPV infection increased with the length of time spent working outdoors. Multiple HPV types were more common in individuals frequently exposed to the sun, a finding attributed to UV-induced immunosuppression. Possible interactions between the mutagenic and immunosuppressive activity of the UV radiation and the properties of the HPV types found in some SCCs are likely to be very diverse and are not elucidated at present, although, as outlined above, the viral proteins that are anti-apoptotic³²⁴ and cause a delay in DNA repair may be important.

Finally for HPV, it should be noted that the suggestion¹³ that some HPV types might play a role in the aetiology of squamous cell cancers in the conjunctiva of the eye in coun-

tries, such as Uganda, where exposure to sunlight is very high, has not been confirmed in more recent studies.^{82, 316}

Recently a polyomavirus has been identified in the tumour cells of Merkel cell carcinoma (a tumour of the dermis with neuroendocrine features and a very poor prognosis), which is not found in uninvolved tissue from the patients or in any other type of skin tumour.²⁷⁵ These tumours arise predominantly on sun-exposed areas of the skin in elderly and immunosuppressed individuals.³⁰⁸ Although rare, its incidence in the USA has increased 3-fold over the past 15 years, possibly due to the ageing of the population and extensive sun exposure. Currently, there is no information available regarding local or systemic immune responses to the polyomavirus antigens, particularly to evaluate whether there could be a role for UV-induced immunosuppression as a risk factor in the tumourigenesis.

Bacterial infections. In contrast to viruses where the acquired immune response, particularly the T cell component, is critical for the control of infection, innate defence mechanisms may be more important for bacteria, especially those infecting cutaneous or mucosal surfaces.³⁸ Glaser et al.¹³⁰ have shown that UV irradiation of healthy volunteers induced up-regulation in the expression of several antimicrobial peptides which form part of the innate immune response of skin. The enhanced expression continued for at least 6 days after the irradiation. Thus one reason for the lack of bacterial infections of human skin following solar UV radiation exposure could be the production of these antimicrobial peptides. They may be particularly relevant when burning of the skin has occurred and bacterial infections might be expected in blistered areas. The contrast between this result and the rodent models of bacterial infection, where microbial load and severity of symptoms increased due to UV-induced suppression of acquired immunity, may relate to the site of infection, the size of the inoculum, and differences in gene regulation and in antimicrobial peptides between species. If the Glaser et al. results¹³⁰ are confirmed in other human studies, it may be necessary to consider whether innate immune responses, which tend to be up-regulated by UV radiation, or acquired immune responses which tend to be down-regulated by UV radiation, are most important in the control of specific infections, especially at early stages in the process.

The effect of UV-induced immunosuppression on vaccination

The immunosuppressive effects of UV radiation have been demonstrated in several animal models of vaccination, both if the exposure occurs prior to (for example¹⁶⁵), or after^{340, 341} the vaccine has been administered. Thus it is of much interest to consider whether exposure to solar UV radiation could adversely affect the immune response to vaccines in human subjects.

There has been only one published experimental human study in which volunteers were whole-body irradiated with solar simulated UV radiation before being vaccinated with hepatitis B surface antigen.²⁹² There was little effect of exposure on the T cell or antibody response to the vaccine except in irradiated subjects with a particular IL-1 β polymorphism (which affects the production of this cytokine) who had lower levels of antibody to the hepatitis protein,²⁹⁴ and in irradiated subjects with high cutaneous *cis*-urocanic acid (see Fig. 2-3) who had suppressed T cell responses to the hepatitis protein.²⁹³ Thus UV radiation adversely affected the generation of immune responses to hepatitis B vaccine, but only in certain individuals.

Only a few studies to date have evaluated whether season or latitude have any effect on immune responses to vaccination. These factors are frequently used as crude measures of personal exposure to solar UV radiation. In a meta-analysis of 10 case-control studies and 13 prospective trials of BCG vaccination against tuberculosis, where the geographical latitude of

the study site was recorded, it was found that the efficacy of protection increased with increasing distance from the equator, perhaps because of diminishing UV-induced immunosuppression.⁶⁵ Most recently, children living in northern Israel who had been injected with the measles-mumps-rubella vaccine at age 12 months were assessed for their antibody response to the rubella component at age 4-5 years.¹⁹⁴ In this area of the world, the UV Index in the summer reaches 10-12, while in the winter the peak values are 2-4. The children vaccinated in the winter months had significantly higher antibody levels compared with the children vaccinated in the summer months, and a bigger percentage had generated adequate levels. Thus the season when the subjects were vaccinated made a difference to the rubella antibody level 3-4 years later. These results require corroboration in more locations with marked differences in ambient solar UV radiation throughout the year, and using other viral vaccines. If it is true that, due to differences in solar UV radiation and hence effects on immune responses, vaccination in the summer leads to decreased immunity to the vaccine compared with vaccination in the winter, several practical implications follow. For example, it might be recommended to undertake vaccination only at times of the year when solar UV radiation is minimal, to ask individuals to limit their sun exposure for a few days before and after vaccination, and not to vaccinate an obviously sunburnt subject, especially on or through a site of erythema.

UV-induced immunosuppression and melanoma

Solar UV radiation is a risk factor for CMM and UV radiation is recognised to be immunosuppressive. It is not clear as yet if these two factors are linked. Muller et al.²²¹ have suggested that immune responses in newborn children, whose skin is immunologically immature, could determine melanoma outcomes in later life. Antigen applied at this time does not induce an immune response, but instead there is generation of antigen-specific T regulatory cells which then persist for life. Thus, if a melanoma antigen arises during this neonatal period, T regulatory cells specific for it will be produced, with the capacity to dampen effective anti-tumour immunity in adulthood. In addition, exposure of neonatal skin to UV radiation induces a poor inflammatory response compared with adult skin, thus limiting the development of an immune response. A micro-array study has identified several genes involved in enhanced immune responses in melanomas harbouring the BRAF mutations compared with non-mutated melanomas.¹⁶⁹ Another approach has centred on cytokine gene polymorphisms which might result in functional changes and influence susceptibility to CMM.^{231, 279}

UV-induced immunosuppression and non-melanoma skin cancer

The development of NMSC is controlled, at least in part, by the immune system, and by exposure to sunlight. For SCCs this is particularly apparent as the number of such tumours is greatly increased on sun-exposed areas of the body in organ transplant recipients (OTR) who are therapeutically immunosuppressed to prevent rejection of the transplant. These drugs suppress T cell activity predominantly and therefore T cell function is thought to play a major role in the immunological control of SCCs. UV radiation is known to suppress the production of the T helper 1 cytokines (see Fig. 2-3) which protect against SCCs in mice.³³⁷ In addition, untreated human SCCs contain many infiltrating T cells of which about 50% are T regulatory cells.⁶³ Furthermore, blood vessels in the tumours do not express E-selectin, a molecule that skin-homing T cells require for their entry into the skin from blood. Thus SCCs exclude the skin-homing T cells that could destroy the tumour cells.

A histological study of human BCCs revealed T regulatory cells surrounding the tumour aggregates and immunosuppressive cytokines within the tumours.¹⁷⁰ Only immature dendritic cells were found intratumorally, implying poor antigen presentation to T cells. All

these factors suggest a lack of immunity in BCCs, although an obvious inflammatory response is also seen,¹⁷⁰ together with an increase in the expression of pro-inflammatory cytokines.¹¹⁷ Thus there is evidence for both an anti-tumour response and an attenuated state of immunity in BCCs.

UV-induced sun allergy

Polymorphic light eruption (PLE) is the most common of the disorders that are provoked by sunlight, occurring in about 5-20% of the population. It is most frequent in the spring or early summer, or during a sunny holiday, following the first exposure to an intense dose of sunlight, and is characterised by red, itchy skin eruptions (Fig. 2-4). After repeated exposures, the lesions are less likely to occur in most subjects – a process called hardening. The effectiveness with which various UV wavelengths induce PLE is unclear and may depend on a complex mixture of factors such as dose, the genetic background of the individual and the cutaneous antigen provoked. Until recently it was thought that the prevalence of PLE increased with increasing distance from the equator, explained by the more marked change in seasonal ambient solar UV radiation at higher latitude. However, a recent large scale European survey found that latitude made no difference to the prevalence, suggesting that exposure to UV radiation could trigger the disease equally in countries with different patterns of solar UV irradiation throughout the year.²⁶¹



Fig. 2-4. Subject with polymorphic light eruption showing pruritic skin eruptions on sun-exposed body sites (photograph supplied by Dr S. Ibbotson, University of Dundee, Scotland).

PLE is immunologically-mediated, with increased immunosurveillance, and resistance to the immunosuppression that follows UV radiation. The subjects with PLE are thought to respond to photo-induced neoantigens in the skin by a form of delayed type hypersensitivity and the lack of immunosuppression may be due to reduced neutrophil and macrophage infiltration into the irradiated skin and possibly reduced numbers of T regulatory cells in the winter months.³⁵⁹ The impact of these alterations from normal is illustrated by finding that the prevalence of PLE is 7.5% in people with skin cancer compared with 21.4% in gender and age-matched controls without skin cancer.¹⁹¹ This implies that the immunological differences in the response of the PLE subjects to UV radiation may confer protection against skin cancer, and it also illustrates the evolutionary significance and potential advantages and disadvantages of UV-induced immunosuppression.

UV-induced vitamin D and its impact on health

For the majority of individuals, most of their vitamin D is derived from sun exposure. The additional sources of vitamin D are natural food stuffs, such as oily fish, supplemented foods, such as margarines and milk, and, in some cases, oral supplements. It has become clear recently that vitamin D status is also dependent on genetic differences in the metabolism of vitamin D.³⁴⁴ A recent study in Denmark showed that the cumulative personal summer solar UV radiation dose correlated weakly with the vitamin D status of the individual in the summer and in the following winter.³¹² Dietary intake of vitamin D appears to influence vitamin

D status during the winter, at least at high latitudes, and this may provide an explanation for the observed weak correlation between the vitamin D status in the winter and summer, in these locations.^{144, 201} Recent simple model computations, based on UK data for ambient UV radiation, indicate that sun exposures in the summer may indeed be inefficient in maintaining a sufficiently high vitamin D status in the winter.⁹¹

The pathway to the formation of the active form of vitamin D, 1,25-dihydroxyvitamin D (1,25(OH)₂D), after skin exposure to UV radiation¹⁵² is outlined in Fig. 2-5. Many cell types possess the enzymatic machinery to produce 1,25(OH)₂D, (reviewed in¹⁵³). The concentration of 25-hydroxyvitamin D (25(OH)D) in the serum is commonly used as a measure of a person's vitamin D status. Traditionally, the values considered as deficient, insufficient, sufficient and excessive are <25 (or <27.5), 25-50, 50-250 and >250 nmol.L⁻¹ respectively. More recently, it is suggested that the minimum level that provides the best health benefits should be increased from 50 to at least 75 nmol.L⁻¹, with the optimum between 90-100 nmol.L⁻¹^{131, 47, 76, 138, 154} although it should be noted that not all agree with this opinion.²⁷⁰ Any health benefit of maintaining a high serum 25(OH)D status has not been established,²⁵⁹ and, indeed, may even be detrimental as has been shown recently for pancreatic cancer where a concentration of ≥ 100 nmol.L⁻¹ was associated with a 2-fold increase in risk.³⁰³

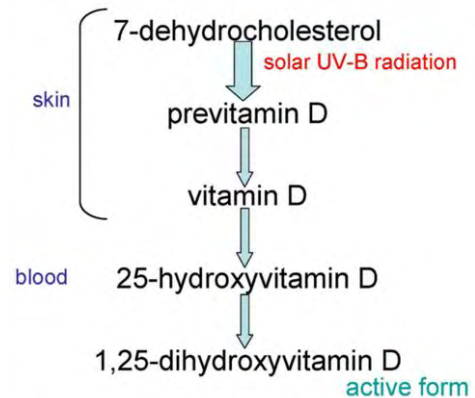


Fig. 2-5. Synthesis of the active form of vitamin D (1,25(OH)₂D) after solar UV-B irradiation of the skin.

By constructing an action spectrum for the conversion of 7-dehydrocholesterol to previtamin D₃ in human skin (see Table 1-6 in Chapter 1), it was concluded that the most effective wavelength for the production of previtamin D₃ was between 295 and 300 nm with a maximum at 297 nm, and no production above 315 nm, i.e. UV-B wavelengths only.²⁰³ Although the accuracy of the original data can be questioned (reviewed in²³⁴), this spectrum was standardised by the CIE in 2006⁶¹ and extended mathematically to 330 nm. It has been used subsequently in several studies for weighting the solar spectra to obtain effective doses for potential vitamin D production at various latitudes throughout the year (See Chapter 1 and refs^{106, 173, 175, 207, 254}). It is vital to obtain the best possible information in this regard so that accurate guidance can be given to the general public and to health agencies concerning personal exposure to sunlight in order to maximise vitamin D production while minimising any harmful effects of the UV radiation. Very few studies to date have measured the actual effect of known doses of UV radiation on 25(OH)D levels. However, one study published very recently has shown that the concentration of 25(OH)D in the majority of fair-skinned subjects rises to sufficient levels (≥50nmol.L⁻¹) (although this may be sub-optimal) following simulated summer sun exposure (at latitude 53.5°N) of 13 minutes, three times weekly for 6 weeks, to 35% of the skin surface area.²⁶² Here it should be noted that the subjects were whole-body irradiated whereas, under natural conditions, people lying on their backs or fronts in the sun are irradiated either on the anterior or the posterior surface, rather than both at the same time. Thus the sunbathing time to achieve the equivalent magnitude of vitamin D synthesis would require an exposure of about 26 minutes. Other confounding factors include posture, orientation with respect to the sun and nearby shade, leading to the conclusion that considerably longer than 26 minutes would be required, typically greater than one hour.⁹⁰

Based on the action spectrum for the production of previtamin D, the potential for synthesis of vitamin D is dependent on levels of ambient solar UV-B radiation. The amount

of solar UV-B radiation that reaches the surface of the Earth varies greatly, depending on the solar zenith angle (highest in the summer and decreasing to as little as 5% of this value at mid-latitudes in the winter months) which also accounts for its strong diurnal variation (typically 50-60% of daily solar UV radiation is incident in the 4 hour period around local noon) (see Chapter 1 for further details). It depends also on parameters such as ozone, cloud cover, air pollution and altitude. Furthermore, there are large interpersonal variations in the efficiency of previtamin D₃ production for a given dose of solar UV-B radiation. This may depend on skin colour (about 6-fold more UV-B radiation appears to be required if the skin is dark compared with fair skin⁶⁴), age (about 50% less is made by the same dose of UV-B radiation in an 80-year-old compared with a 20-year-old²⁰²), obesity (leads to less bioavailability of vitamin D as it is sequestered in fat tissue³²), baseline vitamin D status³⁵ and whether the irradiated skin site is one that has been repeatedly exposed, such as the face, as this affects the quantity of UV-B radiation reaching the deeper epidermal layers, rich in 7-dehydrocholesterol.⁴² Hence it is very difficult to provide a single, simple message regarding the optimal sun exposure for vitamin D production that is appropriate for everyone in a particular location.

The vitamin D status of populations in different countries has been assessed and generally shows that many people of all ages are below what is considered sufficient. For example, the US National Health and Nutritional Examination Survey, 2000-2004, found the prevalence of vitamin D insufficiency (serum 25(OH)D <50 nmol.L⁻¹) was 26% in men and 33% in women, and the overall deficiency (<27.5 nmol.L⁻¹) was 5%.³⁶⁶ A survey in 2005 of people aged 65 and above living in England demonstrated that 57% of women and 49% of men were vitamin D-insufficient (<50 nmol.L⁻¹) with 13% of women and 8% of men being deficient (<25 nmol.L⁻¹).¹⁵¹ Data from a national survey of the U.S. population indicated that the average concentration of 25(OH)D in the serum decreased by 20% over the past few decades.¹²⁴ It might be predicted that there would be a latitudinal gradient in vitamin D status at the overall population level, i.e., a decrease with increasing distance from the Equator. Perhaps surprisingly, this was not found in a recent meta-regression analysis of world populations, although a small but statistically significant gradient was shown if the analysis was limited to those with fair skin (-0.7 ± 0.3 nmol.L⁻¹ 25(OH)D per higher degree latitude north or south).¹⁴² Moreover, vitamin D levels in post-menopausal women in Europe showed the opposite gradient: low levels in the south and high levels in the north.¹⁹⁷ In a different multi-centre global study of post-menopausal women, 25(OH)D levels were assessed in a single laboratory, thus eliminating the considerable variability in measurements between centres.¹⁸² A small, although statistically significant, overall negative gradient was found for 25(OH)D concentration and latitude between 15° and 65°; the gradient was three-fold steeper for readings in the winter than in the summer (about -0.6 vs. -0.2 nmol.L⁻¹ per degree). Factors such as diet, food fortification, taking sunshine holidays in the winter months and outdoor activities may account, at least in part, for the dampening in the anticipated negative gradient in vitamin D status with increasing latitude. Thus the latitude of residence is not strongly correlated with vitamin D status and latitude may not be an appropriate proxy for vitamin D levels in ecological studies. Rather the actual levels in individuals within study groups should be determined, if at all possible.

Vitamin D has been recognised for almost a hundred years as preventing rickets in children, osteomalacia (the rickets equivalent) in adults, osteoporosis and bone fractures. More recently the role of UV radiation and vitamin D in regulating immune responses has been revealed and evidence gathered to indicate that it might protect human subjects against a wide and increasing range of common diseases. These aspects are considered below.

Immune and other effects of vitamin D

The active form of vitamin D ($1,25(\text{OH})_2\text{D}$) acts mainly through binding to, and activation of, the vitamin D receptor (VDR), which is present in many cells including those of the immune system. There are about 200 VDR variants (such as *FokI*, *TaqI*, *BsmI*, *ApaI*) which can affect susceptibility to infectious diseases and to skin tumours. The VDR- $1,25(\text{OH})_2\text{D}$ complex alters the function and expression of more than 200 genes. $1,25(\text{OH})_2\text{D}$ can inhibit the maturation of dendritic cells and hence reduce the presentation of antigens to the lymphocytes and can also act directly on T cells to inhibit their proliferation and to suppress the production of immunostimulatory cytokines. Recently, $1,25(\text{OH})_2\text{D}$ was shown to directly induce the development of T regulatory cells which have the potential to suppress proinflammatory cytokines and to prevent the activation of autoreactive T cells.¹⁶⁶ Such activity is likely to be of importance in protection against autoimmunity (reviewed in⁵⁰). In contrast, in vitamin D insufficiency, there is deregulation of the normal cytokine responses, leading to the overexpression of the immunostimulatory cytokines. Other non-immune targets for vitamin D may also play crucial roles in the prevention of autoimmunity.

The active form, $1,25(\text{OH})_2\text{D}$, is also important in innate immunity by inducing a range of antimicrobial peptides.^{50, 353} Thus it has the potential to provide protection against a range of infectious diseases. Finally, as malignant cells express the VDR, $1,25(\text{OH})_2\text{D}$ may protect against cancer by up-regulating the adherence of and signalling between cells, inhibiting proliferation, enhancing differentiation, stabilising the cell cycle, promoting apoptosis, and inhibiting neoangiogenesis (reviewed in¹¹⁹).

Cancer

In our 2007 assessment²³⁵ we reviewed the evidence available at that time indicating that increasing exposure to the sun reduced the risk of several internal cancers. Vitamin D was suggested as the protective factor. A recent review summarises the ecological studies associating solar UV-B radiation, vitamin D, and cancer.¹³⁷ In many of these, latitude or ambient solar UV radiation was used as a proxy for exposure to UV radiation and hence of vitamin D status. As outlined above, vitamin D status cannot be assumed to decrease as the distance from the equator increases but is affected by many factors including skin colour, diet, outdoor activities, obesity, clothing habits and number of sunshine holidays, and VDR polymorphisms can also alter the risk of disease. While the ecological approach on its own has little power to prove the involvement of any potential causal factor, it has led to considerable and increasing interest in trying to evaluate the importance of solar UV radiation and of vitamin D in protection against internal cancers. In 2008 the International Agency for Research on Cancer (IARC), after a careful formal evaluation, concluded that there was some evidence for a link between sun exposure and a reduced risk of colorectal cancer and adenoma (polyps), limited evidence for such an association in breast cancer, and none in prostate cancer.¹⁶² Other investigators disagree with the cautious approach of the IARC.¹³⁵ New information which will help to resolve this issue is becoming available. For example, in 2010, a remarkable set of pooled cohort studies conducted in Europe, the USA and Asia was published which revealed no inverse correlation between serum $25(\text{OH})\text{D}$ levels and the later incidences of five types of “rarer” cancers (upper gastrointestinal, ovary, endometrial, kidney and non-Hodgkin lymphoma), but an increased risk of pancreatic cancer in the group with the highest $25(\text{OH})\text{D}$ levels (reviewed in⁴³). One difficulty in this area lies in distinguishing whether a low vitamin D status causes an increased risk of cancer, or whether the low vitamin D status is a consequence of poor general health. In addition it is possible, although not likely, that the assessment of cancer risk based on vitamin D status in adulthood may not reflect the cumulative effects of vitamin D through a whole lifetime. To illustrate recent advances in this

area, a short overview of observational studies relating vitamin D to colorectal, breast and prostate cancer is given below.

Colorectal cancer. A recent meta-analysis of 7 epidemiological studies showed that the highest quintile (compared to the lowest) of circulating 25(OH)D concentration was associated with a 30% decrease in the risk of colorectal adenoma.³⁴⁷ Adenomas are benign tumours developing from epithelial tissue and have cancerous potential. The IARC meta-analysis concluded that there was evidence that lower 25(OH)D levels were associated with an increased risk of colorectal cancer.¹⁶² For example, in a pooled analysis of 5 studies, subjects with 25(OH)D levels greater than 95 nmol.L⁻¹ had a 55% lower risk of colorectal cancer compared with subjects with levels less than 40 nmol.L⁻¹.¹³³ The inverse association of pre-diagnostic 25(OH)D levels and colorectal cancer has been demonstrated across a broad range of ethnicities - Japanese, Latino, African-American, White, and Native Hawaiian ancestry,³⁶⁰ and in a study of over half a million participants in 10 western European countries.¹⁶⁷ The influence of vitamin D status on survival in patients with colorectal cancer was established retrospectively: a higher pre-diagnosis 25(OH)D level was associated with a significant improvement in overall survival and in colorectal cancer-specific mortality.²²⁸ Also, Freedman and colleagues¹¹¹ showed that the risk of dying from colorectal cancer in individuals with serum 25(OH)D levels higher than 80 nmol.L⁻¹ was approximately one-quarter compared with those having levels less than 50 nmol.L⁻¹. Thus there is good evidence to date that low 25(OH)D levels are associated with an increased incidence of colorectal cancer incidence and risk of death. One drawback of these studies is that vitamin D status is usually based on a single 25(OH)D level, although in cohort studies, this is at least usually from blood taken prior to the diagnosis of adenoma or colorectal cancer. It is possible that lifetime exposure to UV radiation (and the resulting vitamin D status) is a better measure, but is often not available. It is not yet clear whether supplementation with vitamin D or increased exposure to solar UV-B radiation can modulate the risk in humans significantly, although experiments in mice with diets deficient in, and supplemented with, vitamin D indicate that this is the case.²¹⁹

Breast cancer. The IARC review concluded that there was limited evidence for an association between vitamin D insufficiency and the risk of breast cancer.¹⁶² In the USA¹³⁴ and other countries,²¹⁷ the incidence of breast cancer increases with distance from the equator and decreasing regional solar UV-B radiation, even after adjustment for possible confounding factors such as obesity and smoking. Data from two observational studies suggest that women with pre-diagnostic 25(OH)D levels of about 130 nmol.L⁻¹ have a 50% lower risk of breast cancer than those with levels less than 32 nmol.L⁻¹.¹²⁰ However, in a recent nested case-control study in Sweden, there was only a weak, non-statistically significant decrease in the risk of breast cancer associated with higher pre-diagnostic 25(OH)D levels.⁵ Furthermore, a recent meta-analysis of observational epidemiological studies, investigating the association between serum 25(OH)D levels (generally a single sample, taken before diagnosis) and risk of breast cancer incidence or mortality, showed no significant correlation.³⁶⁸ A large clinical trial in post-menopausal women, randomised to receive either vitamin D (400 IU daily) and calcium daily or placebo and followed for an average of 7 years, revealed no difference in the incidence of breast cancer between the two groups.⁵⁸ It is possible that the vitamin D dose may have been insufficient to achieve protective levels, or some undetected premalignant breast lesions may have been present at the start of the study, or a longer follow-up period may have been required. Higher ambient levels of sunlight or outdoor occupations have also been inversely linked to mortality from breast cancer.¹¹⁰ Further work is required to understand whether exposure to solar UV-B radiation (and vitamin D) is beneficial in reducing the risk of developing, and death from, breast cancer.

Prostate cancer. Initial studies indicated an inverse association between the risk of prostate cancer and sunlight exposure^{33, 136, 168} or the level of 25(OH)D,^{104, 128, 178, 246} but subsequent reports have not substantiated these findings. Neither the IARC meta-analysis¹⁶² nor a more recent meta-analysis of 10 longitudinal studies³⁶⁹ found an association between 25(OH)D level and the risk of prostate cancer. Recent observational analyses also demonstrated either no statistically significant association^{2, 317} or even a possible increased risk of aggressive disease with the highest 25(OH)D levels.² Any associations between particular polymorphisms in the VDR and the risk of prostate cancer remain inconclusive,³⁷⁰ and there is no evidence that dietary or supplemental vitamin D offer significant protection (for example¹⁸¹).

Skin cancers. There is mounting evidence that vitamin D and its receptor are involved in protection against NMSC; for example, vitamin D can regulate the differentiation of normal skin cells and reduce the proliferation of murine BCC cell lines.²⁸ Also, topical vitamin D₃ applied daily reduced the number and size of BCCs in BCC-susceptible mice,³⁶¹ while mice lacking the gene that codes for the VDR were more susceptible to UV-induced skin tumours than the wild type mice.¹⁰⁰ However, a nested case-control study of subjects where vitamin D status was assessed prior to the diagnosis of BCC (up to 11 years prediagnosis),¹² demonstrated that the risk of BCC increased linearly with increasing serum 25(OH)D level. Thus, in the context of BCC, vitamin D is not protective, although the carcinogenic effect of high UV radiation, particularly as experienced in acute intermittent doses, may overwhelm any positive effects of vitamin D production in the skin.

Autoimmune diseases

Ecological and observational studies suggest that lower solar UV radiation and/or vitamin D status may be important risk factors for several autoimmune diseases. Two examples, multiple sclerosis (MS) and type 1 diabetes mellitus (T1DM), are described below.

Multiple sclerosis. MS, the result of an immune-mediated destruction of myelin-producing cells in the central nervous system, is the most common disabling neurological disorder of young adults. Its incidence has increased over the past 20 years and this does not appear to be an artifact of better diagnosis. The underlying aetiology of MS is unknown, but one of the most striking characteristics is the strong positive latitudinal gradient in occurrence so that the further from the equator, the higher the prevalence.^{1, 208} While there is a clear genetic susceptibility, geographic and temporal patterns have led to the hypothesis that an important risk factor for MS may be low exposure to UV radiation, possibly working through inadequate synthesis of vitamin D.²⁰⁹ This suggestion is supported by results using a variety of approaches, as summarised below, but it should be noted that a new study using a mouse model of MS (experimental autoimmune encephalomyelitis) has revealed that chronic exposure to UV radiation can suppress the clinical symptoms of the disease and that this occurs independent of vitamin D production.²² Thus the ability of the UV radiation to suppress the immune response may be of critical importance in reducing susceptibility to MS, acting through the mechanisms outlined in Fig. 2-3, rather than through vitamin D.

Although the latitudinal gradient in prevalence of MS may have weakened in recent years in the USA,¹⁰ in other countries there is persistence of a gradient in incidence,³⁰⁹ or prevalence.^{296, 310} Evidence from several studies suggests that low ambient UV radiation^{296, 299, 357} or low exposure to the sun prenatally or in childhood³³⁰ may represent a particularly significant risk for MS.

Observational studies have largely supported the suggested link between vitamin D and protection from the onset or progression of MS. In two cohort studies in the USA, higher vitamin D intake or serum 25(OH)D levels were associated with a decreased risk of developing MS;

higher 25(OH)D levels when aged less than 20 years were especially important.^{222, 223} In Tasmania the relapse rates for MS were inversely correlated with ambient erythemal UV radiation and serum 25(OH)D levels.³¹⁸ Variants in genes of the vitamin D pathway^{7, 258} have been shown to be important in risk of MS, although there are conflicting findings in relation to variants in the VDR.^{115, 242, 297} possibly because the role of environmental risk factors was not taken into account.²⁵³

Type 1 diabetes mellitus. T1DM is a T-cell mediated autoimmune disease with environmental and genetic risk factors. As is the case for MS, the incidence of T1DM has increased worldwide over the last two decades^{45, 240} and the age of onset has decreased in some regions.^{14, 15, 56, 62} The incidence or prevalence of T1DM increases with distance from the equator, or is inversely correlated with ambient UV radiation in several countries,^{193, 216, 300} although the magnitude of the effect is generally less than that for MS. For example, in the Diabetes Mondial Project Group (DiaMOND) Study, the incidence of T1DM varied from less than 5 per 100,000 at the equator to 37 per 100,000 in Finland, at 60°N.²¹⁶ In a recent Australian study, there was a strong inverse correlation between the incidence of T1DM (ages 0-14 years) and ambient erythemal UV radiation, but this relationship reversed in high population density (urban) areas,⁹⁹ possibly related to greater sun avoidance with increasing ambient UV radiation in urban areas, compared with rural areas.

Many studies (but not all) note a seasonal variation in the birth of people who later develop T1DM, with summer and autumn births being more common.^{267, 326, 358} One hypothesis to explain this finding is that low vitamin D levels in the mother during the winter preceding birth modulate the developing immune system in the foetus so that the risk of later development of autoimmunity is increased.^{62, 98, 269, 274} Individual-level studies have shown that higher intake of vitamin D (usually as supplements) by the mother or infant may be protective against the later development of islet cell antibodies^{39, 114} or T1DM.^{160, 302, 311} In addition, several reports have revealed that T1DM is more commonly diagnosed in the winter than in the other seasons.^{62, 98, 132, 243, 273, 274} Late winter is the time when vitamin D levels are generally at their lowest. This finding is consistent with the loss of a proposed protective effect of a higher dose of UV radiation or higher vitamin D status. In a recent study of US military personnel, the incidence of T1DM was more than twice as high in African Americans compared with non-African Americans,¹³² a finding possibly explained by deeply pigmented individuals being more likely to be vitamin D-insufficient.²⁴ Dietary and genetic factors may also be involved.

There have been conflicting findings regarding a relationship between VDR polymorphisms and T1DM risk, but a recent meta-regression analysis of 16 studies from 19 regions found that two VDR variants were associated with an increase in T1DM risk with increasing ambient winter UV radiation (long-term average midwinter-month noontime erythemal UV irradiance for the years 1997-2004, based on satellite data), while another VDR variant was associated with a decrease in T1DM risk with increasing ambient winter UV radiation.²⁵³ These results suggest that ambient UV radiation may modulate the association between the VDR genotype and T1DM risk, and further implicate a role for vitamin D in T1DM.

Infectious diseases

Many infectious diseases, especially those caused by viruses affecting the respiratory system, have a seasonal incidence with a peak in the winter months. Although this pattern could be explained by the smaller likelihood of viral inactivation during transmission in the winter compared with the summer, it has also been attributed to reducing levels of vitamin D as the dose of ambient solar UV-B radiation decreases. Lower vitamin D status could diminish innate immunity, particularly the expression of antimicrobial peptides in the airways, thus in-

creasing susceptibility to infection. Definitive evidence to support such a suggestion is lacking currently, although preliminary observations are consistent with vitamin D being protective.^{48, 49} In a clinical trial, supplementation with vitamin D correlated with decreased incidence of symptoms of the common cold and influenza in African-American post-menopausal women, although this endpoint was not one of the original aims of the study and was not rigorously assessed.⁶ More convincingly, in a recent small randomised, double-blind, placebo-controlled trial in children in Japan, the treatment group received a vitamin D₃ supplement (1200 IU daily) and the incidence of laboratory-confirmed influenza A infections was the primary outcome: the incidence of influenza A (but not influenza B) was reduced in the supplemented group compared with the placebo group and, in addition, there was significant protection against asthma attacks.³²⁵ In observational studies, low concentrations of 25(OH)D in the serum were associated with an increased risk of acute respiratory infection in Indian children under 5 years old,³⁴⁶ in young Finnish men serving in the military,¹⁸⁵ and in newborns in Istanbul.¹⁷¹ In addition, in a study of almost 19,000 participants in the American Third National Health and Nutrition Examination Survey, those subjects with serum 25(OH)D levels of less than 25 nmol.L⁻¹ had a 55% higher odds of a self-reported recent upper respiratory tract infection than those with levels greater than 75 nmol.L⁻¹.¹²⁵ It has also been suggested that vitamin D insufficiency may increase the risk of exacerbations of asthma through an association with poorer lung function and an increased chance of contracting viral respiratory infections.^{126, 158} However, whether increasing vitamin D levels by sunlight exposure helps to prevent asthma or to reduce the chance of an exacerbation has not yet been tested, as far as we are aware.

Tuberculosis is caused by infection with *Mycobacterium tuberculosis*. As early as the 19th century, it was recognised that open air sunbaths were beneficial in the treatment of patients with tuberculosis. By the 1920s, heliotherapy was a widely accepted treatment for tuberculosis, although it was not advised by most specialists for acute tuberculosis of all types, including pulmonary, as it could cause death. As a result of this therapeutic approach, susceptibility to tuberculosis or disease progression and vitamin D deficiency have been linked, (reviewed in²⁰⁵), possibly through impaired immunity to *M. tuberculosis* as a result of vitamin D deficiency.⁷⁵ Although early work suggested that treatment of tuberculosis patients with oral vitamin D improved the recovery rate and enhanced the acquired immune response against the bacilli, recent clinical trials of vitamin D supplementation,³⁴⁹ or UV-B irradiation³⁶⁵ did not lead to any improvement in clinical outcome or mortality³⁴⁹ or the immune response to the mycobacteria.³⁶⁵

Further clinical trials are urgently required to assess whether exposure to solar UV-B radiation and sufficient vitamin D status can prevent *M. tuberculosis* infection or reactivation from the latent state, and also reduce the risk of developing other respiratory infections.^{205, 232, 362} VDR polymorphisms need to be taken into account as some are known to confer enhanced susceptibility to particular infections.³⁵³

Cardiovascular diseases

The prevalence of coronary heart disease and hypertension increases with increasing distance from the equator.²⁶⁸ In one study, irradiating hypertensive patients with UV-B radiation reduced their blood pressure into the normal range, while UV-A radiation had no effect.¹⁷⁹ These findings are suggestive of a possible protective effect of UV-B radiation acting through enhanced synthesis of vitamin D. Vitamin D has been shown to regulate blood pressure through the renin-angiotensin system, and to decrease the proliferation of myocardial and vascular smooth muscle cells. A meta-analysis of 18 randomised controlled trials involving more than 57,000 participants demonstrated that a daily intake of vitamin D₃, averaging 520

IU, improved all-cause mortality, partly by decreasing deaths due to cardiovascular disease.¹⁸ Later studies have also shown that lower levels of 25(OH)D and 1,25(OH)₂D were independently associated with higher all-cause and cardiovascular mortality,⁹⁵ including in older adults (aged 65 and above),^{127, 285} and a higher risk of myocardial infarction.¹²⁹ More trials involving solar exposure or vitamin D supplementation are required to confirm a role for vitamin D in reducing the risk of these cardiovascular outcomes.

Personal protection

Effective personal protection can mitigate the adverse health effects from increases in ambient UV radiation, resulting from thinning of the stratospheric ozone layer and/or from climate change and UV-exposure related factors in some regions, e.g., where cloud cover is projected to decrease. Health campaigns in several countries such as the USA, Australia, New Zealand, Canada and the UK (for example: www.cdc.gov/cancer/skin/basic_info/prevention.htm; www.sunsmart.com.au; www.cancernz.org.nz/reducing-your-cancer-risk/sunsmart/; www.msc-smc.ec.gc.ca/education/uvindex/index_e) have tried to increase the public's awareness regarding the inherent dangers of overexposure to the sun. Such messages contain the information that sun exposure increases the risk of skin cancer and that precautions can be taken to reduce this risk. However, understanding in general remains low, one reason being that a single, simple message is not appropriate for all due to variations in place, season and skin phototype.^{295, 371} One potentially useful parameter is the UV Index (discussed in Chapter 1 and ref¹²¹) which is published daily in many countries. Greater efforts are required to make this a useful tool in the management of sun exposure as it is not generally understood by individuals.⁵²

Current advice centres on avoiding sunburn by seeking shade when the sun is most intense, wearing clothing that protects against the penetration of UV radiation, the use of topical sunscreens, and protecting the eyes. Each of these will be discussed briefly in turn.

Shade

The most effective way to reduce exposure to the sun is avoidance, particularly in the middle of the day. Staying indoors is best as most of the sky is blocked and glass transmits less than 10% of solar UV radiation. In one study, dense foliage offered the best outdoor protection and a beach umbrella the least.²¹⁸ The species of tree makes a difference, and the shade varies according to the season and sun angles, with highest protection usually in the summer months.¹²³ Careful consideration must be given to the construction of proper shade, especially the material used and the design of the shading structure to minimise diffuse and scattered UV-B radiation. Adolescents in particular are known to be reluctant to use many protective measures, such as wearing hats, and are frequently sunburnt in countries with high levels of solar irradiation. One successful strategy to reduce exposure to solar UV radiation during school hours, especially at lunch-time, is to erect special sails that provide shade in school playgrounds and which reduce levels of ambient UV-B radiation by at least 94%.⁹⁴

Clothing

Textiles can be a reliable method of personal photoprotection for covered areas of the body, although by no means all are effective. At present there is no uniform standard for labelling such clothing as some tests are performed *in vivo* in a similar fashion to sunscreens, while others are assessed by *in vitro* transmittance giving a UV protection factor (UPF) (reviewed in¹²²). Many variables affect the transmission of UV radiation through textiles, such as the porosity, colour, weight and thickness of the fabric. No information is given currently to in-

dicating how the material responds to stretching, wetness, washing, humidity and ambient temperature.

Despite these limitations, there is increasing use of clothing and hats for the sun protection of children (see Fig. 2-6) and such a method may also be useful for the protection of outdoor workers and others during recreational activities, particularly outdoor sports.²¹⁵ The main aim here is to lessen the risk of sunburn and the development of moles in children.¹⁴⁵ In Australia an occupational standard for exposure to UV radiation has been introduced¹²² which states that outdoor workers should be provided with appropriate clothing (rated UPF50+) plus other items for their protection from solar UV radiation. Further developments in the manufacture of UV-protective textiles are expected.

Sunscreens

Sunscreens can be inorganic – reflecting, scattering and absorbing UV radiation, such as zinc oxide and titanium dioxide, or organic – absorbing UV radiation, such as cinnamate and salicylate (reviewed in¹⁸⁸). They give different levels of protection against sunburn ranging from sun protection factors (SPFs) of 6 to more than 50. Sunscreens of SPF 30 are recommended for use in some official health guidelines.¹⁶¹ They were designed originally to protect against sunburn but also protect against other acute effects of solar UV radiation such as sunburn cell formation in the skin, cutaneous DNA damage, immunosuppression and reactivation of latent HSV. With regard to the more chronic effects of solar UV radiation, the regular use of sunscreens reduces the incidence of actinic keratoses³¹³ and SCCs, with a tendency (although not statistically significant) towards decreasing the incidence of BCCs.¹³⁹ The beneficial effect of sunscreens in preventing SCCs was revealed to be long-lasting, up to at least 8 years after the end of a trial in which they had been applied daily to the head, neck, hands and forearms.³³¹ Furthermore, sunscreen use attenuates the development of new moles in children on body sites that are intermittently sun-exposed.¹¹⁶ Such protection may reduce their risk of CMM later in life, although the efficacy of sunscreens in preventing melanoma remains controversial.^{83, 89, 140, 159} Although research in yeasts has indicated that UV-B irradiated titanium dioxide may be mutagenic,²⁵¹ other work shows no skin absorption of such sunscreen components and no evidence of toxicity in humans exposed via this route.²³³

One concern expressed about the widespread and increasing use of sunscreens is that a vitamin D-insufficient or deficient state could result, with reduced protection against a range of diseases. Although such an outcome has been demonstrated under very strictly controlled conditions, in real life it is unlikely to occur for a variety of reasons (reviewed in²³⁷). First, a fraction of the incident UV photons is transmitted through the sunscreen; for example for a product with SPF 30, 3.3% of the erythemal UV irradiation will be transmitted. Secondly, and probably most importantly, sunscreens are rarely applied at the concentration that is used to give the tested level of protection, 2 mg.cm⁻². Most commonly, subjects use only about 0.5 mg.cm⁻². Apart from ignorance about the correct level to use, 2 mg.cm⁻² feels ex-



Fig. 2-6. Children wearing sun-protective hats and clothing (photograph supplied by Dr A. Lesiak, Medical University of Lodz, Poland).

cessive, is often visually unattractive and is costly. The relationship between the quantity of sunscreen applied and the SPF is uncertain as one study finds a linear relationship²⁹ while another finds a non-linear relationship with, for example, a sunscreen of SPF16 being reduced to SPF2 when used at 0.5 mg.cm^{-2} .¹⁰³ Because almost all sunscreens are under-applied, calls have been made for the labelling to be changed.^{86, 229, 260, 343} Thirdly, the coverage of the sunscreen is inevitably uneven and the frequency of re-application is often inadequate. Fourthly, sunscreens are rarely applied to all areas of the exposed body surface. Finally, it has been demonstrated in several recent surveys that sunscreen users often expose themselves to more sun than non-sunscreen users and therefore are less likely to develop vitamin D insufficiency.^{16, 17, 312}

A “sensible” approach is advocated for the use of sunscreens. The SunSmart programme in the United Kingdom stresses the need to avoid sunburn and emphasises the fact that the amount of sun exposure required to ensure production of sufficient vitamin D is less than the amount that causes sunburn.³⁰⁷ In Europe, Diffey recommends that sunscreens with high SPF values are not applied all day every day but are reserved for times of exposure to intense solar UV radiation, during a sunshine holiday and during recreational activities in the middle of a summer day.⁸⁷ This contrasts with the position statement issued in 2007 in Australia and New Zealand that considered the risks and benefits of sun exposure.⁴⁶ In both countries, the local UV Index throughout the day is used as the Sunsmart UV Alert: use of sunscreen is recommended if the value is 3 or higher. Media reports in several countries have begun to highlight the suggested health benefits of vitamin D and have tended to emphasise the negative aspects of sun protection while promoting sun exposure (for example²⁸¹). Changing attitudes towards sun behaviour have been studied in Queensland: evidence of a recent reduction in sun protection practices in this high solar UV radiation environment was found which could lead to a significant increase in the incidence of skin cancer in future years.³⁷¹

Other topical or oral agents that protect against UV-induced skin damage

In most individuals, it is likely that some DNA photodamage will occur due to solar UV radiation, even if various methods of photoprotection are used. Thus, alternatives are being sought which function beyond absorption or avoidance of UV radiation,²⁰⁶ some of the most promising of which are described below.

Skin creams have been developed containing DNA repair enzymes (Advanced Night Repair Concentrate) with the aim of minimising skin cancer risk in susceptible individuals especially if they are unavoidably exposed to the sun.^{174, 199} When applied topically, they protect against the immunosuppression that follows solar UV radiation. In addition, RNA fragments (UV-C-irradiated rabbit globulin mRNAs which decrease sunburn cell formation and DNA damage), applied topically to human skin at the time of irradiation, minimise UV-induced immunosuppression.¹⁷⁴

An approach creating considerable interest at present concentrates on substances that are applied topically or taken orally, and that could be used alongside the sunscreens to provide additional protection. Compounds that activate the tanning pathway, such as melanocyte-stimulating hormone, reduce inflammation and promote DNA repair when applied topically.²⁰ Both oral⁷³ and topical^{291, 367} nicotinamide (vitamin B3) protect against UV-induced immunosuppression of the tuberculosis skin test (Mantoux reaction), and a topical mixture of vitamin C, ferulic acid and α -tocopherol also provides substantial photoprotection.²²⁴ Over a three year study period, subjects taking angiotensin converting enzyme (ACE) inhibitors and angiotensin receptor blockers by the oral route had a lower incidence of skin cancer than non-users.⁶⁰ Supplementation of the diet with the probiotic bacterium *Lactobacillus johnsonii* for

several weeks prior to exposure to solar UV radiation accelerated the recovery of immune function in the irradiated skin.²⁴⁷ Green tea polyphenols have long been known to protect against many of the damaging effects of UV radiation in human skin, acting by a variety of cellular, molecular, and biochemical mechanisms (reviewed in³⁷³). Most recently a green tea extract applied topically to the skin of subjects before UV radiation reduced the epithelial damage,²¹³ and, in another study, both green and white tea extracts also applied topically to human skin after UV radiation protected against several of the effects of UV radiation on cutaneous immunity.⁴⁴

Cost-effectiveness of sun protection education and sunscreens

The SunWise programme which runs in schools in the USA teaches children how to protect themselves from overexposure to the sun. It has been evaluated to determine its cost-effectiveness.¹⁸³ Assuming that the programme continues until 2015 at the current funding levels, it is estimated to avert more than 50 premature deaths, 11,000 skin cancer cases and loss of 960 quality-adjusted life-years amongst the subjects taking part. In addition to the morbidity and mortality benefits, for every dollar invested in SunWise, between 2-4 dollars in medical care costs and productivity losses would be saved. Thus SunWise is considered a successful and worthwhile investment. A similar exercise has been undertaken in Australia where the equivalent programme, SunSmart, was started in the early 1980s.²⁸⁸ Only the incidence of melanoma was included in the calculation as there is lack of coverage of BCC and SCC incidences in cancer registries. On a national scale, the programme is estimated to avert the loss of 120,000 disability-adjusted life-years over the next 20 years, with associated reductions in health care costs. Every dollar invested in SunSmart will return AU\$2.30 in terms of health costs, although further returns are likely if societal perspectives are included. Therefore SunSmart is considered excellent value for money.

There is interest also in determining the cost-effectiveness of public education campaigns promoting the use of sunscreens for the prevention of actinic keratoses and NMSC. Gordon et al.¹³¹ have published the first such study in which the cost effectiveness of advising a cohort of Australians living in sub-tropical Queensland to apply sunscreen daily versus *ad hoc* use over a 5 year period was calculated. The cost of the programme was US\$0.74 per person and the saving to the government was US\$109 per person, providing much better value for the expenditure. It was concluded that community-based interventions that promote regular sunscreen use in fair-skinned subjects living in sub-tropical or tropical environments are cost-effective in protecting against skin cancer. Such analyses for other public health advice regarding personal protection from the detrimental effects of solar UV radiation would be beneficial. Any savings in the costs for human health from protecting the ozone layer are unknown at the present time.

Eye protection

The eye is naturally protected from overhead solar irradiation by its location within the bony orbit of the skull and by the brow, lids and eyelashes. Hence, the structures of the eye are only infrequently exposed to direct solar UV radiation, although exposure via scattering can be considerable. In Norval et al.²³⁵ the interaction of solar UV-B radiation with target tissues in the eye was discussed and the importance of peripheral light focussing when considering ocular protection.

Sunglasses are the most practical and effective method of protecting the eye. The International Organization for Standardization continuously modifies its standards for sunglasses and related eyewear (ISO 12312-2, 2009). Although most sunglasses manufactured currently provide protection from axially incident ambient UV radiation, they may permit UV

irradiation from above, from ground reflections and laterally if they are poorly fitting. One study in India found that all branded and most unbranded sunglasses provided good protection against penetration of UV-A radiation but satisfactory protection against UV-B radiation was not provided by all sunglasses, whether branded or unbranded.⁹⁷ In another study, excellent protection from UV radiation was achieved by some inexpensive sunglasses, that was superior in some cases to branded products.⁵⁹ In general, apart from absorption of UV radiation, the more expensive sunglasses have lenses of better quality but much of the increased cost is accounted for by the designer frames and logos. Ideally sunglasses should meet international standards, and be wrap-around in design or have side shields in the case of prescription lenses. Goggles are recommended at high altitudes and for snow sports.

It has been confirmed recently that UV-blocking contact lenses are capable of protecting the cornea, aqueous humour, and crystalline lens from UV-induced pathologic changes.⁵⁴ The conjunctiva and lids are not protected by such lenses and they should not be considered as substitutes for sunglasses. The UV radiation absorber is incorporated into the polymer of the contact lens and the absorption properties vary with thickness across the lens.³³⁸ For example a minus (negative) contact lens to correct myopia is thicker at the edge than the centre and would provide more protection to the periphery of the cornea and from peripheral rays than the centre of the lens.

Risks associated with the use of substitutes for ozone depleting substances

As a part of the Montreal Protocol, signatories are committed to the development and use of acceptable alternatives or replacements for the ozone depleting substances (ODSs). The introduction of new chemicals, or old chemicals for new uses, may result in increases in human exposures to these chemicals; thus the substitutes need to be evaluated not only for their ability to replace ODSs *per se* but also for their ability to do so within a framework of acceptable risk. From a regulatory standpoint, at least within the USA, such evaluation is being undertaken by the Significant New Alternative Policy (SNAP) programme of the Environmental Protection Agency, details of which are provided in an online supplement to this paper. However, much of the information to which the SNAP programme has access is not publicly available. As a consequence, while the SNAP programme is discussed in detail in the online supplement, the focus of this section is the information in published research papers.

While there are probably several hundred chemicals and chemical mixtures being used as replacements for ODSs in various applications, there is little recent information on their toxicity. However, a number of reviews have summarized the limited older data available on the toxicity of a number of the classes of the chemicals that serve as ODS substitutes and their degradation products.^{101, 102, 320-323} Of the substitutes discussed, probably the most toxic is sulfuryl fluoride, a fumigant proposed to replace methyl bromide. Fatalities have been reported from acute occupational exposures and the occupational exposure limit has been set very low (5 ppmv).³²³ For the hydrofluoroethers (HFEs), carcinogenicity, mutagenicity, reproductive toxicity or systemic chronic toxicity are thought unlikely. Overexposure under occupational conditions is possible, although the levels needed for severe effects, e.g. cardiac sensitization are extremely high (>100,000 ppmv).³²⁰ There are little or no specific data for the hydrofluoropolyethers (HFPEs), but by analogy, the expectation is that the HFPEs will not pose any risks to humans from carcinogenicity, mutagenicity or reproductive toxicity. The information on perfluoro-n-alkanes is similar to that of the HFPEs, that is, they have low toxicity, low flammability, and low corrosiveness. Degradation products from these classes of chemicals include a variety of toxic compounds such as carbonyl fluoride, hydrogen fluoride, hydrogen chloride, formaldehyde, formic acid, and acetic acid but there are

little if any data on the atmospheric concentrations of these compounds.³²⁰⁻³²² The findings for hydrofluorocarbons (HFCs) with regard to reproductive toxicity indicate little reason for concern. Exposure to degradation products, such as carbonyl fluoride and, by analogy, sodium fluoride, have shown some developmental effects in animals. There are insufficient data on the reproductive effects of other degradation products, including trifluoroacetic acid and formic acid, to draw any conclusions about safety.^{101, 102}

Possible health effects of the interactions between climate change and ozone depletion

The World Health Organisation has stated that human health should be at the centre of concerns about climate change and is working to ensure that the issue of health has prominence at various international conferences, including the United Nations Framework Convention on Climate Change in Copenhagen 2009. At a meeting of the Commonwealth Health Ministers in May 2009, the view was expressed that local adverse health effects due to climate change were actually occurring already, and require urgent public health management.²¹⁰ When considering possible interactions between stratospheric ozone depletion and climate change, it is not possible at present to come to any firm general conclusions regarding their impact on human health as so little research has been published in this area, perhaps due to the lack of interdisciplinary approaches.

Many assessments predict the effect of climate change on increasing the incidence of allergic diseases and several infectious diseases, such as malaria, Lyme disease (a bacterial infection spread by ticks) and leishmaniasis (a protozoal infection spread by sand-fly bites) in different parts of the world, but do not include changes in solar UV-B radiation.^{53, 143, 245} Climate factors suggested to affect infectious and other human diseases include increased water temperature leading to increased survival of waterborne agents, increased rainfall leading to increased breeding sites for insect vectors, increased humidity leading to enhanced microbial survival in the environment, decreased seasonal exposure to solar UV-B radiation leading to lower vitamin D levels with diminished protective effects, increased atmospheric pollutants leading to less efficient mucociliary action, and changing rainfall patterns and ocean temperatures that result from long-term natural variabilities such as the El Niño Southern Oscillation events.¹⁰⁷ One obvious uncertainty for solar UV radiation is whether people will spend more or less time outdoors in sunlight in the future as temperatures rise but as humidity, storms, floods and drought also increase.

The following summarises the present sparse knowledge regarding interactions between climate change and ozone depletion with respect to human health.

Skin cancer

On the basis of previous results obtained from photocarcinogenic experiments in mice housed at different temperatures, van der Leun and de Gruijl³²⁸ suggested several years ago that rising temperatures due to global warming might enhance the induction of skin cancer by solar UV radiation. This has been tested by correlating the incidence of skin cancer in fair-skinned people in 10 regions of the USA with measured annual UV irradiance and temperature (average daily maximum temperature in the summer months) in each of the regions. The analysis showed a predominant influence of the UV radiation but also a statistically significant influence of temperature.³²⁹ For the same UV irradiance, each one degree Celsius increase in temperature resulted in an estimated 3% increase in the incidence of BCC, and 6% of SCC. This consequence may therefore represent a significant hazard in terms of global health. Fur-

thermore, high temperatures and humidity, as experienced in the tropics and as predicted for some areas for the future, may increase the deleterious effects of UV-B radiation on human health, including suppression of immunity to infectious diseases and skin cancers.¹⁶⁴

Infectious diseases

One study of illness in children aged less than six years, presenting as emergency cases in Sydney, found that the maximum daily temperature was a risk factor for both fever and gastroenteritis, while increasing UV Index was inversely correlated with gastroenteritis incidence; air quality was not a significant risk factor.¹⁸⁶

A group in Philadelphia has assessed the seasonality of both invasive pneumonia, caused by *Streptococcus pneumoniae*, and invasive meningococcal disease and tested associations with acute (day-to-day) environmental factors. For pneumonia, the weekly incidence in Philadelphia County was greatest in the winter months. This pattern correlated with extended periods of lowest solar UV radiation and, to a much lesser extent, with temperature.³⁵² The limited solar UV radiation available at higher latitudes, (Chapter 1) could aid the survival of the bacterium or could adversely affect innate immunity, possibly through the lack of vitamin D. As temperature is not a major factor in the seasonality of invasive pneumonia, global warming is unlikely to affect the incidence of the disease significantly, although increased cloud cover could reduce ambient UV radiation and hence lower the vitamin D status. For invasive meningitis, the number of cases in Philadelphia was highest in the late winter and early spring.¹⁷⁷ A one-unit increase in the UV Index 1-4 days prior to the onset of symptoms was associated with a 46% decrease in the odds of disease. The dose of solar UV-B radiation could affect transmission from a colonised subject or the infectivity of the bacteria.

Thus, although the evidence to date is sparse, ozone depletion leading to increased solar UV-B radiation, or decreases in UV radiation projected for the future (Chapter 1), in combination with other environmental factors, could impact significantly on the incidence of particular infectious diseases.

Dermatoses

Chronic actinic dermatitis (CAD) is an uncommon eczematous photosensitivity disease affecting mainly sun-exposed sites on the body. The provoking wavelengths are within the UV-B waveband in almost all patients.¹⁴⁸ As more cases have been diagnosed since 1991 in the Pusan region of South Korea than in previous years, the relationship between various climate factors and the incidence of CAD was investigated.¹⁸⁴ Recent changes in the climate of Pusan include increased air temperature all year round, expanding desertification with Asian dust and a year-by-year increase in sunshine duration. A close correlation was found between the number of cases of CAD and increased ambient sunshine. This emphasises the relationship between solar UV radiation and photosensitivity disorders and how climate change can affect their incidence.

Environmental effects

UV radiation in sunlight is a major factor in causing the death of microorganisms in the environment that are pathogenic for humans. It acts by direct effects on genomic DNA or by the generation of reactive oxygen species. UV radiation can inactivate human pathogens present in drinking water. For example, natural sunlight was tested recently for its ability to reduce the infectivity in drinking water of bacteria, viruses and protozoa that can cause disease in human subjects.⁷⁴ Other reports demonstrated that insolation rapidly inactivated the protozoan *Cryptosporidium parvum* in environmental waters, with UV-B radiation identified as the most effective waveband.^{66, 176} Interactions between temperature, pH and water transparency

will affect the UV-induced reduction in infectivity of this microorganism.⁶⁶ Sagripanti et al.²⁷¹ examined the inactivation of the virulent bacterium *Burkholderia pseudomallei* by sunlight under different environmental conditions such as in rain water and in seawater, and showed that an increase in exposure to solar UV-B radiation led to increased microbiocidal activity. Sunlight exposure is an important mechanism for inactivating certain microorganisms in sewage in shallow sea water, provided the water is clear.³⁴ One study has revealed that inactivation of some bacterial species in fresh water occurred more rapidly in the summer than in the winter, and that inactivation by sunlight increased with increasing salinity of the water.²⁹⁰ The efficiency of inactivation of microorganisms by exposure to sunlight in the environment is determined by a complex mixture of factors including the amount and type of photoproducts produced, the ability to repair the damage, the ambient temperature,²⁴⁴ the pH and salinity of the water, and the solar spectrum. At least 60-94% of the killing of bacteria by solar exposure is suggested to be due to the UV-B component of sunlight.⁶⁷

Further work is required to assess possible interactions between changes in climate, such as global warming, and solar UV-B radiation on the viability of pathogenic microorganisms in the environment.

Gaps in knowledge

Stratospheric ozone depletion leading to increased solar UV-B radiation has had adverse health effects on human populations, the most serious and widespread being skin cancer and cortical cataract. Such an increase in solar UV-B radiation can be beneficial in increasing vitamin D status and thus lowering the risk of developing a range of diseases. Although the ozone layer is projected to recover slowly in the coming decades, continuing vigilance is required regarding exposure to the sun: for ageing populations who are more susceptible to a number of serious diseases in which UV radiation plays a part but also for young people, as risk for at least some UV-related diseases may be largely determined by early-life exposures. Personal protection to prevent sunburn is recommended whilst ensuring enough sun exposure to provide sufficient vitamin D. When climate change is considered together with ozone depletion, any health effects, either advantageous or disadvantageous, are hard to assess currently as the impact of such a change on societies and behaviour is not clear. However, it may be more difficult to maintain adequate vitamin D status from exposure to the sun at mid to high latitudes. Many gaps in our knowledge remain, some of which are summarised in Table 2-1.

Table 2-1. Suggested gaps in current knowledge regarding solar UV-B radiation and human health

Subject	Key questions
The eye	What are the wavelength dependencies for cataract development? Does solar UV-B radiation play a role in age-related macular degeneration? What role does solar UV-B radiation play in uveal melanoma?
The skin	What is the UV wavelength dependency for melanoma induction? What is the interaction between solar UV radiation and the human papillomaviruses that are involved in squamous cell carcinoma? Does vaccination in the summer months or in a sun-exposed individual lead to a suppressed immune response against some vaccines? What is the mechanism for the induction of T regulatory cells following UV radiation?

	<p>Does solar UV radiation induce innate defence mechanisms in human skin that can control bacterial and other infections?</p> <p>Is there a balance between the positive and negative effects of UV-induced immunosuppression?</p> <p>What is the optimal vitamin D status for all its health benefits, and how much solar UV-B radiation is required to attain it in people of different skin colour living at different latitudes at different times of the year?</p> <p>Is exposure to UV-B radiation and/or vitamin D status linked directly with protection against certain internal cancers, autoimmune diseases and infectious diseases?</p> <p>Can all the potential benefits of vitamin D adequacy be met from supplementation?</p>
Protection measures	<p>What is the most effective health message to give the general public regarding “safe” sun exposure?</p> <p>How can public understanding and use of the UV Index be improved?</p> <p>Can components of our diet or substances applied topically provide protection for the eye and skin against the harmful effects of UV radiation?</p> <p>Is additional photoprotection required after cataract surgery?</p> <p>Should the SPF of sunscreens be modified to reflect the actual concentration commonly used by the public?</p> <p>Is it important to measure and publicise the immune protection factor of sunscreens?</p>
Effects from climate change/ozone depletion interactions	<p>Does an increase in temperature combined with increased solar UV-B radiation cause enhanced adverse effects in the eye and/or skin?</p> <p>Will sun exposure behaviour alter with climate change conditions?</p> <p>What effect does climate change have on lifestyle factors which influence personal sun exposure such as sunshine holidays, clothing, diet and tanning?</p> <p>Does climate change alter the daily solar UV-B radiation reaching the earth’s surface?</p> <p>Does climate change affect the efficacy of solar UV radiation to inactivate pathogenic microorganisms in water supplies?</p> <p>Will populations migrate to environments that have more favourable climates (cooler, better water supplies, etc.), but increase/decrease the risks of harmful effects of solar UV-B radiation or vitamin D insufficiency?</p>

References

- 1 Acheson ED and Bachrach CA, 1960, The distribution of multiple sclerosis in U. S. veterans by birthplace, *Am. J. Hyg.*, **72**, 88-99.
- 2 Ahn J, Peters U, Albanes D, Purdue MP, Abnet CC, Chatterjee N, Horst RL, Hollis BW, Huang WY, Shikany JM and Hayes RB, 2008, Serum vitamin D concentration and prostate cancer risk: a nested case-control study, *J. Nat. Cancer. Inst.*, **100**, 796-804.
- 3 AIHW and AACR, 2008, Cancer in Australia: an overview, 2008, Australian Institute of Health and Welfare Report No. Cancer series, no 46, Canberra. <http://www.aihw.gov.au/publications/can/ca08/ca08.pdf>
- 4 Alamartine E, Berthoux P, Mariat C, Cambazard F and Berthoux F, 2003, Interleukin-10 promoter polymorphisms and susceptibility to skin squamous cell carcinoma after renal transplantation, *J. Invest. Dermatol.*, **120**, 99-103.
- 5 Almquist M, Bondeson AG, Bondeson L, Malm J and Manjer J, 2010, Serum levels of vitamin D, PTH and calcium and breast cancer risk - a prospective nested case-control study, *Int. J. Cancer*, **127**, 2159-2168.
- 6 Aloia JF and Li-Ng M, 2007, Re: epidemic influenza and vitamin D, *Epidemiol. Infect.*, **135**, 1095-1096.
- 7 ANZgene, 2009, Genome-wide association study identifies new multiple sclerosis susceptibility loci on chromosomes 12 and 20, *Nat. Genet.*, **41**, 824-828.

- 8 Applebaum KM, Karagas MR, Hunter DJ, Catalano PJ, Byler SH, Morris S and Nelson HH, 2007, Polymorphisms in nucleotide excision repair genes, arsenic exposure, and non-melanoma skin cancer in New Hampshire, *Environ. Health Perspect.*, **115**, 1231-1236.
- 9 Armstrong BK, Krickler A and English DR, 1997, Sun exposure and skin cancer, *Australasian. J. Dermatol.*, **38 Suppl 1**, S1-6.
- 10 Ascherio A and Munger KL, 2007, Environmental risk factors for multiple sclerosis. Part II: Noninfectious factors, *Ann. Neurol.*, **61**, 504-513.
- 11 Asgari MM, Kiviat NB, Critchlow CW, Stern JE, Argenyi ZB, Raugi GJ, Berg D, Odland PB, Hawes SE and de Villiers EM, 2008, Detection of human papillomavirus DNA in cutaneous squamous cell carcinoma among immunocompetent individuals, *J. Invest. Dermatol.*, **128**, 1409-1417.
- 12 Asgari MM, Tang J, Warton ME, Chren MM, Quesenberry CP, Jr., Bikle D, Horst RL, Orentreich N, Vogelmann JH and Friedman GD, 2010, Association of Prediagnostic Serum Vitamin D Levels with the Development of Basal Cell Carcinoma, *J. Invest. Dermatol.*, **130**, 1438-1443.
- 13 Ateenyi-Agaba C, Weiderpass E, Smet A, Dong W, Dai M, Kahwa B, Wabinga H, Katongole-Mbidde E, Franceschi S and Tommasino M, 2004, Epidermodysplasia verruciformis human papillomavirus types and carcinoma of the conjunctiva: a pilot study, *Br. J. Cancer*, **90**, 1777-1779.
- 14 Atkinson MA and Eisenbarth GS, 2001, Type 1 diabetes: new perspectives on disease pathogenesis and treatment, *Lancet*, **358**, 221-229.
- 15 Australasian Paediatric Endocrine Group, 2005, Clinical practice guidelines: Type 1 diabetes in children and adolescents, National Health and Medical Research Council, Publisher site <http://www.nhmrc.gov.au/publications/synopses/cp102syn.htm>, accessed September, 2010.
- 16 Autier P, 2009, Sunscreen abuse for intentional sun exposure, *Br. J. Dermatol.*, **161**, 40-45.
- 17 Autier P, Boniol M and Dore JF, 2007, Sunscreen use and increased duration of intentional sun exposure: still a burning issue, *Int. J. Cancer*, **121**, 1-5.
- 18 Autier P and Gandini S, 2007, Vitamin D supplementation and total mortality: a meta-analysis of randomized controlled trials, *Arch. Intern. Med.*, **167**, 1730-1737.
- 19 Ayala M, Strid H, Jacobsson U and Soderberg PG, 2007, p53 expression and apoptosis in the lens after ultraviolet radiation exposure, *Invest. Ophthalmol. Vis. Sci.*, **48**, 4187-4191.
- 20 Barnetson RS, Ooi TK, Zhuang L, Halliday GM, Reid CM, Walker PC, Humphrey SM and Kleinig MJ, 2006, [Nle4-D-Phe7]-alpha-melanocyte-stimulating hormone significantly increased pigmentation and decreased UV damage in fair-skinned Caucasian volunteers, *J. Invest. Dermatol.*, **126**, 1869-1878.
- 21 Bath-Hextall F, Leonardi-Bee J, Smith C, Meal A and Hubbard R, 2007, Trends in incidence of skin basal cell carcinoma. Additional evidence from a UK primary care database study, *Int. J. Cancer*, **121**, 2105-2108.
- 22 Becklund BR, Severson KS, Vang SV and Deluca HF, 2010, UV radiation suppresses experimental autoimmune encephalomyelitis independent of vitamin D production, *Proc. Nat. Acad. Sci. USA.*, **107**, 6418-6423.
- 23 Beissert S and Loser K, 2008, Molecular and cellular mechanisms of photocarcinogenesis, *Photochem. Photobiol.*, **84**, 29-34.
- 24 Benitez-Aguirre PZ, Wood NJ, Biesheuvel C, Moreira C and Munns CF, 2009, The natural history of vitamin D deficiency in African refugees living in Sydney, *Med. J. Aust.*, **190**, 426-428.

- 25 Bennett MF, Robinson MK, Baron ED and Cooper KD, 2008, Skin immune systems and inflammation: protector of the skin or promoter of aging?, *J. Invest. Dermatol. Symp. Proc.*, **13**, 15-19.
- 26 Berkhout RJ, Bouwes Bavinck JN and ter Schegget J, 2000, Persistence of human papillomavirus DNA in benign and (pre)malignant skin lesions from renal transplant recipients, *J. Clin. Microbiol.*, **38**, 2087-2096.
- 27 Bialek-Szymanska A, Misiuk-Hojlo M and Witkowska K, 2007, Risk factors evaluation in age- related macular degeneration, *Klinika Oczna*, **109**, 127-130.
- 28 Bikle DD, 2004, Vitamin D and skin cancer, *J. Nutr.*, **134**, 3472S-3478S.
- 29 Bimczok R, Gers-Barlag H, Mundt C, Klette E, Bielfeldt S, Rudolph T, Pflucker F, Heinrich U, Tronnier H, Johncock W, Klebon B, Westenfelder H, Flosser-Muller H, Jenni K, Kockott D, Lademann J, Herzog B and Rohr M, 2007, Influence of applied quantity of sunscreen products on the sun protection factor--a multicenter study organized by the DGK Task Force Sun Protection, *Skin Pharmacol. Physiol.*, **20**, 57-64.
- 30 Birt B, Cowling I, Coyne S and Michael G, 2007, The effect of the eye's surface topography on the total irradiance of ultraviolet radiation on the inner canthus, *J. Photochem. Photobiol. B.*, **87**, 27-36.
- 31 Bischoff-Ferrari HA, Giovannucci E, Willett WC, Dietrich T and Dawson-Hughes B, 2006, Estimation of optimal serum concentrations of 25-hydroxyvitamin D for multiple health outcomes, *Am. J. Clin. Nutr.*, **84**, 18-28.
- 32 Blum M, Dolnikowski G, Seyoum E, Harris SS, Booth SL, Peterson J, Saltzman E and Dawson-Hughes B, 2008, Vitamin D(3) in fat tissue, *Endocrine*, **33**, 90-94.
- 33 Bodiwala D, Luscombe CJ, French ME, Liu S, Saxby MF, Jones PW, Fryer AA and Strange RC, 2003, Associations between prostate cancer susceptibility and parameters of exposure to ultraviolet radiation, *Cancer Lett.*, **200**, 141-148.
- 34 Boehm AB, Yamahara KM, Love DC, Peterson BM, McNeill K and Nelson KL, 2009, Covariation and photoinactivation of traditional and novel indicator organisms and human viruses at a sewage-impacted marine beach, *Environ. Sci. Technol.*, **43**, 8046-8052.
- 35 Bogh MK, Schmedes AV, Philipsen PA, Thieden E and 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**, 546-553.
- 36 Bono A, Tolomio E, Bartoli C, Carbone A, Tomatis S, Zurrada S and Santinami M, 2008, Metamorphosis of melanoma. Trends in size and thickness of cutaneous melanoma over one decade at the Istituto Nazionale Tumori, Milan, *Tumori*, **94**, 11-13.
- 37 Box NF, Duffy DL, Irving RE, Russell A, Chen W, Griffyths LR, Parsons PG, Green AC and Sturm RA, 2001, Melanocortin-1 receptor genotype is a risk factor for basal and squamous cell carcinoma, *J. Invest. Dermatol.*, **116**, 224-229.
- 38 Braff MH and Gallo RL, 2006, Antimicrobial peptides: an essential component of the skin defensive barrier, *Curr. Top. Microbiol. Immunol.*, **306**, 91-110.
- 39 Brekke HK and Ludvigsson J, 2007, Vitamin D supplementation and diabetes-related autoimmunity in the ABIS study, *Pediatr. Diabetes*, **8**, 11-14.
- 40 Brewster DH, Bhatti LA, Inglis JH, Nairn ER and Doherty VR, 2007, Recent trends in incidence of nonmelanoma skin cancers in the East of Scotland, 1992-2003, *Br. J. Dermatol.*, **156**, 1295-1300.
- 41 Brudnik U, Branicki W, Wojas-Pelc A and Kanas P, 2009, The contribution of melanocortin 1 receptor gene polymorphisms and the agouti signalling protein gene

- 8818A>G polymorphism to cutaneous melanoma and basal cell carcinoma in a Polish population, *Exp. Dermatol.*, **18**, 167-174.
- 42 Bruls WA, Slaper H, van der Leun JC and Berrens L, 1984, Transmission of human epidermis and stratum corneum as a function of thickness in the ultraviolet and visible wavelengths, *Photochem. Photobiol.*, **40**, 485-494.
- 43 Byers T, 2010, Anticancer vitamins du Jour--The ABCED's so far, *Am. J. Epid.*, **172**, 1-3.
- 44 Camouse MM, Domingo DS, Swain FR, Conrad EP, Matsui MS, Maes D, Declercq L, Cooper KD, Stevens SR and Baron ED, 2009, Topical application of green and white tea extracts provides protection from solar-simulated ultraviolet light in human skin, *Exp. Dermatol.*, **18**, 522-526.
- 45 Campbell-Stokes PL and Taylor BJ, 2005, Prospective incidence study of diabetes mellitus in New Zealand children aged 0 to 14 years, *Diabetologia*, **48**, 643-648.
- 46 Cancer Council Australia, 2007, Risks and benefits of sun exposure position statement, Cancer Council Australia, <http://www.cancer.org.au/File/PolicyPublications/PSRisksBenefitsSunExposure03May07.pdf>, accessed September, 2010.
- 47 Cannell JJ and Hollis BW, 2008, Use of vitamin D in clinical practice, *Alternat. Med. Rev.*, **13**, 6-20.
- 48 Cannell JJ, Vieth R, Umhau JC, Holick MF, Grant WB, Madronich S, Garland CF and Giovannucci E, 2006, Epidemic influenza and vitamin D, *Epidemiol. Infect.*, **134**, 1129-1140.
- 49 Cannell JJ, Zasloff M, Garland CF, Scragg R and Giovannucci E, 2008, On the epidemiology of influenza, *Virology*, **5**, 29.
- 50 Cantorna MT, Yu S and Bruce D, 2008, The paradoxical effects of vitamin D on type 1 mediated immunity, *Mol. Aspects Med.*, **29**, 369-375.
- 51 Carless MA, Kraska T, Lintell N, Neale RE, Green AC and Griffiths LR, 2008, Polymorphisms of the VDR gene are associated with presence of solar keratoses on the skin, *Br. J. Dermatol.*, **159**, 804-810.
- 52 Carter OB and Donovan RJ, 2007, Public (Mis)understanding of the UV Index, *J. Health. Commun.*, **12**, 41-52.
- 53 Casimiro E, Calheiros J, Santos FD and Kovats S, 2006, National assessment of human health effects of climate change in Portugal: approach and key findings, *Environ. Health Perspect.*, **114**, 1950-1956.
- 54 Chandler HL, Reuter KS, Sinnott LT and Nichols JJ, 2010, Prevention of UV-induced damage to the anterior segment using class I UV-absorbing hydrogel contact lenses, *Invest. Ophthalmol. Vis. Sci.*, **51**, 172-178.
- 55 Chang YM, Barrett JH, Bishop DT, Armstrong BK, Bataille V, Bergman W, Berwick M, Bracci PM, Elwood JM, Ernstoff MS, Gallagher RP, Green AC, Gruijs NA, Holly EA, Ingvar C, Kanetsky PA, Karagas MR, Lee TK, Le Marchand L, Mackie RM, Olsson H, Osterlind A, Rebbeck TR, Sasieni P, Siskind V, Swerdlow AJ, Titus-Ernstoff L, Zens MS and Newton-Bishop JA, 2009, Sun exposure and melanoma risk at different latitudes: a pooled analysis of 5700 cases and 7216 controls, *Int. J. Epidemiol.*, **38**, 814-830.
- 56 Charkaluk ML, Czernichow P and Levy-Marchal C, 2002, Incidence data of childhood-onset type I diabetes in France during 1988-1997: the case for a shift toward younger age at onset, *Pediat. Res.*, **52**, 859-862.
- 57 Chen AC, McMillan NA and Antonsson A, 2008, Human papillomavirus type spectrum in normal skin of individuals with or without a history of frequent sun exposure, *J. Gen. Virol.*, **89**, 2891-2897.

- 58 Chlebowski RT, Johnson KC, Kooperberg C, Pettinger M, Wactawski-Wende J, Rohan T, Rossouw J, Lane D, O'Sullivan MJ, Yasmeen S, Hiatt RA, Shikany JM, Vitolins M, Khandekar J and Hubbell FA, 2008, Calcium plus vitamin D supplementation and the risk of breast cancer, *J. Nat. Cancer. Inst.*, **100**, 1581-1591.
- 59 Chou B and Cullen A, 1986, Optical radiation protection by non-prescription sunglasses, *Can. J. Optom.*, **48**, 17-22.
- 60 Christian JB, Lapane KL, Hume AL, Eaton CB and Weinstock MA, 2008, Association of ACE inhibitors and angiotensin receptor blockers with keratinocyte cancer prevention in the randomized VATTC trial, *J. Nat. Cancer. Inst.*, **100**, 1223-1232.
- 61 CIE, 2006, Action Spectrum for the Production of Previtamin D3 in Human Skin, Commission Internationale d'Eclairage Report No. CIE Technical report 174-2006 Vienna. http://www.cie.co.at/div6/cie_174-2006.htm
- 62 Cinek O, Sumnik Z and Vavrinec J, 2003, Continuing increase in incidence of childhood-onset type 1 diabetes in the Czech Republic 1990-2001, *Eur. J. Pediatr.*, **162**, 428-429.
- 63 Clark RA, Huang SJ, Murphy GF, Mollet IG, Hijnen D, Muthukuru M, Schanbacher CF, Edwards V, Miller DM, Kim JE, Lambert J and Kupper TS, 2008, Human squamous cell carcinomas evade the immune response by down-regulation of vascular E-selectin and recruitment of regulatory T cells, *J. Exp. Med.*, **205**, 2221-2234.
- 64 Clemens TL, Adams JS, Henderson SL and Holick MF, 1982, Increased skin pigment reduces the capacity of skin to synthesise vitamin D3, *Lancet*, **1**, 74-76.
- 65 Colditz GA, Brewer TF, Berkey CS, Wilson ME, Burdick E, Fineberg HV and Mosteller F, 1994, Efficacy of BCG vaccine in the prevention of tuberculosis. Meta-analysis of the published literature, *J. Am. Med. Assoc.*, **271**, 698-702.
- 66 Connelly SJ, Wolyniak EA, Williamson CE and Jellison KL, 2007, Artificial UV-B and solar radiation reduce in vitro infectivity of the human pathogen *Cryptosporidium parvum*, *Environ. Sci. Technol.*, **41**, 7101-7106.
- 67 Coohill TP and Sagripanti JL, 2009, Bacterial inactivation by solar ultraviolet radiation compared with sensitivity to 254 nm radiation, *Photochem. Photobiol.*, **85**, 1043-1052.
- 68 Coory M, Baade P, Aitken J, Smithers M, McLeod GR and Ring I, 2006, Trends for in situ and invasive melanoma in Queensland, Australia, 1982-2002, *Cancer Causes Control*, **17**, 21-27.
- 69 Dal H, Boldemann C and Lindelof B, 2007, Does relative melanoma distribution by body site 1960-2004 reflect changes in intermittent exposure and intentional tanning in the Swedish population?, *Eur. J. Dermatol.*, **17**, 428-434.
- 70 Dal H, Boldemann C and Lindelof B, 2008, Trends during a half century in relative squamous cell carcinoma distribution by body site in the Swedish population: support for accumulated sun exposure as the main risk factor, *J. Dermatol.*, **35**, 55-62.
- 71 Dalmas M, England K, Boffa MJ, Degaetano J and Gatt P, 2007, Cutaneous melanoma in the Maltese Islands: 2000-2004, *Eur. J. Cancer.*, **43**, 1604-1610.
- 72 Damian DL, Halliday GM, Taylor CA and Barnetson RS, 1998, Ultraviolet radiation induced suppression of Mantoux reactions in humans, *J. Invest. Dermatol.*, **110**, 824-827.
- 73 Damian DL, Patterson CR, Stapelberg M, Park J, Barnetson RS and Halliday GM, 2008, UV radiation-induced immunosuppression is greater in men and prevented by topical nicotinamide, *J. Invest. Dermatol.*, **128**, 447-454.

- 74 Davies CM, Roser DJ, Feitz AJ and Ashbolt NJ, 2009, Solar radiation disinfection of drinking water at temperate latitudes: inactivation rates for an optimised reactor configuration, *Water Res.*, **43**, 643-652.
- 75 Davies PD, 1985, A possible link between vitamin D deficiency and impaired host defence to Mycobacterium tuberculosis, *Tubercle*, **66**, 301-306.
- 76 Dawson-Hughes B, Heaney RP, Holick MF, Lips P, Meunier PJ and Vieth R, 2005, Estimates of optimal vitamin D status, *Osteopor. Int.*, **16**, 713-716.
- 77 De Fabo EC, Noonan FP, Fears T and Merlino G, 2004, Ultraviolet B but not ultraviolet A radiation initiates melanoma, *Cancer. Res.*, **64**, 6372-6376.
- 78 de Feraudy S, Ridd K, Richards LM, Kwok PY, Revet I, Oh D, Feeney L and Cleaver JE, 2010, The DNA Damage-Binding Protein XPC Is a Frequent Target for Inactivation in Squamous Cell Carcinomas, *Am J Pathol*, **177**, 555-562.
- 79 de Gruijl FR, 2008, UV-induced immunosuppression in the balance, *Photochem. Photobiol.*, **84**, 2-9.
- 80 de Gruijl FR, Koehl GE, Voskamp P, Strik A, Rebel HG, Gaumann A, de Fijter JW, Tensen CP, Bavinck JN and Geissler EK, 2010, Early and late effects of the immunosuppressants rapamycin and mycophenolate mofetil on UV carcinogenesis, *Int J Cancer*, **127**, 796-804.
- 81 de Gruijl FR, Longstreth J, Norval M, Cullen AP, Slaper H, Kripke ML, Takizawa Y and van der Leun JC, 2003, Health effects from stratospheric ozone depletion and interactions with climate change, *Photochem. Photobiol. Sci.*, **2**, 16-28.
- 82 de Koning MN, Waddell K, Magyezi J, Purdie K, Proby C, Harwood C, Lucas S, Downing R, Quint WG and Newton R, 2008, Genital and cutaneous human papillomavirus (HPV) types in relation to conjunctival squamous cell neoplasia: A case-control study in Uganda, *Infect. Agents Cancer*, **3**, 12.
- 83 Dennis LK, Beane Freeman LE and VanBeek MJ, 2003, Sunscreen use and the risk for melanoma: a quantitative review, *Ann. Intern. Med.*, **139**, 966-978.
- 84 Dennis LK, Vanbeek MJ, Beane Freeman LE, Smith BJ, Dawson DV and Coughlin JA, 2008, Sunburns and risk of cutaneous melanoma: does age matter? A comprehensive meta-analysis, *Ann. Epidemiol.*, **18**, 614-627.
- 85 Detorakis ET and Spandidos DA, 2009, Pathogenetic mechanisms and treatment options for ophthalmic pterygium: trends and perspectives (Review), *Int. J. Mol. Med.*, **23**, 439-447.
- 86 Diffey B, 2000, Has the sun protection factor had its day?, *Br. Med. J.*, **320**, 176-177.
- 87 Diffey B, 2008, A behavioral model for estimating population exposure to solar ultraviolet radiation, *Photochem. Photobiol.*, **84**, 371-375.
- 88 Diffey BL, 2002, Sources and measurement of ultraviolet radiation, *Methods*, **28**, 4-13.
- 89 Diffey BL, 2009, Sunscreens as a preventative measure in melanoma: an evidence-based approach or the precautionary principle?, *Br. J. Dermatol.*, **161**, 25-27.
- 90 Diffey BL, 2010, Is casual exposure to summer sunlight effective at maintaining adequate vitamin D status?, *Photodermatol. Photoimmunol. Photomed.*, **26**, 172-176.
- 91 Diffey BL, 2010, Modelling the seasonal variation of vitamin D due to sun exposure, *Br. J. Dermatol.*, **162**, 1342-1348.
- 92 Dobbins S, Wakefield M, Hill D, Girgis A, Aitken JF, Beckmann K, Reeder AI, Herd N, Fairthorne A and Bowles KA, 2008, Prevalence and determinants of Australian adolescents' and adults' weekend sun protection and sunburn, summer 2003-2004, *J. Am. Acad. Dermatol.*, **59**, 602-614.

- 93 Dobbinson SJ, Wakefield MA, Jamsen KM, Herd NL, Spittal MJ, Lipscomb JE and Hill DJ, 2008, Weekend sun protection and sunburn in Australia trends (1987-2002) and association with SunSmart television advertising, *Am. J. Prev. Med.*, **34**, 94-101.
- 94 Dobbinson SJ, White V, Wakefield MA, Jamsen KM, White V, Livingston PM, English DR and Simpson JA, 2009, Adolescents' use of purpose built shade in secondary schools: cluster randomised controlled trial, *Br. Med. J.*, **338**, b95.
- 95 Dobnig H, Pilz S, Scharnagl H, Renner W, Seelhorst U, Wellnitz B, Kinkeldei J, Boehm BO, Weihrauch G and Maerz W, 2008, Independent association of low serum 25-hydroxyvitamin d and 1,25-dihydroxyvitamin d levels with all-cause and cardiovascular mortality, *Arch. Intern. Med.*, **168**, 1340-1349.
- 96 Dong X, Lofgren S, Ayala M and Soderberg PG, 2007, Maximum tolerable dose for avoidance of cataract after repeated exposure to ultraviolet radiation in rats, *Exp. Eye Res.*, **84**, 200-208.
- 97 Dongre AM, Pai GG and Khopkar US, 2007, Ultraviolet protective properties of branded and unbranded sunglasses available in the Indian market in UV phototherapy chambers, *Indian. J. Dermatol. Venereol. Leprol.*, **73**, 26-28.
- 98 Durruty P, Ruiz F and Garcia de los Rios M, 1979, Age at diagnosis and seasonal variation in the onset of insulin-dependent diabetes in Chile (Southern hemisphere), *Diabetologia*, **17**, 357-360.
- 99 Elliott JC, Lucas RM, Clements MS and Bambrick HJ, 2010, Population density determines the direction of the association between ambient ultraviolet radiation and type 1 diabetes incidence, *Pediatr. Diabetes*, **11**, 394-402.
- 100 Ellison TI, Smith MK, Gilliam AC and MacDonald PN, 2008, Inactivation of the vitamin D receptor enhances susceptibility of murine skin to UV-induced tumorigenesis, *J. Invest. Dermatol.*, **128**, 2508-2517.
- 101 Ema M, Naya M, Yoshida K and Nagaosa R, 2009, Reproductive and developmental toxicity of degradation products of refrigerants in experimental animals, *Reprod. Toxicol.*, **29**, 1-9.
- 102 Ema M, Naya M, Yoshida K and Nagaosa R, 2009, Reproductive and developmental toxicity of hydrofluorocarbons used as refrigerants, *Reprod. Toxicol.*, **29**, 125-131.
- 103 Faurschou A and Wulf HC, 2007, The relation between sun protection factor and amount of sunscreen applied in vivo, *Br. J. Dermatol.*, **156**, 716-719.
- 104 Feldman D, Skowronski RJ and Peehl DM, 1995, Vitamin D and prostate cancer, *Adv. Exp. Med. Biol.*, **375**, 53-63.
- 105 Fernandez A, Hu S and Kirsner RS, 2008, Sirolimus: a potential chemopreventive agent, *J. Invest. Dermatol.*, **128**, 2352.
- 106 Fioletov VE, McArthur LJ, Mathews TW and Marrett L, 2010, Estimated ultraviolet exposure levels for a sufficient vitamin D status in North America, *J. Photochem. Photobiol. B.*, **100**, 57-66.
- 107 Fisman DN, 2007, Seasonality of infectious diseases, *Ann. Rev. Pub. Hlth.*, **28**, 127-143.
- 108 Fletcher AE, Bentham GC, Agnew M, Young IS, Augood C, Chakravarthy U, de Jong PT, Rahu M, Seland J, Soubrane G, Tomazzoli L, Topouzis F, Vingerling JR and Vioque J, 2008, Sunlight exposure, antioxidants, and age-related macular degeneration, *Arch. Ophthalmol.*, **126**, 1396-1403.
- 109 Forslund O, Iftner T, Andersson K, Lindelof B, Hradil E, Nordin P, Stenquist B, Kirnbauer R, Dillner J and de Villiers EM, 2007, Cutaneous human papillomaviruses found in sun-exposed skin: Beta-papillomavirus species 2 predominates in squamous cell carcinoma, *J. Infect. Dis.*, **196**, 876-883.

- 110 Freedman DM, Dosemeci M and McGlynn K, 2002, Sunlight and mortality from breast, ovarian, colon, prostate, and non-melanoma skin cancer: a composite death certificate based case-control study, *Occ. Environ. Med.*, **59**, 257-262.
- 111 Freedman DM, Looker AC, Chang SC and Graubard BI, 2007, Prospective study of serum vitamin D and cancer mortality in the United States, *J. Nat. Cancer. Inst.*, **99**, 1594-1602.
- 112 Fris M, Cejkova J and Midelfart A, 2007, Changes in aqueous humour following single or repeated UVB irradiation of rabbit cornea, *Graefes Arch. Clin. Exp. Ophthalmol.*, **245**, 1705-1711.
- 113 Fris M, Cejkova J and Midelfart A, 2008, The effect of single and repeated UVB radiation on rabbit lens, *Graefes Arch. Clin. Exp. Ophthalmol.*, **246**, 551-558.
- 114 Fronczak CM, Baron AE, Chase HP, Ross C, Brady HL, Hoffman M, Eisenbarth GS, Rewers M and Norris JM, 2003, In utero dietary exposures and risk of islet autoimmunity in children, *Diab. Care*, **26**, 3237-3242.
- 115 Fukazawa T, Yabe I, Kikuchi S, Sasaki H, Hamada T, Miyasaka K and Tashiro K, 1999, Association of vitamin D receptor gene polymorphism with multiple sclerosis in Japanese, *J. Neurol. Sci.*, **166**, 47-52.
- 116 Gallagher RP, Rivers JK, Lee TK, Bajdik CD, McLean DI and Coldman AJ, 2000, Broad-spectrum sunscreen use and the development of new nevi in white children: A randomized controlled trial, *J. Am. Med. Assoc.*, **283**, 2955-2960.
- 117 Gambichler T, Skrygan M, Hyun J, Bechara F, Tomi NS, Altmeyer P and Kreuter A, 2006, Cytokine mRNA expression in basal cell carcinoma, *Arch. Dermatol. Res.*, **298**, 139-141.
- 118 Gandini S, Raimondi S, Gnagnarella P, Dore JF, Maisonneuve P and Testori A, 2009, Vitamin D and skin cancer: a meta-analysis, *Eur. J. Cancer.*, **45**, 634-641.
- 119 Garland CF, Gorham ED, Mohr SB and Garland FC, 2009, Vitamin D for cancer prevention: global perspective, *Ann. Epidemiol.*, **19**, 468-483.
- 120 Garland CF, Gorham ED, Mohr SB, Grant WB, Giovannucci EL, Lipkin M, Newmark H, Holick MF and Garland FC, 2007, Vitamin D and prevention of breast cancer: pooled analysis, *J. Steriod Biochem. Mol. Biolo.*, **103**, 708-711.
- 121 Geller AC, Hufford D, Miller DR, Sun T, Wyatt SW, Reilley B, Bewerse B, Lisco J, Brooks D, Grupenhoff J, Weary P, Lew RA and Koh HK, 1997, Evaluation of the Ultraviolet Index: media reactions and public response, *J. Am. Acad. Dermatol.*, **37**, 935-941.
- 122 Gies P, 2007, Photoprotection by clothing, *Photodermatol. Photoimmunol. Photomed.*, **23**, 264-274.
- 123 Gies P, Elix R, Lawry D, Gardner J, Hancock T, Cockerell S, Roy C, Javorniczky J and Henderson S, 2007, Assessment of the UVR protection provided by different tree species, *Photochem. Photobiol.*, **83**, 1465-1470.
- 124 Ginde AA, Liu MC and Camargo CA, Jr., 2009, Demographic differences and trends of vitamin D insufficiency in the US population, 1988-2004, *Arch. Intern. Med.*, **169**, 626-632.
- 125 Ginde AA, Mansbach JM and 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**, 384-390.
- 126 Ginde AA, Mansbach JM and Camargo CA, Jr., 2009, Vitamin D, respiratory infections, and asthma, *Curr. Allerg. Asthma Rep.*, **9**, 81-87.
- 127 Ginde AA, Scragg R, Schwartz RS and Camargo CA, Jr., 2009, Prospective study of serum 25-hydroxyvitamin d level, cardiovascular disease mortality, and all-cause mortality in older U.S. Adults, *J. Am. Geriat. Soc.*, **57**, 1595-1603.

- 128 Giovannucci E, 1998, Dietary influences of 1,25(OH)₂ vitamin D in relation to prostate cancer: a hypothesis, *Cancer Causes Control*, **9**, 567-582.
- 129 Giovannucci E, Liu Y, Hollis BW and Rimm EB, 2008, 25-hydroxyvitamin D and risk of myocardial infarction in men: a prospective study, *Arch. Intern. Med.*, **168**, 1174-1180.
- 130 Glaser R, Navid F, Schuller W, Jantschitsch C, Harder J, Schroder JM, Schwarz A and Schwarz T, 2009, UV-B radiation induces the expression of antimicrobial peptides in human keratinocytes in vitro and in vivo, *J. Allergy. Clin. Immunol.*, **123**, 1117-1123.
- 131 Gordon LG, Scuffham PA, van der Pols JC, McBride P, Williams GM and Green AC, 2009, Regular sunscreen use is a cost-effective approach to skin cancer prevention in subtropical settings, *J. Invest. Dermatol.*, **129**, 2766-2771.
- 132 Gorham ED, Barrett-Connor E, Highfill-McRoy RM, Mohr SB, Garland CF, Garland FC and Ricordi C, 2009, Incidence of insulin-requiring diabetes in the US military, *Diabetologia*, **52**, 2087-2091.
- 133 Gorham ED, Garland CF, Garland FC, Grant WB, Mohr SB, Lipkin M, Newmark HL, Giovannucci E, Wei M and Holick MF, 2007, Optimal vitamin D status for colorectal cancer prevention: a quantitative meta analysis, *Am. J. Ind. Hlth.*, **32**, 210-216.
- 134 Grant WB, 2002, An estimate of premature cancer mortality in the U.S. due to inadequate doses of solar ultraviolet-B radiation, *Cancer*, **94**, 1867-1875.
- 135 Grant WB, 2009, A critical review of Vitamin D and Cancer: A report of the IARC Working Group, *Dermato-endocrinol.*, **1**, 25-33.
- 136 Grant WB and Garland CF, 2006, The association of solar ultraviolet B (UVB) with reducing risk of cancer: multifactorial ecologic analysis of geographic variation in age-adjusted cancer mortality rates, *Anticancer. Res.*, **26**, 2687-2699.
- 137 Grant WB and Mohr SB, 2009, Ecological studies of ultraviolet B, vitamin D and cancer since 2000, *Ann. Epidemiol.*, **19**, 446-454.
- 138 Grant WB and Schuitmaker GE, 2010, Health benefits of higher serum 25-hydroxyvitamin D levels in The Netherlands, *J. Steriod Biochem. Mol. Biolo.*, **121**, 456-458.
- 139 Green A, Williams G, Neale R, Hart V, Leslie D, Parsons P, Marks GC, Gaffney P, Battistutta D, Frost C, Lang C and Russell A, 1999, Daily sunscreen application and betacarotene supplementation in prevention of basal-cell and squamous-cell carcinomas of the skin: a randomised controlled trial, *Lancet*, **354**, 723-729.
- 140 Green AC and Williams GM, 2007, Point: sunscreen use is a safe and effective approach to skin cancer prevention, *Cancer Epidemiol. Biomarkers. Prev.*, **16**, 1921-1922.
- 141 Gudbjartsson DF, Sulem P, Stacey SN, Goldstein AM, Rafnar T, Sigurgeirsson B, Benediktsdottir KR, Thorisdottir K, Ragnarsson R, Sveinsdottir SG, Magnusson V, Lindblom A, Kostulas K, Botella-Estrada R, Soriano V, Juberias P, Grasa M, Saez B, Andres R, Scherer D, Rudnai P, Gurzau E, Koppova K, Kiemeney LA, Jakobsdottir M, Steinberg S, Helgason A, Gretarsdottir S, Tucker MA, Mayordomo JI, Nagore E, Kumar R, Hansson J, Olafsson JH, Gulcher J, Kong A, Thorsteinsdottir U and Stefansson K, 2008, ASIP and TYR pigmentation variants associate with cutaneous melanoma and basal cell carcinoma, *Nat. Genet.*, **40**, 886-891.
- 142 Hagenau T, Vest R, Gissel TN, Poulsen CS, Erlandsen M, Mosekilde L and Vestergaard P, 2009, Global vitamin D levels in relation to age, gender, skin pigmentation and latitude: an ecologic meta-regression analysis, *Osteopor. Int.*, **20**, 133-140.

- 143 Haines A, McMichael AJ and Epstein PR, 2000, Environment and health: 2. Global climate change and health, *Can. Med. Assoc. J.*, **163**, 729-734.
- 144 Hanwell HE, Vieth R, Cole DE, Scillitani A, Modoni S, Frusciante V, Ritrovato G, Chiodini I, Minisola S and Carnevale V, 2010, Sun exposure questionnaire predicts circulating 25-hydroxyvitamin D concentrations in Caucasian hospital workers in southern Italy, *J. Steriod Biochem. Mol. Biolo.*, **121**, 334-337.
- 145 Harrison SL, Buettner PG and MacLennan R, 2005, The North Queensland "Sun-Safe Clothing" study: design and baseline results of a randomized trial to determine the effectiveness of sun-protective clothing in preventing melanocytic nevi, *Am. J. Epid.*, **161**, 536-545.
- 146 Harrison SL, MacLennan R and Buettner PG, 2008, Sun exposure and the incidence of melanocytic nevi in young Australian children, *Cancer Epidemiol. Biomarkers. Prev.*, **17**, 2318-2324.
- 147 Harwood CA, Suretheran T, McGregor JM, Spink PJ, Leigh IM, Breuer J and Proby CM, 2000, Human papillomavirus infection and non-melanoma skin cancer in immunosuppressed and immunocompetent individuals, *J. Med. Virol.*, **61**, 289-297.
- 148 Hawk JL, 2004, Chronic actinic dermatitis, *Photodermatol. Photoimmunol. Photomed.*, **20**, 312-314.
- 149 Heitzer E, Lassacher A, Quehenberger F, Kerl H and Wolf P, 2007, UV fingerprints predominate in the PTCH mutation spectra of basal cell carcinomas independent of clinical phenotype, *J. Invest. Dermatol.*, **127**, 2872-2881.
- 150 Hirakawa M, Tanaka M, Tanaka Y, Okubo A, Koriyama C, Tsuji M, Akiba S, Miyamoto K, Hillebrand G, Yamashita T and Sakamoto T, 2008, Age-related maculopathy and sunlight exposure evaluated by objective measurement, *Br. J. Ophthalmol.*, **92**, 630-634.
- 151 Hirani V, Tull K, Ali A and Mindell J, 2010, Urgent action needed to improve vitamin D status among older people in England!, *Age and Ageing*, **39**, 62-68.
- 152 Holick MF, 2003, Vitamin D: A millenium perspective, *J. Cell. Biochem.*, **88**, 296-307.
- 153 Holick MF, 2008, The vitamin D deficiency pandemic and consequences for nonskeletal health: mechanisms of action, *Mol. Aspects Med.*, **29**, 361-368.
- 154 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**, 317-322.
- 155 Holly EA, Aston DA, Char DH, Kristiansen JJ and Ahn DK, 1990, Uveal melanoma in relation to ultraviolet light exposure and host factors, *Cancer. Res.*, **50**, 5773-5777.
- 156 Hu DN, Simon JD and Sarna T, 2008, Role of ocular melanin in ophthalmic physiology and pathology, *Photochem. Photobiol.*, **84**, 639-644.
- 157 Hu DN, Yu GP, McCormick SA, Schneider S and Finger PT, 2005, Population-based incidence of uveal melanoma in various races and ethnic groups, *Am. J. Ophthalmol.*, **140**, 612-617.
- 158 Hughes DA and Norton R, 2009, Vitamin D and respiratory health, *Clin. Exp. Immunol.*, **158**, 20-25.
- 159 Huncharek M and Kupelnick B, 2002, Use of topical sunscreens and the risk of malignant melanoma: a meta-analysis of 9067 patients from 11 case-control studies, *Am. J. Pub. Hlth.*, **92**, 1173-1177.
- 160 Hypponen E, Laara E, Reunanen A, Jarvelin MR and Virtanen SM, 2001, Intake of vitamin D and risk of type 1 diabetes: a birth-cohort study, *Lancet*, **358**, 1500-1503.
- 161 IARC, 2001, Sunscreens, International Agency for Research on Cancer, World Health Organization Report No. 92-832-3005-1, Lyon,

- 162 IARC, 2008, Vitamin D and Cancer, World Health Organization International Agency for Research on Cancer Report No. IARC Working Group Reports; 5, Lyon,
- 163 Iftner T, Elbel M, Schopp B, Hiller T, Loizou JI, Caldecott KW and Stubenrauch F, 2002, Interference of papillomavirus E6 protein with single-strand break repair by interaction with XRCC1, *EMBO J.*, **21**, 4741-4748.
- 164 Ilyas M, 2007, Climate augmentation of erythematous UV-B radiation dose damage in the tropics and global change, *Curr. Sci.*, **93**, 1604-1608.
- 165 Jeevan A, Sharma AK and McMurray DN, 2009, Ultraviolet radiation reduces resistance to Mycobacterium tuberculosis infection in BCG-vaccinated guinea pigs, *Tuberculosis (Edinb)*, **89**, 431-438.
- 166 Jeffery LE, Burke F, Mura M, Zheng Y, Qureshi OS, Hewison M, Walker LS, Lammas DA, Raza K and Sansom DM, 2009, 1,25-Dihydroxyvitamin D3 and IL-2 combine to inhibit T cell production of inflammatory cytokines and promote development of regulatory T cells expressing CTLA-4 and FoxP3, *J. Immunol.*, **183**, 5458-5467.
- 167 Jenab M, Bueno-de-Mesquita HB, Ferrari P, van Duijnhoven FJ, Norat T, Pischon T, Jansen EH, Slimani N, Byrnes G, Rinaldi S, Tjonneland A, Olsen A, Overvad K, Boutron-Ruault MC, Clavel-Chapelon F, Morois S, Kaaks R, Linseisen J, Boeing H, Bergmann MM, Trichopoulou A, Misirli G, Trichopoulos D, Berrino F, Vineis P, Panico S, Palli D, Tumino R, Ros MM, van Gils CH, Peeters PH, Brustad M, Lund E, Tormo MJ, Ardanaz E, Rodriguez L, Sanchez MJ, Dorronsoro M, Gonzalez CA, Hallmans G, Palmqvist R, Roddam A, Key TJ, Khaw KT, Autier P, Hainaut P and Riboli E, 2010, Association between pre-diagnostic circulating vitamin D concentration and risk of colorectal cancer in European populations: a nested case-control study, *Br. Med. J.*, **340**, b5500.
- 168 John EM, Dreon DM, Koo J and Schwartz GG, 2004, Residential sunlight exposure is associated with a decreased risk of prostate cancer, *J. Steroid Biochem. Mol. Biol.*, **89-90**, 549-552.
- 169 Kannengiesser C, Spatz A, Michiels S, Eychene A, Dessen P, Lazar V, Winnepenninckx V, Lesueur F, Druillennec S, Robert C, van den Oord JJ, Sarasin A and Bressac-de Paillerets B, 2008, Gene expression signature associated with BRAF mutations in human primary cutaneous melanomas, *Mol. Oncol.*, **1**, 425-430.
- 170 Kaporis HG, Guttman-Yassky E, Lowes MA, Haider AS, Fuentes-Duculan J, Darabi K, Whynot-Ertelt J, Khatcherian A, Cardinale I, Novitskaya I, Krueger JG and Carucci JA, 2007, Human basal cell carcinoma is associated with Foxp3+ T cells in a Th2 dominant microenvironment, *J. Invest. Dermatol.*, **127**, 2391-2398.
- 171 Karatekin G, Kaya A, Salihoglu O, Balci H and Nuhoglu A, 2009, Association of subclinical vitamin D deficiency in newborns with acute lower respiratory infection and their mothers, *Eur. J. Clin. Nutr.*, **63**, 473-477.
- 172 Karlsson PM and Fredrikson M, 2007, Cutaneous malignant melanoma in children and adolescents in Sweden, 1993-2002: the increasing trend is broken, *Int. J. Cancer*, **121**, 323-328.
- 173 Kazantzidis A, Bais AF, Zempila MM, Kazadzis S, den Outer PN, Koskela T and Slaper H, 2009, Calculations of the human vitamin D exposure from UV spectral measurements at three European stations, *Photochem. Photobiol. Sci.*, **8**, 45-51.
- 174 Ke MS, Camouse MM, Swain FR, Oshtory S, Matsui M, Mammone T, Maes D, Cooper KD, Stevens SR and Baron ED, 2008, UV protective effects of DNA repair enzymes and RNA lotion, *Photochem. Photobiol.*, **84**, 180-184.
- 175 Kimlin MG and Schallhorn KA, 2004, Estimations of the human 'vitamin D' UV exposure in the USA, *Photochem. Photobiol. Sci.*, **3**, 1067-1070.

- 176 King BJ, Hoefel D, Daminato DP, Fanok S and Monis PT, 2008, Solar UV reduces *Cryptosporidium parvum* oocyst infectivity in environmental waters, *J. Appl. Microbiol.*, **104**, 1311-1323.
- 177 Kinlin LM, Spain CV, Ng V, Johnson CC, White AN and Fisman DN, 2009, Environmental exposures and invasive meningococcal disease: an evaluation of effects on varying time scales, *Am. J. Epid.*, **169**, 588-595.
- 178 Konety BR, Johnson CS, Trump DL and Getzenberg RH, 1999, Vitamin D in the prevention and treatment of prostate cancer, *Sem Urolog. Oncol.*, **17**, 77-84.
- 179 Krause R, Buhning M, Hopfenmuller W, Holick MF and Sharma AM, 1998, Ultraviolet B and blood pressure, *Lancet*, **352**, 709-710.
- 180 Kripke ML, 1974, Antigenicity of murine skin tumors induced by ultraviolet light, *J. Nat. Cancer. Inst.*, **53**, 1333-1336.
- 181 Kristal AR, Cohen JH, Qu P and Stanford JL, 2002, Associations of energy, fat, calcium, and vitamin D with prostate cancer risk, *Cancer Epidemiol. Biomarkers. Prev.*, **11**, 719-725.
- 182 Kuchuk NO, van Schoor NM, Pluijm SM, Chines A and Lips P, 2009, Vitamin D status, parathyroid function, bone turnover, and BMD in postmenopausal women with osteoporosis: global perspective, *J. Bone Mineral Res.*, **24**, 693-701.
- 183 Kyle JW, Hammitt JK, Lim HW, Geller AC, Hall-Jordan LH, Maibach EW, De Fabo EC and Wagner MC, 2008, Economic evaluation of the US Environmental Protection Agency's SunWise program: sun protection education for young children, *Pediatrics.*, **121**, e1074-1084.
- 184 Kyu-Won C, Chae-Young L, Yeong-Kyu L, Young-Hun K and Ki-Ho K, 2009, A Korean experience with chronic actinic dermatitis during an 18-year period: meteorological and photoimmunological aspects, *Photodermatol. Photoimmunol. Photomed.*, **25**, 286-292.
- 185 Laaksi I, Ruohola JP, Tuohimaa P, Auvinen A, Haataja R, Pihlajamaki H and Ylikomi T, 2007, An association of serum vitamin D concentrations < 40 nmol/L with acute respiratory tract infection in young Finnish men, *Am. J. Clin. Nutr.*, **86**, 714-717.
- 186 Lam LT, 2007, The association between climatic factors and childhood illnesses presented to hospital emergency among young children, *Int. J. Environ. Hlth. Res.*, **17**, 1-8.
- 187 Lange JR, Palis BE, Chang DC, Soong SJ and Balch CM, 2007, Melanoma in children and teenagers: an analysis of patients from the National Cancer Data Base, *J. Clin. Oncol.*, **25**, 1363-1368.
- 188 Lautenschlager S, Wulf HC and Pittelkow MR, 2007, Photoprotection, *Lancet*, **370**, 528-537.
- 189 Lea CS, Scotto JA, Buffler PA, Fine J, Barnhill RL and Berwick M, 2007, Ambient UVB and melanoma risk in the United States: a case-control analysis, *Ann. Epidemiol.*, **17**, 447-453.
- 190 Leiter U and Garbe C, 2008, Epidemiology of melanoma and nonmelanoma skin cancer - the role of sunlight, *Adv. Exp. Med. Biol.*, **624**, 89-103.
- 191 Lembo S, Fallon J, O'Kelly P and Murphy GM, 2008, Polymorphic light eruption and skin cancer prevalence: is one protective against the other?, *Br. J. Dermatol.*, **159**, 1342-1347.
- 192 Levell NJ, Beattie CC, Shuster S and Greenberg DC, 2009, Melanoma epidemic: a midsummer night's dream?, *Br. J. Dermatol.*, **161**, 630-634.
- 193 Li XH, Li TL, Yang Z, Liu ZY, Wei YD, Jin SX, Hong C, Qin RL, Li YQ, Dorman JS, Laporte RE and Wang KA, 2000, A nine-year prospective study on the incidence of childhood type 1 diabetes mellitus in China, *Biomed. Environ. Sci.*, **13**, 263-270.

- 194 Linder N, Abudi Y, Abdalla W, Badir M, Amitai Y, Samuels J, Mendelson E and Levy I, 2009, Effect of season of inoculation on immune response to rubella vaccine in children, *J. Trop. Pediat.*, DOI: 10.1093/tropej/fmp1104.
- 195 Linos E, Swetter SM, Cockburn MG, Colditz GA and Clarke CA, 2009, Increasing burden of melanoma in the United States, *J. Invest. Dermatol.*, **129**, 1666-1674.
- 196 Lipozencic J, Jurakic-Toncic R, Rados J and Celic D, 2008, Epidemiology of nonmelanoma and melanoma skin cancer in Zagreb, Croatia, *Acta Dermatovenerol. Croatica*, **16**, 193-203.
- 197 Lips P, Duong T, Oleksik A, Black D, Cummings S, Cox D and Nickelsen T, 2001, A global study of vitamin D status and parathyroid function in postmenopausal women with osteoporosis: baseline data from the multiple outcomes of raloxifene evaluation clinical trial, *J. Clin. Endocrinol. Metab.*, **86**, 1212-1221.
- 198 Longstreth J, de Gruijl FR, Kripke ML, Abseck S, Arnold F, Slaper HI, Velders G, Takizawa Y and van der Leun JC, 1998, Health risks, *J. Photochem. Photobiol. B.*, **46**, 20-39.
- 199 Lucas CR, Ke MS, Matsui MS, Maes D, Cooper KD, Stevens SR and Baron ED, 2008, Immune protective effect of a moisturizer with DNA repair ingredients, *J. Cosmet. Dermatol.*, **7**, 132-135.
- 200 Mabruk MJ, Toh LK, Murphy M, Leader M, Kay E and Murphy GM, 2009, Investigation of the effect of UV irradiation on DNA damage: comparison between skin cancer patients and normal volunteers, *J. Cutan. Pathol.*, **36**, 760-765.
- 201 Macdonald HM, Mavroeidi A, Barr RJ, Black AJ, Fraser WD and Reid DM, 2008, Vitamin D status in postmenopausal women living at higher latitudes in the UK in relation to bone health, overweight, sunlight exposure and dietary vitamin D, *Bone*, **42**, 996-1003.
- 202 MacLaughlin J and Holick MF, 1985, Aging decreases the capacity of human skin to produce vitamin D₃, *J. Clin. Invest.*, **76**, 1536-1538.
- 203 MacLaughlin JA, Anderson RR and Holick MF, 1982, Spectral character of sunlight modulates photosynthesis of previtamin D₃ and its photoisomers in human skin, *Science*, **216**, 1001-1003.
- 204 Mainster MA and Turner PL, 2009, Blue-blocking intraocular lenses: myth or reality?, *Am. J. Ophthalmol.*, **147**, 8-10.
- 205 Martineau AR, Honecker FU, Wilkinson RJ and Griffiths CJ, 2007, Vitamin D in the treatment of pulmonary tuberculosis, *J. Steriod Biochem. Mol. Biolo.*, **103**, 793-798.
- 206 Matsui MS, Hsia A, Miller JD, Hanneman K, Scull H, Cooper KD and Baron E, 2009, Non-sunscreen photoprotection: antioxidants add value to a sunscreen, *J. Invest. Dermatol. Symp. Proc.*, **14**, 56-59.
- 207 McKenzie RL, Liley JB and Bjorn LO, 2009, UV radiation: balancing risks and benefits, *Photochem. Photobiol.*, **85**, 88-98.
- 208 McLeod JG, Hammond SR and Hallpike JF, 1994, Epidemiology of multiple sclerosis in Australia. With NSW and SA survey results, *Med. J. Aust.*, **160**, 117-122.
- 209 McMichael AJ and Hall AJ, 1997, Does immunosuppressive ultraviolet radiation explain the latitude gradient for multiple sclerosis?, *Epidemiol.*, **8**, 642-645.
- 210 McMichael AJ, Neira M, Bertollini R, Campbell-Lendrum D and Hales S, 2009, Climate change: a time of need and opportunity for the health sector, *Lancet*, **374**, 2123-2125.
- 211 Meyer LM, Dong X, Wegener A and Soderberg P, 2008, Dose dependent cataractogenesis and Maximum Tolerable Dose (MTD(2.3:16)) for UVR 300 nm-induced cataract in C57BL/6J mice, *Exp. Eye Res.*, **86**, 282-289.

- 212 Mitchell DL, Fernandez AA, Nairn RS, Garcia R, Paniker L, Trono D, Thames HD and Gimenez-Conti I, 2010, Ultraviolet A does not induce melanomas in a Xiphophorus hybrid fish model, *Proc. Nat. Acad. Sci. USA.*, **107**, 9329-9334.
- 213 Mnich CD, Hoek KS, Virkki LV, Farkas A, Dudli C, Laine E, Urošević M and Dummer R, 2009, Green tea extract reduces induction of p53 and apoptosis in UVB-irradiated human skin independent of transcriptional controls, *Exp. Dermatol.*, **18**, 69-77.
- 214 Mody VC, Kakar M, Elfving A and Lofgren S, 2008, Drinking water supplementation with ascorbate is not protective against UVR-B-induced cataract in the guinea pig, *Acta Ophthalmol.*, **86**, 188-195.
- 215 Moehrle M, 2008, Outdoor sports and skin cancer, *Clin. Dermatol.*, **26**, 12-15.
- 216 Mohr SB, Garland CF, Gorham ED and Garland FC, 2008, The association between ultraviolet B irradiance, vitamin D status and incidence rates of type 1 diabetes in 51 regions worldwide, *Diabetologia*, **51**, 1391-1398.
- 217 Mohr SB, Garland CF, Gorham ED, Grant WB and Garland FC, 2008, Relationship between low ultraviolet B irradiance and higher breast cancer risk in 107 countries, *Breast J.*, **14**, 255-260.
- 218 Moise AF and Aynsley R, 1999, Ambient ultraviolet radiation levels in public shade settings, *Int. J. Biometeorol.*, **43**, 128-138.
- 219 Mokady E, Schwartz B, Shany S and Lamprecht SA, 2000, A protective role of dietary vitamin D3 in rat colon carcinogenesis, *Nutr. Cancer.*, **38**, 65-73.
- 220 Montella A, Gavin A, Middleton R, Autier P and Boniol M, 2009, Cutaneous melanoma mortality starting to change: a study of trends in Northern Ireland, *Eur. J. Cancer.*, **45**, 2360-2366.
- 221 Muller HK, Malley RC, McGee HM, Scott DK, Wozniak T and Woods GM, 2008, Effect of UV radiation on the neonatal skin immune system- implications for melanoma, *Photochem. Photobiol.*, **84**, 47-54.
- 222 Munger KL, Levin LI, Hollis BW, Howard NS and Ascherio A, 2006, Serum 25-hydroxyvitamin D levels and risk of multiple sclerosis, *J. Am. Med. Assoc.*, **296**, 2832-2838.
- 223 Munger KL, Zhang SM, O'Reilly E, Hernan MA, Olek MJ, Willett WC and Ascherio A, 2004, Vitamin D intake and incidence of multiple sclerosis, *Neurology*, **62**, 60-65.
- 224 Murray JC, Burch JA, Streilein RD, Iannacchione MA, Hall RP and Pinnell SR, 2008, A topical antioxidant solution containing vitamins C and E stabilized by ferulic acid provides protection for human skin against damage caused by ultraviolet irradiation, *J. Am. Acad. Dermatol.*, **59**, 418-425.
- 225 Nagano T, Kunisada M, Yu X, Masaki T and Nishigori C, 2008, Involvement of interleukin-10 promoter polymorphisms in nonmelanoma skin cancers-a case study in non-Caucasian skin cancer patients, *Photochem. Photobiol.*, **84**, 63-66.
- 226 Narbutt J, Lesiak A, Skibinska M, Wozniacka A, van Loveren H, Sysa-Jedrzejowska A, Lewy-Trenda I, Omulecka A and Norval M, 2005, Suppression of contact hypersensitivity after repeated exposures of humans to low doses of solar simulated radiation, *Photochem. Photobiol. Sci.*, **4**, 517-522.
- 227 Neale RE, Davis M, Pandeya N, Whiteman DC and Green AC, 2007, Basal cell carcinoma on the trunk is associated with excessive sun exposure, *J. Am. Acad. Dermatol.*, **56**, 380-386.
- 228 Ng K, Meyerhardt JA, Wu K, Feskanich D, Hollis BW, Giovannucci EL and Fuchs CS, 2008, Circulating 25-hydroxyvitamin D levels and survival in patients with colorectal cancer, *J. Clin. Oncol.*, **26**, 2984-2991.

- 229 Nicol I, Gaudy C, Gouvernet J, Richard MA and Grob JJ, 2007, Skin protection by sunscreens is improved by explicit labeling and providing free sunscreen, *J. Invest. Dermatol.*, **127**, 41-48.
- 230 Nikolaou VA, Sypsa V, Stefanaki I, Gogas H, Papadopoulos O, Polydorou D, Plaka M, Tsoutsos D, Dimou A, Mourtzoukou E, Korfitis V, Hatziolou E, Antoniou C, Hatzakis A, Katsambas A and Stratigos AJ, 2008, Risk associations of melanoma in a Southern European population: results of a case/control study, *Cancer Causes Control*, **19**, 671-679.
- 231 Nikolova PN, Pawelec GP, Mihailova SM, Ivanova MI, Myhailova AP, Baltadjieva DN, Marinova DI, Ivanova SS and Naumova EJ, 2007, Association of cytokine gene polymorphisms with malignant melanoma in Caucasian population, *Cancer Immunol. Immunotherap.*, **56**, 371-379.
- 232 Nnoaham KE and Clarke A, 2008, Low serum vitamin D levels and tuberculosis: a systematic review and meta-analysis, *Int. J. Epidemiol.*, **37**, 113-119.
- 233 Nohynek GJ, Antignac E, Re T and Toutain H, 2010, Safety assessment of personal care products/cosmetics and their ingredients, *Toxicol. Appl. Pharmacol.*, **243**, 239-259.
- 234 Norval M, Bjorn LO and de Gruijl FR, 2009, Is the action spectrum for the UV-induced production of previtamin D3 in human skin correct?, *Photochem. Photobiol. Sci.*, **9**, 11-17.
- 235 Norval M, Cullen AP, de Gruijl FR, Longstreth J, Takizawa Y, Lucas RM, Noonan FP and van der Leun JC, 2007, The effects on human health from stratospheric ozone depletion and its interactions with climate change, *Photochem. Photobiol. Sci.*, **6**, 232-251.
- 236 Norval M, McLoone P, Lesiak A and Narbutt J, 2008, The effect of chronic ultraviolet radiation on the human immune system, *Photochem. Photobiol.*, **84**, 19-28.
- 237 Norval M and Wulf HC, 2009, Does chronic sunscreen use reduce vitamin D production to insufficient levels?, *Br. J. Dermatol.*, **161**, 732-736.
- 238 Oberyszyn TM, 2008, Non-melanoma skin cancer: importance of gender, immunosuppressive status and vitamin D, *Cancer Lett.*, **261**, 127-136.
- 239 Olsen CM, Zens MS, Stukel TA, Sacerdote C, Chang YM, Armstrong BK, Bataille V, Berwick M, Elwood JM, Holly EA, Kirkpatrick C, Mack T, Bishop JN, Osterlind A, Swerdlow AJ, Zanetti R, Green AC, Karagas MR and Whiteman DC, 2009, Nevus density and melanoma risk in women: a pooled analysis to test the divergent pathway hypothesis, *Int. J. Cancer*, **124**, 937-944.
- 240 Onkamo P, Vaananen S, Karvonen M and Tuomilehto J, 1999, Worldwide increase in incidence of Type I diabetes, *Diabetologia*, **42**, 1395-1403.
- 241 Oriowo OM, Cullen AP, Chou BR and Sivak JG, 2001, Action spectrum and recovery for in vitro UV-induced cataract using whole lenses, *Invest. Ophthalmol. Vis. Sci.*, **42**, 2596-2602.
- 242 Orton SM, Morris AP, Herrera BM, Ramagopalan SV, Lincoln MR, Chao MJ, Vieth R, Sadovnick AD and Ebers GC, 2008, Evidence for genetic regulation of vitamin D status in twins with multiple sclerosis, *Am. J. Clin. Nutr.*, **88**, 441-447.
- 243 Ostman J, Lonnberg G, Arnqvist HJ, Blohme G, Bolinder J, Ekbom Schnell A, Eriksson JW, Gudbjornsdottir S, Sundkvist G and Nystrom L, 2008, Gender differences and temporal variation in the incidence of type 1 diabetes: results of 8012 cases in the nationwide Diabetes Incidence Study in Sweden 1983-2002, *J. Internal Med.*, **263**, 386-394.

- 244 Pakker H, Martins S, Boelen P, Buma A, Nikaido O and Breeman A, 2000, Effects of temperature on the photoreactivation of ultraviolet-B-induced DNA damage in *Palmaria palmate* (Rhodophyta), *J. Phycol.*, **36**, 334-341.
- 245 Patz JA, Olson SH, Uejio CK and Gibbs HK, 2008, Disease emergence from global climate and land use change, *Med. Clin. N. Am.*, **92**, 1473-1491.
- 246 Peehl DM, 1999, Vitamin D and prostate cancer risk, *Eur. Urol.*, **35**, 392-394.
- 247 Peguet-Navarro J, Dezutter-Dambuyant C, Buetler T, Leclaire J, Smola H, Blum S, Bastien P, Breton L and Gueniche A, 2008, Supplementation with oral probiotic bacteria protects human cutaneous immune homeostasis after UV exposure-double blind, randomized, placebo controlled clinical trial, *Eur. J. Dermatol.*, **18**, 504-511.
- 248 Pellacani G, Lo Scocco G, Vinceti M, Albertini G, Raccagni AA, Baldassari L, Catrani S, Donelli S, Ghetti P, Lanzoni A, Leardini M, Reggiani M, Santini M, Stanganelli I, Virgili A and Seidenari S, 2008, Melanoma epidemic across the millennium: time trends of cutaneous melanoma in Emilia-Romagna (Italy) from 1997 to 2004, *J. Eur. Acad. Dermatol. Venereol.*, **22**, 213-218.
- 249 Pettijohn KJ, Asdigian NL, Aalborg J, Morelli JG, Mokrohisky ST, Dellavalle RP and Crane LA, 2009, Vacations to waterside locations result in nevus development in Colorado children, *Cancer Epidemiol. Biomarkers. Prev.*, **18**, 454-463.
- 250 Pham TQ, Rochtchina E, Mitchell P, Smith W and Wang JJ, 2009, Sunlight-related factors and the 10-year incidence of age-related maculopathy, *Ophthalmic. Epidemiol.*, **16**, 136-141.
- 251 Pinto AV, Deodato EL, Cardoso JS, Oliveira EF, Machado SL, Toma HK, Leitao AC and de Padula M, 2010, Enzymatic recognition of DNA damage induced by UVB-photosensitized titanium dioxide and biological consequences in *Saccharomyces cerevisiae*: evidence for oxidatively DNA damage generation, *Mutat. Res.*, **688**, 3-11.
- 252 Pleasance ED, Cheetham RK, Stephens PJ, McBride DJ, Humphray SJ, Greenman CD, Varela I, Lin ML, Ordonez GR, Bignell GR, Ye K, Alipaz J, Bauer MJ, Beare D, Butler A, Carter RJ, Chen L, Cox AJ, Edkins S, Kokko-Gonzales PI, Gormley NA, Grocock RJ, Haudenschield CD, Hims MM, James T, Jia M, Kingsbury Z, Leroy C, Marshall J, Menzies A, Mudie LJ, Ning Z, Royce T, Schulz-Trieglaff OB, Spiridou A, Stebbings LA, Szajkowski L, Teague J, Williamson D, Chin L, Ross MT, Campbell PJ, Bentley DR, Futreal PA and Stratton MR, 2010, A comprehensive catalogue of somatic mutations from a human cancer genome, *Nature*, **463**, 191-196.
- 253 Ponsonby AL, Pezic A, Ellis J, Morley R, Cameron F, Carlin J and Dwyer T, 2008, Variation in associations between allelic variants of the vitamin D receptor gene and onset of type 1 diabetes mellitus by ambient winter ultraviolet radiation levels: a meta-regression analysis, *Am. J. Epidemiol.*, **168**, 358-365.
- 254 Pope SJ, Holick MF, Mackin S and Godar DE, 2008, Action spectrum conversion factors that change erythemally weighted to previtamin D3-weighted UV doses, *Photochem. Photobiol.*, **84**, 1277-1283.
- 255 Pruthi DK, Guilfoyle R, Nugent Z, Wiseman MC and Demers AA, 2009, Incidence and anatomic presentation of cutaneous malignant melanoma in central Canada during a 50-year period: 1956 to 2005, *J. Am. Acad. Dermatol.*, **61**, 44-50.
- 256 Purdie KJ, Pennington J, Proby CM, Khalaf S, de Villiers EM, Leigh IM and Storey A, 1999, The promoter of a novel human papillomavirus (HPV77) associated with skin cancer displays UV responsiveness, which is mediated through a consensus p53 binding sequence, *EMBO J.*, **18**, 5359-5369.
- 257 Qureshi AA, Laden F, Colditz GA and Hunter DJ, 2008, Geographic variation and risk of skin cancer in US women. Differences between melanoma, squamous cell carcinoma, and basal cell carcinoma, *Arch. Intern. Med.*, **168**, 501-507.

- 258 Ramagopalan SV, Maugeri NJ, Handunnetthi L, Lincoln MR, Orton SM, Dymant DA, Deluca GC, Herrera BM, Chao MJ, Sadovnick AD, Ebers GC and Knight JC, 2009, Expression of the multiple sclerosis-associated MHC class II Allele HLA-DRB1*1501 is regulated by vitamin D, *PLoS Genet.*, **5**, e1000369.
- 259 Reddy KK and Gilchrist BA, 2010, What is all this commotion about vitamin D?, *J. Invest. Dermatol.*, **130**, 321-326.
- 260 Reich A, Harupa M, Bury M, Chrzaszcz J and Starczewska A, 2009, Application of sunscreen preparations: a need to change the regulations, *Photodermatol. Photoimmunol. Photomed.*, **25**, 242-244.
- 261 Rhodes LE, Bock M, Janssens AS, Ling TC, Anastasopoulou L, Antoniou C, Aubin F, Bruckner T, Faivre B, Gibbs NK, Jansen C, Pavel S, Stratigos AJ, de Gruijl FR and Diepgen TL, 2010, Polymorphic light eruption occurs in 18% of europeans and does not show higher prevalence with increasing latitude: multicenter survey of 6,895 individuals residing from the Mediterranean to Scandinavia, *J. Invest. Dermatol.*, **130**, 626-628.
- 262 Rhodes LE, Webb AR, Fraser HI, Kift R, Durkin MT, Allan D, O'Brien SJ, Vail A and Berry JL, 2010, Recommended Summer Sunlight Exposure Levels Can Produce Sufficient (≥ 20 ng ml⁻¹) but Not the Proposed Optimal (≥ 32 ng ml⁻¹) 25(OH)D Levels at UK Latitudes, *J. Invest. Dermatol.*, **130**, 1411-1418.
- 263 Richardson A, Fletcher L, Sneyd M, Cox B and Reeder AI, 2008, The incidence and thickness of cutaneous malignant melanoma in New Zealand 1994-2004, *N. Z. Med. J.*, **121**, 18-26.
- 264 Richmond-Sinclair NM, Pandeya N, Ware RS, Neale RE, Williams GM, van der Pols JC and Green AC, 2009, Incidence of basal cell carcinoma multiplicity and detailed anatomic distribution: longitudinal study of an Australian population, *J. Invest. Dermatol.*, **129**, 323-328.
- 265 Richtig E, Berghold A, Schwantzer G, Ott A, Wolfelmaier F, Karner B, Ludwig R, Denk H, Stering R, Leitner G, Lax S, Okcu M, Gerger A, Kerl H and Smolle J, 2007, Clinical epidemiology of invasive cutaneous malignant melanoma in the Austrian province Styria in the years 2001-2003 and its relationship with local geographical, meteorological and economic data, *Dermatol.*, **214**, 246-252.
- 266 Robinson ES, Hill RH, Jr., Kripke ML and Setlow RB, 2000, The Monodelphis melanoma model: initial report on large ultraviolet A exposures of suckling young, *Photochem. Photobiol.*, **71**, 743-746.
- 267 Roche EF, Lewy H, Hoey HM and Laron Z, 2003, Differences between males and females in the seasonality of birth and month of clinical onset of disease in children with type 1 diabetes mellitus in Ireland, *J. Pediatr. Endocrinol. Metab.*, **16**, 779-782.
- 268 Rostand SG, 1997, Ultraviolet light may contribute to geographic and racial blood pressure differences, *Hypertension*, **30**, 150-156.
- 269 Rothwell PM, Gutnikov SA, McKinney PA, Schober E, Ionescu-Tirgoviste C and Neu A, 1999, Seasonality of birth in children with diabetes in Europe: multicentre cohort study. European Diabetes Study Group, *Br. Med. J.*, **319**, 887-888.
- 270 SACN, 2007, Update on vitamin D: Position Statement by the Scientific Advisory Committee on Nutrition, Scientific Advisory Committee on Nutrition Report No., London. http://www.sacn.gov.uk/pdfs/sacn_position_vitamin_d_2007_05_07.pdf
- 271 Sagripanti JL, Levy A, Robertson J, Merritt A and Inglis TJ, 2009, Inactivation of virulent *Burkholderia pseudomallei* by sunlight, *Photochem. Photobiol.*, **85**, 978-986.
- 272 Salmon PJ, Chan WC, Griffin J, McKenzie R and Rademaker M, 2007, Extremely high levels of melanoma in Tauranga, New Zealand: possible causes and comparisons with Australia and the northern hemisphere, *Australasian. J. Dermatol.*, **48**, 208-216.

- 273 Samuelsson U, Carstensen J, Lofman O and Nordfeldt S, 2007, Seasonal variation in the diagnosis of type 1 diabetes in south-east Sweden, *Diabetes Res. Clin. Pract.*, **76**, 75-81.
- 274 Santos J, Carrasco E, Moore A, Perez-Bravo F and Albala C, 2001, Incidence rate and spatio-temporal clustering of type 1 diabetes in Santiago, Chile, from 1997 to 1998, *Revista de Saude Publica*, **35**, 96-100.
- 275 Sastre-Garau X, Peter M, Avril MF, Laude H, Couturier J, Rozenberg F, Almeida A, Boitier F, Carlotti A, Couturaud B and Dupin N, 2009, Merkel cell carcinoma of the skin: pathological and molecular evidence for a causative role of MCV in oncogenesis, *J. Pathol.*, **218**, 48-56.
- 276 Sathyanarayana UG, Moore AY, Li L, Padar A, Majmudar K, Stastny V, Makarla P, Suzuki M, Minna JD, Feng Z and Gazdar AF, 2007, Sun exposure related methylation in malignant and non-malignant skin lesions, *Cancer Lett.*, **245**, 112-120.
- 277 Scelo G, Boffetta P, Autier P, Hemminki K, Pukkala E, Olsen JH, Weiderpass E, Tracey E, Brewster DH, McBride ML, Kliewer EV, Tonita JM, Pompe-Kirn V, Chia KS, Jonasson JG, Martos C, Giblin M and Brennan P, 2007, Associations between ocular melanoma and other primary cancers: an international population-based study, *Int. J. Cancer*, **120**, 152-159.
- 278 Schmidt-Pokrzywniak A, Jockel KH, Bornfeld N, Sauerwein W and Stang A, 2009, Positive interaction between light iris color and ultraviolet radiation in relation to the risk of uveal melanoma: a case-control study, *Ophthalmol.*, **116**, 340-348.
- 279 Schoof N, von Bonin F, Konig IR, Mossner R, Kruger U, Reich K, Berking C, Volkenandt M, Ziegler A, Bockmann L, Kuschal C, Thoms KM, Kube D and Emmert S, 2009, Distal and proximal interleukin (IL)-10 promoter polymorphisms associated with risk of cutaneous melanoma development: a case-control study, *Genes & Immun.*, **10**, 586-590.
- 280 Schwarz T, 2008, 25 years of UV-induced immunosuppression mediated by T cells-from disregarded T suppressor cells to highly respected regulatory T cells, *Photochem. Photobiol.*, **84**, 10-18.
- 281 Scully M, Wakefield M and Dixon H, 2008, Trends in news coverage about skin cancer prevention, 1993-2006: increasingly mixed messages for the public, *Aust. N. Zealand J. Pub. Hlth.*, **32**, 461-466.
- 282 Seddon JM, Gragoudas ES, Glynn RJ, Egan KM, Albert DM and Blitzer PH, 1990, Host factors, UV radiation, and risk of uveal melanoma. A case-control study, *Arch. Ophthalmol.*, **108**, 1274-1280.
- 283 Segerback D, Strozzyk M, Snellman E and Hemminki K, 2008, Repair of UV dimers in skin DNA of patients with basal cell carcinoma, *Cancer Epidemiol. Biomarkers. Prev.*, **17**, 2388-2392.
- 284 Sekelj S, Dekaris I, Kondza-Krstonijevic E, Gabric N, Predovic J and Mitrovic S, 2007, Ultraviolet light and pterygium, *Coll. Antropol.*, **31**, 45-47.
- 285 Semba RD, Houston DK, Bandinelli S, Sun K, Cherubini A, Cappola AR, Guralnik JM and Ferrucci L, 2010, Relationship of 25-hydroxyvitamin D with all-cause and cardiovascular disease mortality in older community-dwelling adults, *Eur. J. Clin. Nutr.*, **64**, 203-209.
- 286 Setlow RB, Grist E, Thompson K and Woodhead AD, 1993, Wavelengths effective in induction of malignant melanoma, *Proc. Nat. Acad. Sci. USA.*, **90**, 6666-6670.
- 287 Shah CP, Weis E, Lajous M, Shields JA and Shields CL, 2005, Intermittent and chronic ultraviolet light exposure and uveal melanoma: a meta-analysis, *Ophthalmol.*, **112**, 1599-1607.

- 288 Shih ST, Carter R, Sinclair C, Mihalopoulos C and Vos T, 2009, Economic evaluation of skin cancer prevention in Australia, *Prevent. Med.*, **49**, 449-453.
- 289 Sinclair C and Foley P, 2009, Skin cancer prevention in Australia, *Br. J. Dermatol.*, **161**, 116-123.
- 290 Sinton LW, Hall CH, Lynch PA and Davies-Colley RJ, 2002, Sunlight inactivation of fecal indicator bacteria and bacteriophages from waste stabilization pond effluent in fresh and saline waters, *Appl. Environ. Microbiol.*, **68**, 1122-1131.
- 291 Sivapirabu G, Yiasemides E, Halliday GM, Park J and Damian DL, 2009, Topical nicotinamide modulates cellular energy metabolism and provides broad-spectrum protection against ultraviolet radiation-induced immunosuppression in humans, *Br. J. Dermatol.*, **161**, 1357-1364.
- 292 Sleijffers A, Garssen J, de Gruijl FR, Boland GJ, van Hattum J, van Vloten WA and van Loveren H, 2001, Influence of ultraviolet B exposure on immune responses following hepatitis B vaccination in human volunteers, *J. Invest. Dermatol.*, **117**, 1144-1150.
- 293 Sleijffers A, Kammeyer A, de Gruijl FR, Boland GJ, van Hattum J, van Vloten WA, van Loveren H, Teunissen MB and Garssen J, 2003, Epidermal cis-urocanic acid levels correlate with lower specific cellular immune responses after hepatitis B vaccination of ultraviolet B-exposed humans, *Photochem. Photobiol.*, **77**, 271-275.
- 294 Sleijffers A, Yucesoy B, Kashon M, Garssen J, De Gruijl FR, Boland GJ, Van Hattum J, Luster MI and Van Loveren H, 2003, Cytokine polymorphisms play a role in susceptibility to ultraviolet B-induced modulation of immune responses after hepatitis B vaccination, *J. Immunol.*, **170**, 3423-3428.
- 295 Sliney DH and Wengraitis S, 2006, Is a differentiated advice by season and region necessary?, *Prog. Biophys. Mol. Biol.*, **92**, 150-160.
- 296 Sloka JS, Pryse-Phillips WE and Stefanelli M, 2008, The relation of ultraviolet radiation and multiple sclerosis in Newfoundland, *Can. J. Neurol. Sci.*, **35**, 69-74.
- 297 Smolders J, Thewissen M, Peelen E, Menheere P, Cohen Tervaert JW, Damoiseaux J and Hupperts R, 2009, Vitamin D status is positively correlated with regulatory T cell function in patients with multiple sclerosis, *PLoS One*, **4**, e6635.
- 298 Sneyd MJ and Cox B, 2009, Melanoma in Maori, Asian, and Pacific peoples in New Zealand, *Cancer Epidemiol. Biomarkers. Prev.*, **18**, 1706-1713.
- 299 Staples J, Lim L and Ponsonby AL, 2010, Timing of birth influences multiple sclerosis risk in the southern hemisphere, *Br. Med. J.*, **340**.
- 300 Staples JA, Ponsonby AL, Lim LL and McMichael AJ, 2003, Ecologic analysis of some immune-related disorders, including type 1 diabetes, in Australia: latitude, regional ultraviolet radiation, and disease prevalence, *Environ. Health Perspect.*, **111**, 518-523.
- 301 Staples MP, Elwood M, Burton RC, Williams JL, Marks R and Giles GG, 2006, Non-melanoma skin cancer in Australia: the 2002 national survey and trends since 1985, *Med. J. Aust.*, **184**, 6-10.
- 302 Stene LC, Ulriksen J, Magnus P and Joner G, 2000, Use of cod liver oil during pregnancy associated with lower risk of Type I diabetes in the offspring, *Diabetologia*, **43**, 1093-1098.
- 303 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 and 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.

- 304 Struijk L, van der Meijden E, Kazem S, ter Schegget J, de Gruijl FR, Steenbergen RD and Feltkamp MC, 2008, Specific betapapillomaviruses associated with squamous cell carcinoma of the skin inhibit UVB-induced apoptosis of primary human keratinocytes, *J. Gen. Virol.*, **89**, 2303-2314.
- 305 Suarez-Martinez EB, Ruiz A, Matias J, Morales L, Cruz A, Vazquez D, Villa J and Matta JL, 2007, Early-onset of sporadic basal-cell carcinoma: germline mutations in the TP53, PTCH, and XPD genes, *Puerto Rico Hlth. Scie. J.*, **26**, 349-354.
- 306 Sugie N, Fujii N and Danno K, 2002, Cyclosporin-A suppresses p53-dependent repair DNA synthesis and apoptosis following ultraviolet-B irradiation, *Photodermatol. Photoimmunol. Photomed.*, **18**, 163-168.
- 307 SunSmart, 2010, SunSmart Home Page, Cancer Research UK, <http://www.sunsmart.org.uk/index.htm>, accessed September, 2010.
- 308 Swann MH and Yoon J, 2007, Merkel cell carcinoma, *Sem. Oncol.*, **34**, 51-56.
- 309 Taylor B, Lucas R, van der Mei I, Pender M, Dear K, Chapman C, Coulthard A, Dwyer T, Kilpatrick T, McMichael A, Valery P, Williams D and Ponsonby A-L, 2010, Latitudinal variation in incidence and type of first central nervous system demyelinating events, *Mult. Scler.*, **16**, 398-405.
- 310 Taylor BV, Pearson JF, Clarke G, Mason DF, Abernethy DA, Willoughby E and Sabel C, 2010, MS prevalence in New Zealand, an ethnically and latitudinally diverse country, *Mult Scler.*
- 311 The EURODIAB Substudy 2 Study Group, 1999, Vitamin D supplement in early childhood and risk for Type I (insulin-dependent) diabetes mellitus, *Diabetologia*, **42**, 51-54.
- 312 Thieden E, Philipsen PA, Heydenreich J and Wulf HC, 2009, Vitamin D level in summer and winter related to measured UVR exposure and behavior, *Photochem. Photobiol.*, **85**, 1480-1484.
- 313 Thompson SC, Jolley D and Marks R, 1993, Reduction of solar keratoses by regular sunscreen use, *N. Engl. J. Med.*, **329**, 1147-1151.
- 314 Toews GB, Bergstresser PR and Streilein JW, 1980, Epidermal Langerhans cell density determines whether contact hypersensitivity or unresponsiveness follows skin painting with DNFB, *J. Immunol.*, **124**, 445-453.
- 315 Tommasi S, Denissenko MF and Pfeifer GP, 1997, Sunlight induces pyrimidine dimers preferentially at 5-methylcytosine bases, *Cancer. Res.*, **57**, 4727-4730.
- 316 Tornesello ML, Duraturo ML, Waddell KM, Biryahwaho B, Downing R, Balinandi S, Lucas SB, Buonaguro L and Buonaguro FM, 2006, Evaluating the role of human papillomaviruses in conjunctival neoplasia, *Br. J. Cancer.*, **94**, 446-449.
- 317 Travis RC, Crowe FL, Allen NE, Appleby PN, Roddam AW, Tjonneland A, Olsen A, Linseisen J, Kaaks R, Boeing H, Kroger J, Trichopoulou A, Dilis V, Trichopoulos D, Vineis P, Palli D, Tumino R, Sieri S, Bueno-de-Mesquita HB, van Duynhoven FJ, Chirlaque MD, Barricarte A, Larranaga N, Gonzalez CA, Arguelles MV, Sanchez MJ, Stattin P, Hallmans G, Khaw KT, Bingham S, Rinaldi S, Slimani N, Jenab M, Riboli E and Key TJ, 2009, Serum vitamin D and risk of prostate cancer in a case-control analysis nested within the European Prospective Investigation into Cancer and Nutrition (EPIC), *Am. J. Epid.*, **169**, 1223-1232.
- 318 Tremlett H, van der Mei IA, Pittas F, Blizzard L, Paley G, Mesaros D, Woodbaker R, Nunez M, Dwyer T, Taylor BV and Ponsonby AL, 2008, Monthly ambient sunlight, infections and relapse rates in multiple sclerosis, *Neuroepidemiology*, **31**, 271-279.
- 319 Triay E, Bergman L, Nilsson B, All-Ericsson C and Seregard S, 2009, Time trends in the incidence of conjunctival melanoma in Sweden, *Br. J. Ophthalmol.*, **93**, 1524-1528.

- 320 Tsai WT, 2005, Environmental risk assessment of hydrofluoroethers (HFEs), *J. Haz. Matter.*, **119**, 69-78.
- 321 Tsai WT, 2007, Environmental risk assessment of hydrofluoropolyethers (HFPEs), *J. Haz. Matter.*, **139**, 185-192.
- 322 Tsai WT, 2009, Environmental hazards and health risk of common liquid perfluoro-n-alkanes, potent greenhouse gases, *Environ. Int.*, **35**, 418-424.
- 323 Tsai WT, 2010, Environmental and health risks of sulfuryl fluoride, a fumigant replacement for methyl bromide, *J. Environ. Sci. Hlth. C Environ. Carcinog. Ecotoxicol. Rev.*, **28**, 125-145.
- 324 Underbrink MP, Howie HL, Bedard KM, Koop JI and Galloway DA, 2008, E6 proteins from multiple human betapapillomavirus types degrade Bak and protect keratinocytes from apoptosis after UVB irradiation, *J. Virol.*, **82**, 10408-10417.
- 325 Urashima M, Segawa T, Okazaki M, Kurihara M, Wada Y and Ida H, 2010, Randomized trial of vitamin D supplementation to prevent seasonal influenza A in schoolchildren, *Am. J. Clin. Nutr.*, **91**, 1255-1260.
- 326 Vaiserman AM, Carstensen B, Voitenko VP, Tronko MD, Kravchenko VI, Khalangot MD and Mechova LV, 2007, Seasonality of birth in children and young adults (0-29 years) with type 1 diabetes in Ukraine, *Diabetologia*, **50**, 32-35.
- 327 Vajdic CM, Krickler A, Giblin M, McKenzie J, Aitken J, Giles GG and Armstrong BK, 2002, Sun exposure predicts risk of ocular melanoma in Australia, *Int. J. Cancer*, **101**, 175-182.
- 328 van der Leun JC and de Gruijl FR, 2002, Climate change and skin cancer, *Photochem. Photobiol. Sci.*, **1**, 324-326.
- 329 van der Leun JC, Piacentini RD and de Gruijl FR, 2008, Climate change and human skin cancer, *Photochem. Photobiol. Sci.*, **7**, 730-733.
- 330 van der Mei IA, Ponsonby AL, Dwyer T, Blizzard L, Simmons R, Taylor BV, Butzkueven H and Kilpatrick T, 2003, Past exposure to sun, skin phenotype, and risk of multiple sclerosis: case-control study, *Br. Med. J.*, **327**, 316.
- 331 van der Pols JC, Williams GM, Pandeya N, Logan V and Green AC, 2006, Prolonged prevention of squamous cell carcinoma of the skin by regular sunscreen use, *Cancer Epidemiol. Biomarkers. Prev.*, **15**, 2546-2548.
- 332 van Doorn R, Gruis NA, Willemze R, van der Velden PA and Tensen CP, 2005, Aberrant DNA methylation in cutaneous malignancies, *Sem. Oncol.*, **32**, 479-487.
- 333 van Hattem S, Aarts MJ, Louwman WJ, Neumann HA, Coebergh JW, Looman CW, Nijsten T and de Vries E, 2009, Increase in basal cell carcinoma incidence steepest in individuals with high socioeconomic status: results of a cancer registry study in The Netherlands, *Br. J. Dermatol.*, **161**, 840-845.
- 334 van Schanke A, van Venrooij GM, Jongsma MJ, Banus HA, Mullenders LH, van Kranen HJ and de Gruijl FR, 2006, Induction of nevi and skin tumors in Ink4a/Arf Xpa knockout mice by neonatal, intermittent, or chronic UVB exposures, *Cancer. Res.*, **66**, 2608-2615.
- 335 Vojnikovic B, Njiric S, Coklo M and Spanjol J, 2007, Ultraviolet sun radiation and incidence of age-related macular degeneration on Croatian Island Rab, *Coll. Antropol.*, **31**, 43-44.
- 336 Vollmer RT, 2007, Solar elastosis in cutaneous melanoma, *Am. J. Clin. Nutr.*, **128**, 260-264.
- 337 Wakita D, Chamoto K, Ohkuri T, Narita Y, Ashino S, Sumida K, Nishikawa H, Shiku H, Togashi Y, Kitamura H and Nishimura T, 2009, IFN-gamma-dependent type 1 immunity is crucial for immunosurveillance against squamous cell carcinoma in a novel mouse carcinogenesis model, *Carcinogenesis*, **30**, 1408-1415.

- 338 Walsh JE, Koehler LV, Fleming DP and Bergmanson JP, 2007, Novel method for determining hydrogel and silicone hydrogel contact lens transmission curves and their spatially specific ultraviolet radiation protection factors, *Eye Contact Lens*, **33**, 58-64.
- 339 Wang GS, Zhang M, Li XP, Zhang H, Chen W, Kan M and Wang YM, 2009, Ultraviolet B exposure of peripheral blood mononuclear cells of patients with systemic lupus erythematosus inhibits DNA methylation, *Lupus*, **18**, 1037-1044.
- 340 Wang L, Saito K, Toda M, Hori T, Torii M, Ma N, Katayama N, Shiku H, Kuribayashi K and Kato T, 2010, UV irradiation after immunization induces type 1 regulatory T cells that suppress Th2-type immune responses via secretion of IL-10, *Immunobiology*, **215**, 124-132.
- 341 Wang L, Toda M, Saito K, Hori T, Horii T, Shiku H, Kuribayashi K and Kato T, 2008, Post-immune UV irradiation induces Tr1-like regulatory T cells that suppress humoral immune responses, *Int. Immunol.*, **20**, 57-70.
- 342 Wang LE, Li C, Strom SS, Goldberg LH, Brewster A, Guo Z, Qiao Y, Clayman GL, Lee JJ, El-Naggar AK, Prieto VG, Duvic M, Lippman SM, Weber RS, Kripke ML and Wei Q, 2007, Repair capacity for UV light induced DNA damage associated with risk of nonmelanoma skin cancer and tumor progression, *Clin. Cancer Res.*, **13**, 6532-6539.
- 343 Wang SQ and Dusza SW, 2009, Assessment of sunscreen knowledge: a pilot survey, *Br. J. Dermatol.*, **161**, 28-32.
- 344 Wang TJ, Zhang F, Richards JB, Kestenbaum B, van Meurs JB, Berry D, Kiel DP, Streeten EA, Ohlsson C, Koller DL, Peltonen L, Cooper JD, O'Reilly PF, Houston DK, Glazer NL, Vandenput L, Peacock M, Shi J, Rivadeneira F, McCarthy MI, Anneli P, de Boer IH, Mangino M, Kato B, Smyth DJ, Booth SL, Jacques PF, Burke GL, Goodarzi M, Cheung CL, Wolf M, Rice K, Goltzman D, Hidioglou N, Ladouceur M, Wareham NJ, Hocking LJ, Hart D, Arden NK, Cooper C, Malik S, Fraser WD, Hartikainen AL, Zhai G, Macdonald HM, Forouhi NG, Loos RJ, Reid DM, Hakim A, Dennison E, Liu Y, Power C, Stevens HE, Jaana L, Vasani RS, Soranzo N, Bojunga J, Psaty BM, Lorentzon M, Foroud T, Harris TB, Hofman A, Jansson JO, Cauley JA, Uitterlinden AG, Gibson Q, Jarvelin MR, Karasik D, Siscovick DS, Econs MJ, Kritchevsky SB, Florez JC, Todd JA, Dupuis J, Hypponen E and Spector TD, 2010, Common genetic determinants of vitamin D insufficiency: a genome-wide association study, *Lancet*, **376**, 180-188.
- 345 Waster PK and Ollinger KM, 2009, Redox-dependent translocation of p53 to mitochondria or nucleus in human melanocytes after UVA- and UVB-induced apoptosis, *J. Invest. Dermatol.*, **129**, 1769-1781.
- 346 Wayse V, Yousafzai A, Mogale K and Filteau S, 2004, Association of subclinical vitamin D deficiency with severe acute lower respiratory infection in Indian children under 5 y, *Eur. J. Clin. Nutr.*, **58**, 563-567.
- 347 Wei MY, Garland CF, Gorham ED, Mohr SB and Giovannucci E, 2008, Vitamin D and prevention of colorectal adenoma: a meta-analysis, *Cancer Epidemiol. Biomarkers. Prev.*, **17**, 2958-2969.
- 348 Weis E, Shah CP, Lajous M, Shields JA and Shields CL, 2006, The association between host susceptibility factors and uveal melanoma: a meta-analysis, *Arch. Ophthalmol.*, **124**, 54-60.
- 349 Wejse C, Gomes VF, Rabna P, Gustafson P, Aaby P, Lisse IM, Andersen PL, Glerup H and Sodemann M, 2009, Vitamin D as supplementary treatment for tuberculosis: a double-blind, randomized, placebo-controlled trial, *Am. J. Resp. Criti. Care Med.*, **179**, 843-850.

- 350 Welsh MM, Applebaum KM, Spencer SK, Perry AE, Karagas MR and Nelson HH, 2009, CTLA4 variants, UV-induced tolerance, and risk of non-melanoma skin cancer, *Cancer. Res.*, **69**, 6158-6163.
- 351 Welsh MM, Karagas MR, Applebaum KM, Spencer SK, Perry AE and Nelson HH, 2008, A role for ultraviolet radiation immunosuppression in non-melanoma skin cancer as evidenced by gene-environment interactions, *Carcinogenesis*, **29**, 1950-1954.
- 352 White AN, Ng V, Spain CV, Johnson CC, Kinlin LM and Fisman DN, 2009, Let the sun shine in: effects of ultraviolet radiation on invasive pneumococcal disease risk in Philadelphia, Pennsylvania, *BMC Infect. Dis.*, **9**, 196.
- 353 White JH, 2008, Vitamin D signaling, infectious diseases, and regulation of innate immunity, *Infect. Immun.*, **76**, 3837-3843.
- 354 Whiteman DC, Bray CA, Siskind V, Green AC, Hole DJ and Mackie RM, 2008, Changes in the incidence of cutaneous melanoma in the west of Scotland and Queensland, Australia: hope for health promotion?, *Eur. J. Cancer. Prev.*, **17**, 243-250.
- 355 Whiteman DC, Bray CA, Siskind V, Hole D, MacKie RM and Green AC, 2007, A comparison of the anatomic distribution of cutaneous melanoma in two populations with different levels of sunlight: the west of Scotland and Queensland, Australia 1982-2001, *Cancer Causes Control*, **18**, 485-491.
- 356 Widyarini S, Domanski D, Painter N and Reeve VE, 2006, Estrogen receptor signaling protects against immune suppression by UV radiation exposure, *Proc. Nat. Acad. Sci. USA.*, **103**, 12837-12842.
- 357 Willer CJ, Dymant DA, Sadovnick AD, Rothwell PM, Murray TJ and Ebers GC, 2005, Timing of birth and risk of multiple sclerosis: population based study, *Br. Med. J.*, **330**, 120.
- 358 Willis JA, Scott RS, Darlow BA, Lewy H, Ashkenazi I and Laron Z, 2002, Seasonality of birth and onset of clinical disease in children and adolescents (0-19 years) with type 1 diabetes mellitus in Canterbury, New Zealand, *J. Pediat. Endocrinol. Metab.*, **15**, 645-647.
- 359 Wolf P, Byrne SN and Gruber-Wackernagel A, 2009, New insights into the mechanisms of polymorphic light eruption: resistance to ultraviolet radiation-induced immune suppression as an aetiological factor, *Exp. Dermatol.*, **18**, 350- 356.
- 360 Woolcott CG, Wilkens LR, Nomura AM, Horst RL, Goodman MT, Murphy SP, Henderson BE, Kolonel LN and Le Marchand L, 2010, Plasma 25-hydroxyvitamin D levels and the risk of colorectal cancer: the multiethnic cohort study, *Cancer Epidemiol. Biomarkers. Prev.*, **19**, 130-134.
- 361 Xiao T, Tang J, Wu A, Shpall E, Khaimsky I, So P and Epstein E, 2009, Hedgehog signaling of BCC is inhibited by Vitamin D: Implication for a chemopreventive agent against BCC carcinogenesis, *J. Invest. Dermatol.*, **129**, s32 (abstr.).
- 362 Yamshchikov AV, Desai NS, Blumberg HM, Ziegler TR and Tangpricha V, 2009, Vitamin D for treatment and prevention of infectious diseases: a systematic review of randomized controlled trials, *Endocrine Practice*, **15**, 438-449.
- 363 Yang G, Curley D, Bosenberg MW and Tsao H, 2007, Loss of xeroderma pigmentosum C (Xpc) enhances melanoma photocarcinogenesis in Ink4a-Arf-deficient mice, *Cancer. Res.*, **67**, 5649-5657.
- 364 Yarak S, Ogawa MM, Hirata S and de Almeida FA, 2009, Prevalence of acquired melanocytic naevi in Brazilian schoolchildren, *Clin. Exp. Dermatol.*, **35**, 581-587.
- 365 Yesudian PD, Berry JL, Wiles S, Hoyle S, Young DB, Haylett AK, Rhodes LE and Davies P, 2008, The effect of ultraviolet B-induced vitamin D levels on host

- resistance to *Mycobacterium tuberculosis*: a pilot study in immigrant Asian adults living in the United Kingdom, *Photodermatol. Photoimmunol. Photomed.*, **24**, 97-98.
- 366 Yetley EA, 2008, Assessing the vitamin D status of the US population, *Am. J. Clin. Nutr.*, **88**, 558S-564S.
- 367 Yiasemides E, Sivapirabu G, Halliday GM, Park J and Damian DL, 2009, Oral nicotinamide protects against ultraviolet radiation-induced immunosuppression in humans, *Carcinogenesis*, **30**, 101-105.
- 368 Yin L, Grandi N, Raum E, Haug U, Arndt V and Brenner H, 2010, Meta-analysis: Serum vitamin D and breast cancer risk, *Eur J Cancer*, **46**, 2196-2205.
- 369 Yin L, Raum E, Haug U, Arndt V and Brenner H, 2009, Meta-analysis of longitudinal studies: Serum vitamin D and prostate cancer risk, *Cancer Epid.*, **33**, 435-445.
- 370 Yin M, Wei S and Wei Q, 2009, Vitamin D Receptor Genetic Polymorphisms and Prostate Cancer Risk: A Meta-analysis of 36 Published Studies, *Int J Clin Exp Med*, **2**, 159-175.
- 371 Youl PH, Janda M and Kimlin M, 2009, Vitamin D and sun protection: the impact of mixed public health messages in Australia, *Int. J. Cancer*, **124**, 1963-1970.
- 372 Yu GP, Hu DN and McCormick SA, 2006, Latitude and incidence of ocular melanoma, *Photochem. Photobiol.*, **82**, 1621-1626.
- 373 Yusuf N, Irby C, Katiyar SK and Elmets CA, 2007, Photoprotective effects of green tea polyphenols, *Photodermatol. Photoimmunol. Photomed.*, **23**, 48-56.
- 374 Zanetti R, Rosso S, Martinez C, Nieto A, Miranda A, Mercier M, Loria DI, Osterlind A, Greinert R, Navarro C, Fabbrocini G, Barbera C, Sancho-Garnier H, Gafa L, Chiarugi A and Mossotti R, 2006, Comparison of risk patterns in carcinoma and melanoma of the skin in men: a multi-centre case-case-control study, *Br. J. Cancer.*, **94**, 743-751.
- 375 Zhou L, Beuerman RW, Ang LP, Chan CM, Li SF, Chew FT and Tan DT, 2009, Elevation of human alpha-defensins and S100 calcium-binding proteins A8 and A9 in tear fluid of patients with pterygium, *Invest. Ophthalmol. Vis. Sci.*, **50**, 2077-2086.

Chapter 3. Effects of solar ultraviolet radiation on terrestrial ecosystems. Patterns, mechanisms, and interactions with climate change

C. L. Ballaré^a, M. M. Caldwell^b, S. D. Flint^b, S. A. Robinson^c and J. F. Bornman^d

^a*IFEVA and Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Facultad de Agronomía, Universidad de Buenos Aires, Av. San Martín 4453, Buenos Aires (C1417DSE), Argentina*

^b*Department of Wildland Resources and the Ecology Center, 5230 Old Main Hill, Utah State University, Logan, UT 84322-5230, USA*

^c*Institute for Conservation Biology and Environmental Management, University of Wollongong, Northfields Avenue, NSW 2522, Australia*

^d*International Global Change Centre, University of Waikato, Private Bag 3105, Hamilton 3240, New Zealand*

Summary

Ultraviolet radiation (UV) is a minor fraction of the solar spectrum reaching the ground surface. In this assessment we summarize the results of previous work on the effects of the UV-B component (280-315 nm) on terrestrial ecosystems, and draw attention to important knowledge gaps in our understanding of the interactive effects of UV radiation and climate change. We highlight the following points: (i) The effects of UV-B on the growth of terrestrial plants are relatively small and, because the Montreal Protocol has been successful in limiting ozone depletion, the reduction in plant growth caused by increased UV-B radiation in areas affected by ozone decline since 1980 is unlikely to have exceeded 6%. (ii) Solar UV-B radiation has large direct and indirect (plant-mediated) effects on canopy arthropods and microorganisms. Therefore, trophic interactions (herbivory, decomposition) in terrestrial ecosystems appear to be sensitive to variations in UV-B irradiance. (iii) Future variations in UV radiation resulting from changes in climate and land-use may have more important consequences on terrestrial ecosystems than the changes in UV caused by ozone depletion. This is because the resulting changes in UV radiation may affect a greater range of ecosystems, and will not be restricted solely to the UV-B component. (iv) Several ecosystem processes that are not particularly sensitive to UV-B radiation can be strongly affected by UV-A (315-400 nm) radiation. One example is the physical degradation of plant litter. Increased photodegradation (in response to reduced cloudiness or canopy cover) will lead to increased carbon release to the atmosphere via direct and indirect mechanisms.

Introduction

Terrestrial ecosystems represent the largest store of active organic carbon in the biosphere,¹²⁸ and include biomes of widely variable climate regimes with a diverse set of organisms adapted to this range of conditions.³⁶ Key ecosystem services include food and fibre production, as well as protection of watersheds and water quality and regulation of atmospheric composition.¹⁹

Terrestrial ecosystems are being perturbed directly and indirectly by anthropogenic activity. Increased temperature and atmospheric CO₂, and altered precipitation patterns, are generally considered to be the most important climate change factors affecting terrestrial ecosystems. Superimposed on those drivers are changes in the levels of solar UV-B radiation re-

sulting from stratospheric ozone depletion and other atmospheric factors (Chapter 1). Model calculations that incorporate satellite measurements of ozone, and cloud and aerosol reflectivity, show a significant increase in UV-B radiation reaching the Earth's surface between 1979 and 2008; this increase occurred at all latitudes except the equatorial zone, with the largest increments taking place at mid to high latitudes in the Southern Hemisphere⁵⁹ (see also Chapter 1).

Recovery of stratospheric ozone, due to the successful implementation of the Montreal Protocol, is predicted over the decades ahead (see Chapter 1 and ref.⁹⁶). However, the additional effects of climate change on ozone chemistry and UV transmission through the atmosphere make future UV levels at the Earth's surface much more difficult to predict (Chapter 1). Changes in UV-B radiation also occur in response to environmental and anthropogenic factors other than ozone depletion. For example, changes in cloudiness (associated with climate change) and aerosol concentrations may also affect UV irradiance at regional, or even global scales (see Chapter 1 and ref.¹). Reduced cloud cover and conditions of increased aridity, predicted by current climate models for some regions,^{53, 62, 142} are likely to have strong effects on the UV irradiance received at ground level. Furthermore, deforestation or changes in agricultural practices that alter plant canopy cover or structure may have important effects on UV levels received by vegetation, canopy arthropods, and microbes in terrestrial ecosystems. These changes in UV radiation are predicted to occur over a greater geographic area than that affected by ozone depletion (Chapter 1) and may therefore affect a much more diverse range of terrestrial ecosystems.

In this report, we consider recent advances in our understanding of the effects of UV radiation on terrestrial ecosystems, and assess the biological consequences of changes in UV radiation resulting from ozone depletion and other climate change factors. In the first part, we build upon our latest report³⁰ and yearly updates¹⁻³ and present an analysis of the responses to UV-B radiation of the various components (trophic levels) and processes (trophic-level interactions; biogeochemical cycles) of terrestrial ecosystems. Next, we highlight recent progress in the understanding of the basic mechanisms of plant responses to UV-B radiation. Finally, we briefly address technical issues associated with the design and interpretation of experiments intended to evaluate biological effects of UV-B radiation. This assessment is mainly concerned with UV-B radiation effects, but because climate change may also result in significant variation in UV-A levels [for example, due to changes in clouds, Chapter 1], the effects of this spectral region will be considered in those cases where there is sufficient information to anticipate possible ecological consequences.

Effects of UV radiation on organisms at different trophic levels

Primary producers

Growth responses. The general conclusion that has emerged from studies with terrestrial plants is that photosynthesis (CO₂ fixation per unit leaf area) is not significantly affected by changes in UV-B radiation when plants are grown under natural conditions. However, UV-B radiation may have subtle inhibitory effects on biomass accumulation, often correlated with a reduction in the rate of leaf area expansion. The primary literature reporting on these effects has been discussed in previous reports³⁰ and in several reviews^{9, 29, 102, 130}.

In this report, we have focused on a selected number of reviews and meta-analyses of published information that permit a quantitative assessment of the sensitivity of plant growth to ozone-induced variations in UV-B levels under field conditions. One such study is a meta-

analysis of experiments carried out in polar regions in both hemispheres¹⁰². This analysis considered results from both UV-B attenuation (reduction through filtering or screening) and supplementation (addition of UV-B radiation using lamps) studies, and provides rough estimates of dose-response functions, where parameters such as leaf area and biomass are plotted against the dose of UV-B radiation received by plants (Fig. 3-1A). The authors of this analysis concluded that the effects of UV-B radiation on plants (mosses and angiosperms) of Arctic and Antarctic ecosystems are similar to those reported for higher plants of lower latitudes (Ballaré *et al.*⁹; Searles *et al.*¹²⁹). The response is characterized by small reductions in leaf area and growth rate (biomass accumulation) as UV-B radiation increases (Fig. 3-1A), and is accompanied by responses at the biochemical and physiological levels (see following section on Protection and Acclimation).

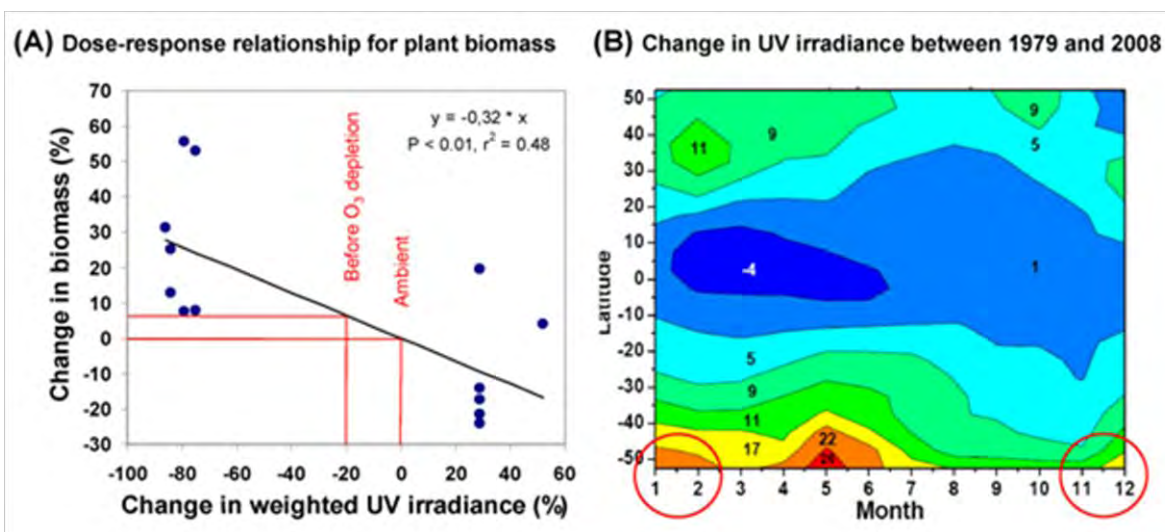


Fig. 3-1. A quantitative estimate of the reduction in the growth of the primary producers that may have occurred as a consequence of increased UV-B radiation between 1979 and 2008. **(A)** Change in aboveground biomass as a function of experimentally-imposed changes in weighted UV irradiance. The growth data are derived from a meta-analysis of field studies in high-latitude ecosystems (which involved experimental attenuation or supplementation of ambient solar UV-B radiation), and are expressed as % change in relation to the growth of the plants receiving ambient solar radiation¹⁰². The UV doses are weighted using the generalised plant function²⁸, and expressed as % change relative to the ambient level [Note that, for this function, a 10 % increase in UV corresponds to a 5% reduction in ozone; i.e., a RAF of 2 (see McKenzie *et al.*⁹⁷). The red lines focus on the example discussed in the text. For areas where ozone depletion over the last three decades has led to a 20 % increase in the summertime levels of weighted UV radiation (areas approximately designated by the red circles in panel B), the difference in plant growth between 1979 and the present would be 6% or less, given the slope of the dose-response relationship and assuming that all other factors are equal. **(B)** Percentage change in UV irradiance (numbers inside the coloured areas), weighted using the generalised plant function²⁸, as a function of time of the year and latitude (between 55° S and 55° N), between 1979 and 2008 (data from Herman⁵⁹). Note that the relative changes in weighted UV irradiance at 50° to 55° S are much greater near the winter solstice, but the absolute irradiance levels are very low during the winter and vegetation is less physiologically active and possibly snow-covered at that time of year.

The slope of the plant biomass response to UV-B irradiance derived from this meta-analysis (-0.32; Fig. 3-1A) indicates an approximate 1% reduction in growth for each 3% increase in weighted UV-B irradiance. If this slope is considered in the context of the changes in weighted UV-B irradiance that occurred over the last 30 years (Fig. 3-1B)⁶⁰, it is possible to produce an estimate of the magnitude of the changes in the growth of the primary producers that may have occurred as a consequence of ozone depletion. Thus, for example, in areas such as the southern tip of South America (at 55° S), where ozone depletion has led to a 20%

increase in the summertime levels of UV-B radiation, (the areas approximately designated by the red circles in Fig. 3-1B), the estimated difference in plant growth rate between the present and 1979 would be 6% or less (see red lines in Fig. 3-1A).

This analysis has several strengths, which are summarized below.

- 1) The analysis produces a quantitative estimate of the effects of changes in UV-B radiation on the growth of terrestrial primary producers.
- 2) The estimate agrees well with quantitative data produced by other analyses of field experiments. For example, the UV-B attenuation experiments carried out in southern South America in the late 1990s (the peak in ozone-depletion), indicated that the negative effect of the enhanced UV-B radiation on plant growth was ~3-4% (Ballaré *et al.*⁹). Furthermore, a comprehensive meta-analysis of UV-B supplementation studies¹²⁹ concluded that the average response to treatments that simulated 10 to 20 % depletion of ozone was a 6% reduction in plant biomass. A more recent meta-analysis⁸⁵ yielded results that were quantitatively consistent with those of Searles and co-workers¹²⁹, and suggested that the average sensitivity to UV-B radiation would be lower in woody perennials than in herbaceous plants.
- 3) Combining results from several studies reduces effects of random variation in individual experiments. The coefficient of variation in individual field studies in natural ecosystems is frequently >10%. Because the number of replicates in these studies is normally low, due to cost and logistic limitations, it is clear that responses of the magnitude predicted by the analysis presented in this report are unlikely to be detected as statistically significant in individual studies.

At the same time, the analysis presented here has some limitations. First, it assumes a linear dose-response relationship, which is not necessarily the case. Second, it assumes that the growth responses measured in experiments where the UV-B radiation levels are abruptly increased or decreased (by supplementation or filtering techniques) would hold true for conditions where the UV-B irradiance received by the ecosystems changes gradually over a period of several years.

Protection and acclimation. Terrestrial plants have highly efficient protective mechanisms against the damaging effects of solar radiation, and this is one of the reasons why increased UV-B radiation resulting from ozone reduction has only modest consequences on plant growth (Fig. 3-1A). As sessile photosynthetic organisms, they are continuously exposed to extreme variations in the levels of solar radiation, including the UV-B component. Plants acclimate to changes in UV-B levels through several defense responses, including morphological changes, accumulation of effective UV-screening compounds, production of increased amounts of antioxidants, stimulation of DNA repair, as well as other regulatory adjustments. Plant acclimation is mediated by UV-B-induced changes in gene expression via UV-B-specific and non-specific signaling pathways.⁶⁸ Numerous mechanisms of acclimation and adaptation have been detailed in previous reports.^{1-3, 30}

Depending on the degree of stress, acclimation responses are likely to involve an energy cost with consequent redistribution of resources for production of protective compounds or structures. As an example, the metabolic cost of accumulating increased levels of UV-absorbing compounds in response to abrupt increases in UV-B radiation was calculated for an Antarctic leafy liverwort. That cost represented only 2% of the carbon fixed by photosynthesis, but such a cost could have cumulative effects on plants growing in polar regions that are

already constrained by short growing seasons.¹³² In an experiment with a native Patagonian shrub (*Grindelia chiloensis*), plants responded to attenuation of solar UV-B radiation with more plant biomass, greater height and increased leaf area, which correlated with a reduction of 10% in the glucose equivalent used in the synthesis of UV-B protective resin.¹⁵⁶ From these experiments, it may be inferred that energy is allocated from growth to protection when plants are exposed to natural sunlight with its UV-B component. The magnitude of the energy cost is likely to be species-specific and dependent on environmental conditions. Protective responses other than production of secondary metabolites are also likely to incur a cost to the plant.

Genotypes within a given species of plant can differ in their tolerance to UV-B radiation.^{41, 74, 141} Genotypic differences in acclimation to UV-B radiation may contribute to the variation in growth responses that has been documented in field studies (see, e.g., scattering in Fig. 3-1A), and may allow for directional selection for UV-B tolerance within plant populations in response to long-term changes in UV-B levels. A recent short-term study⁶⁷ assessed the natural variation in constitutive (inherent) and induced protection of the photosynthetic function from UV-induced damage using over 200 lines (varieties) of *Arabidopsis thaliana*, a member of the mustard family (Brassicaceae). Constitutive protection did not correlate with the latitudinal distribution (and presumed gradation in natural UV-B radiation) of the populations tested. Also, among lines from high altitudes, both constitutively highly tolerant and moderately tolerant populations were found. However, lines from lower latitudes were found to activate UV defenses more readily than those of higher latitudes. Correlation between acclimative/adaptive response to UV-B radiation and habitat origin has also been reported in studies with other species.¹⁵² Jansen *et al.*⁶⁷ point out that some of the differences reported in the literature may be explained by the selection of parameters used to measure plant resistance to UV-B radiation, as well as confounding effects of environmental variation in factors other than UV-B radiation (see also Torabinejad and Caldwell¹⁴¹).

UV-B radiation and other variables of the biotic and abiotic environment can interact to produce cross-tolerance (i.e., tolerance to one stress induced by another stress), as well as resilience to subsequent stress due to the establishment of a level of protection.⁷³ Cross-tolerance has been documented for a number of environmental stressors (examples in Izaguirre *et al.*⁶⁵ and Mittler *et al.*¹⁰¹) and has, in some instances, been attributed to the activation of common signaling pathways. For example, in an analysis of gene-expression responses to pulses of drought, cold, and high UV-B radiation under laboratory conditions, plants were found to exhibit commonalities in their reactions to the various stressors, involving a core set of stress-related genes.⁷⁶ A well-documented case of UV-induced protection against other stress factors is the effect of solar UV-B radiation increasing plant resistance to insect herbivory.¹⁰ UV-B radiation induces the synthesis of several secondary metabolites, including those of the phenylpropanoid pathway, which act as effective UV-absorbing sunscreens.⁶⁸ The response usually involves an increase in the concentration of these compounds as well as differential regulation and shifts in their relative abundance.^{37, 64, 105, 126, 139} Studies that combined detailed analyses of plant tissue chemistry and herbivory bioassays suggest the effect of UV-B radiation increasing plant resistance against herbivorous insects may be at least partially mediated by changes in phenolic metabolites, which may have toxic effects on plant consumers⁴⁴ (see also section on Consumers and decomposers).

From the point of view of modeling the quantitative impacts of changes in UV radiation on plant growth (Fig. 3-1), an important implication of acclimation/adaptation responses is that the slope of the dose-response relationship may change depending on the duration of the experiment. Thus, in a short-term experiment (days), where plants have little time to acclimate to changes in the light environment, changes in UV-B radiation may trigger larger

effects on growth than those produced by gradual increases in UV-B irradiance over a period of several years.

Consumers and decomposers

Canopy arthropods. Some of the most prominent and best characterized effects of solar UV-B radiation in terrestrial ecosystems have been documented at the interface between plants and plant-eating (herbivorous) insects.^{9, 11, 14, 29, 119} Generally, the intensity of herbivory on plants grown under field conditions increases if the UV-B in the solar spectrum is attenuated using filters.²⁹

The “anti-herbivore” effect of UV-B radiation can be considerable. The dose response relationship published in our last report,³⁰ and reproduced here in Fig. 3-2, indicates a doubling in the intensity of herbivory by insects with an attenuation of 25% in the level of solar UV-B radiation. This strong effect of attenuation of solar UV-B radiation on levels of herbivory has been confirmed in more recent studies.⁴⁴ Importantly, the slope of this response is substantially steeper than the one shown in Fig. 3-1A for the effects of UV-B radiation on plant growth. Hence, there is reason to suspect that the increases in UV-B that occurred as a consequence of ozone depletion and other environmental factors (Fig. 3-1B) may have caused larger effects on levels of herbivory than directly on primary productivity. Similarly, herbivory is likely an important determinant of the impacts of future variations in UV-B levels (increases or decreases) on biomass production and losses of biomass to herbivory.

The conclusion regarding quantitative impacts has several caveats. First, it is difficult to estimate the biological effects (quantitative changes in herbivory levels) that may have occurred over a time span of three decades from responses obtained in short-term experiments, where the UV-B levels are instantaneously manipulated with filters. In the long-term, plants may have adjusted to the enhanced doses of UV-B caused by ozone reduction and the insects adapted to the gradual changes in plant tissue quality elicited by the higher UV-B levels. Second, although the effect of UV-B radiation increasing plant resistance to herbivory has been extensively documented, cases have been reported where an increase in UV-B radiation resulted in increased levels of insect

herbivory or differences in the responses between species of insects.^{29, 82, 83} Therefore, in any given ecosystem, different species of insects may have a range of responses to the changes in plant tissue quality caused by enhanced UV-B radiation. An implication of this variation in the response is that changes in UV-B radiation resulting from ozone depletion (or recovery), clouds and aerosols (Chapter 1), or from other sources, such as changes in canopy cover and architecture, have great potential to alter the species composition and diversity of the community of canopy insects.

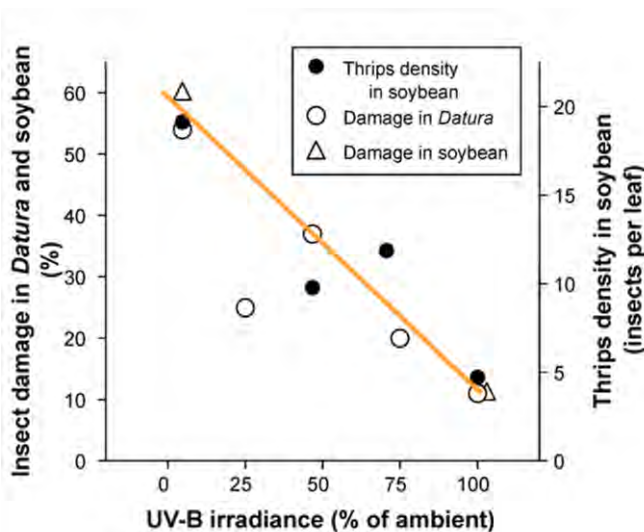


Fig. 3-2. Changes in insect herbivory in response to experimental attenuation of the UV-B irradiance received by the plant canopy. The graph shows the effect of attenuating the UV-B component of solar radiation on the intensity of insect herbivory by thrips (a piercing-sucking insect) in soybean crops⁹⁴, and leaf beetles (chewing insects) in plants of the common annual weed *Datura ferox*.¹⁰

The mechanisms that mediate the effects of solar UV-B radiation on insect herbivory have been studied in some detail. The conclusion emerging from that body of work is that some of these effects are a consequence of a direct action of UV-B radiation on the insects, whereas others are indirect, i.e., mediated by changes in the quality of plant tissues.

Direct deleterious effects of UV-B radiation on insect performance (e.g., increased mortality of larvae) were documented some time ago.^{20, 95} However, recent research has demonstrated that UV-B radiation may also serve as a signal to canopy arthropods (insects, spiders, etc.) that elicits changes in behaviour.^{86, 87, 93, 94} Direct perception of solar UV-B radiation has been demonstrated in field studies with thrips, *Caliothrips phaseoli*, a common crop pest.^{93, 94} Presumably, specific UV-B sensitivity plays a role in the mechanisms that allow canopy arthropods to locate favourable feeding positions or areas of low UV-B exposure within the plant canopy.^{92, 104, 106} Although not directly connected with herbivory studies, Li and co-workers demonstrated that females of a jumping spider species (*Phintella vittata*) choose a mate based on sex-specific UV-B reflectance patterns,^{86, 87} and observational studies with hornets showed that flight activity correlated better with solar UV-B irradiance than with other environmental variables.¹⁴⁸ Mazza and co-workers proposed that specific perception of UV-B in thrips is achieved by a combination of broad-band UV receptors and filtering compounds in the insect's visual system.⁹² Studies in vertebrates also suggested perception of UV-B in poison dart frogs.⁵⁶ The finding that some animals can react specifically to UV-B under natural conditions has important implications for our understanding of the ecological roles of UV-B radiation, and suggests that changes in the UV-B environment in plant communities may have complex effects on the behaviour of animals in the canopy. However, the quantitative significance of direct behavioural responses of animals to UV-B radiation in defining response patterns at the ecosystem level (e.g. changes in rates of herbivory) has yet to be established.

Indirect effects of solar radiation on animals (i.e., effects mediated by changes in the plant host) have been extensively documented in bioassays where the insects themselves are not exposed to the UV-B radiation treatments. Thus, "choice" and "no-choice" bioassays with herbivorous insects have shown that ambient solar UV-B radiation can produce changes in the plant tissues that affect choice of sites for insect feeding^{10, 123} and oviposition (egg-laying),^{34, 52} as well as insect growth and survival.^{13, 65, 81, 82, 157} The increase in plant resistance to herbivory by insects has been correlated with UV-B-induced variations in a number of tissue quality traits, such as nitrogen content⁵⁸, leaf phenolics,^{64, 81, 82, 95, 124} cyanogenic compounds,⁸⁹ and defense-related proteins such as inhibitors of insect proteinases.^{65, 136, 137} Increased accumulation of phenolic compounds in plant tissues is one of the most consistently reported responses to UV-B radiation. These phenolic compounds contribute to filtering out UV-B photons before they reach sensitive molecules in the interior tissues (mesophyll). However, they are also thought to play a role in direct defense against herbivores.^{44, 47, 61, 63, 84, 100, 134} In fact, UV-B radiation and insect damage trigger partially overlapping patterns of phenolic compounds in some plant species.⁶⁴ A partial convergence in response also has been evidenced in studies that measured changes in gene expression elicited by herbivory/wounding treatments and exposure to UV-B radiation.^{24, 65}

These observations have lent support to the idea that the effects of solar UV-B radiation on interactions between plants and insects may be mediated by stimulation of the hormonal signaling cascades that plants activate to defend themselves against herbivore attack.^{30, 64, 65, 136} Recent studies in a species of wild tobacco (*Nicotiana attenuata*) have indicated that some effects of solar UV-B radiation on plant defense against insects require biosynthesis of jasmonates (which are the principal hormones that orchestrate plant defense responses against insects), while others do not. Among the responses to UV-B radiation that do not depend on

jasmonate signaling are the accumulation of flavonoids and other phenolic compounds with potential anti-herbivore activity. On the other hand, the UV-B-induced accumulation of several polyamine conjugates is totally dependent on jasmonate production, and UV-B strongly enhances the expression of defense-related proteins (proteinase inhibitors) triggered by herbivory through a jasmonate-dependent pathway.⁴⁴ Solar UV-B radiation does not increase accumulation of jasmonates in *N. attenuata*, but increases sensitivity to jasmonates, presumably via regulation of some of the downstream components involved in jasmonate signaling. The increased sensitivity to jasmonate thus leads to stronger defense responses in plants exposed to UV-B radiation compared to those grown under attenuated levels of UV-B.⁴⁴ Bioassays carried out in the field have indicated that those effects of UV-B radiation on plant chemistry that require jasmonate signaling play a quantitatively important role in the mechanisms whereby solar UV-B increases plant resistance to herbivorous insects.^{34, 44} Detection of significant effects of solar UV-B on jasmonate signaling is important, because recent field studies have shown that the impacts of elevated concentrations of atmospheric CO₂ on the intensity of herbivory (more herbivory under elevated CO₂) may be caused by a reduced activation of the jasmonate pathway of plant defense.¹⁵⁵ Thus, improved understanding of the effects of UV-B radiation on the mechanisms of defense may be useful for analyzing the impacts of multiple environmental factors (such as UV-B, CO₂, etc.), as well as for the design or selection of crop varieties with increased resistance to herbivory.

Microbial communities. Solar UV-B radiation is one of several environmental factors that influence the biodiversity of microbes growing on a range of materials, including the surfaces of leaves and dead plant material (plant litter). By altering the microbial communities that are present, UV-B radiation can thus affect microbial decomposition, which is globally an important process, since it affects the potential for carbon sequestration in terrestrial ecosystems and the flux of CO₂ to the atmosphere. For example, experimental attenuation of UV-B radiation reaching the surface of plant litter in a field study carried out in Tierra del Fuego (southern Patagonia) changed the species composition of fungal communities on the litter, and increased the rate of microbial decomposition.¹⁰⁸ Another recent study reporting changes in plant litter following exposure of branches of alder and birch trees to solar UV radiation indicated changes in tissue chemistry that subsequently influenced the microbial release of CO₂ as the litter was decomposing.⁷⁹ While it is difficult to generalize from such studies, they do indicate that UV radiation can have complex effects on microbial decomposition.

Live foliage can provide a habitat for a diverse set of microbes,⁸⁸ and the composition of these microbial communities can be influenced by solar UV-B radiation striking the leaf surfaces.⁷⁰ Furthermore, studies in maize have shown that the effects of UV-B radiation on bacterial diversity depend on the plant genotype, suggesting that at least some of the effects of UV-B are indirect (i.e., mediated by changes in the plant, such as changes in plant surface chemistry).¹³⁵ In parallel with these studies that focused on microbial diversity on the leaf surface, other researchers have shown that solar UV-B radiation can also alter plant resistance to leaf pathogens. When ambient UV-B radiation was filtered out from areas of tea crops during the wet season in Sri Lanka, the relative abundance of *Xanthomonas* spp. (a phyllosphere bacterium) increased, and this correlated with an increase in the incidence of the fungus that causes blister blight, the major leaf disease of tea plants.⁵⁵ A recent study in maize⁸ found a genetic correlation between low bacterial diversity on leaf surfaces and resistance to fungal blight. This suggests that some dominant bacteria may suppress other bacteria and, at the same time, increase resistance of plants to fungal infection. These studies are beginning to reveal the nature of the interactions between microbial organisms that take place on living foliage. Progress in this direction will increase understanding of the biological implications of the effects of UV-B radiation on microbial diversity.

As in the case of plant-herbivore interactions, the effects of UV-B radiation on plant-associated microbes may be direct (i.e., UV-B acting directly on the microorganisms) or indirect (mediated by UV-B-induced changes in the plant tissues). Indirect effects have not been studied to the same level of detail as plant-insect interactions. However, given the evidence showing that solar UV-B can interact with jasmonate signaling,⁴⁴ and the well-established fact that jasmonates play a central role in plant defense responses against certain types of pathogens,¹¹² it seems likely that changes in UV-B levels will result in variations in plant resistance to pathogen attack.

Finally, experimentally imposed changes in UV radiation aboveground can alter the quantity and diversity of microbes in the soil⁶⁹ or microfauna below the surface in peatlands.^{120, 129} Unlike the leaf surface, this is an environment devoid of UV radiation. Consequently, shifts in microbial species composition are indirect UV effects, which may be mediated by processes such as changes in root exudates,^{117, 118} or in the case of peat, through changes in the plant tissues or exudates of the peat.¹²⁰ Although alterations in the populations of microorganisms and microfauna below the surface have been demonstrated, the broader significance of these changes for ecosystem function is still unclear.

Effects of UV radiation on biogeochemical cycles

In this section we highlight recent advances in the understanding of UV effects on biogeochemical cycles and their implications for predicting the responses of terrestrial ecosystems to variations in UV resulting from ozone and climate change. For further discussion of the subject, the reader is referred to Chapter 5.

Carbon cycle

Of particular importance for the changing carbon balance of terrestrial ecosystems is net ecosystem exchange (NEE), the balance between gross photosynthesis of the vegetation and the total efflux of CO₂ from the ecosystem. As discussed previously (see Growth responses), manipulative field studies did not reveal general effects of UV-B radiation on net photosynthesis (carbon assimilation per unit leaf area), even though shoot biomass can show some sensitivity to variations in UV-B irradiance (Fig. 3-1A).^{102, 129} Another pathway whereby changes in UV-B radiation may affect ecosystems is through belowground processes. Alterations in plant roots and associated microorganisms (mycorrhizae),¹⁵⁴ soil microbial communities¹¹⁷ and microfauna⁴⁰ have been reported in response to aboveground manipulations of UV radiation. However, a general perspective of the chain of events causing these belowground responses, and their significance for ecosystem function is still lacking. Therefore, at this point, there is little evidence to show how NEE will respond to variations in UV-B radiation.

A component of NEE that appears to be influenced by solar UV radiation is the photodegradation of plant litter. Although litter decomposition is largely a biological process involving microbes, purely physical photodegradation (degradation under the action of light) can play a prominent role in arid and semiarid ecosystems,⁶ which represent *ca* 40 % of the Earth's land surface. Recent studies demonstrate a sizable effect of solar radiation in driving mass loss from above-ground organic matter in a range of terrestrial environments.^{4-6, 21, 23, 125} The activity spectrum for photodegradation indicates that effective wavelengths extend beyond the UV-B region, and even include part of the visible spectrum^{5, 22} (Fig. 3-3). Therefore, because the irradiances in the UV-A and visible regions are much higher than in the UV-B, the rate of photodegradation is unlikely to have increased significantly in response to changes in the solar spectrum resulting from ozone depletion.

However, because the effects of UV-A and short-wave visible radiation can be quite large, photodegradation could be strongly enhanced by increases in the amount of radiation resulting from decreased cloud cover or conditions of increased aridity.⁵ Photodegradation affects predominantly the lignin fraction of plant litter, reducing its abundance when the material is exposed to sunlight (Fig. 3-4). Because lignin is known to play a key role in retarding biological (microbial) decomposition,¹³⁸ increases in photodegradation as a result of climate change may have important consequences, accelerating microbial respiration and hence carbon release to the atmosphere.⁵ This indirect effect of increased photodegradation may be particularly important in scenarios of greater variability in climate, with increased alternation between dry periods (which may favour photodegradation) and periods of abundant precipitation (which favour microbial activity).

Nitrogen oxides

Trace gases of nitrogen, NO_x (NO and NO₂), are present in small quantities in the atmosphere, but are very important in a variety of chemical reactions (Chapter 6). These and other oxides of nitrogen, NO_y, can play important roles in atmospheric chemistry. One of those, nitrous oxide, N₂O, is now considered to be the single most important ozone-depleting emission, exceeding the contribution of chlorofluorocarbons.¹¹⁵ Plant shoots have been shown to emit NO_x when exposed to solar UV radiation,⁵⁷ with NO_x likely originating from leaf tissues. Other nitrogen oxides (NO_y) from conifers appear to emanate from the surfaces of foliage when exposed to UV-B radiation.¹¹⁴ There is a suggestion that global NO_x emissions from boreal forests might be roughly equivalent to those from industrial and traffic sources.⁵⁷ Although several uncertainties remain, this suggests an important role for solar UV-B radiation interacting with plant tissues in the production of reactive nitrogen.

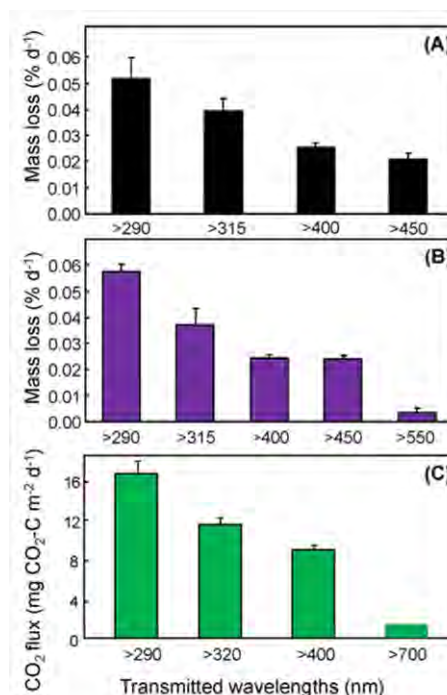


Fig. 3-3. Experimental attenuation of specific regions of the solar spectrum demonstrates that both UV (<400 nm) and visible (400-700 nm) radiation can drive photodegradation in the field. (A) Mass loss of grass litter exposed to solar radiation transmitted through different cut-off filters in a semi-arid grassland. (B) Mass loss of artificial cellulose-lignin substrates with 10% lignin concentration exposed to solar radiation transmitted through different cut-off filters. Adapted from Austin and Ballaré⁵ (C) CO₂ evolution from leaves exposed to solar radiation transmitted through different cut-off filters. Adapted from Brandt *et al.*²²

Methane

Although the release of methane into the atmosphere had been generally considered to occur only under conditions of very low oxygen, measurable release of methane from vegetation in an atmosphere with normal oxygen levels has been reported.⁷⁵ This has led to considerable controversy.^{98, 99, 103, 147, 149, 150} Although interpretations vary, it appears that methane can be produced from plant pectins through a photochemical process driven by solar UV radiation.¹⁴⁷ Recent estimates suggest that the quantity of methane emitted from terrestrial ecosystems by this process is not relevant from the perspective of the global methane budget.¹⁶ However, methane is the next most important greenhouse gas after water vapour and CO₂, and thus the potential importance of this process clearly deserves attention (Chapter 1).

Interactions with other climate change factors

Changes to incident UV radiation may occur in response to changes in climate and land use, as discussed earlier. Such changes could affect both UV-B and UV-A levels, and the effects are likely to be greater than those that have resulted from stratospheric ozone depletion (see Chapter 1 and ref⁷). For example, decreasing cloud cover in some regions (Fig. 3-5)¹⁴² will increase transmittance of UV through the atmosphere (Chapter 1), and also through the plant canopy if the reduction in clouds is accompanied by conditions of increased aridity (as predicted by some models, Fig. 3-6)^{53, 62} and reduced vegetative cover. Similarly, in polar and alpine regions, vegetation is often protected for many months of the year by layers of snow and ice that effectively block solar radiation. Reductions in these protective layers due to climate warming will increase the duration of exposure to UV-B radiation and, particularly in the Southern Hemisphere, would coincide with ozone-depletion events.¹³¹ This increased UV-B radiation is likely to be combined with changes in water availability and exposure to temperature extremes.^{17, 18, 111}

Understanding how ecosystems will adapt to these changes requires identification of likely new combinations of stressors at a regional level, as well as studies that con-

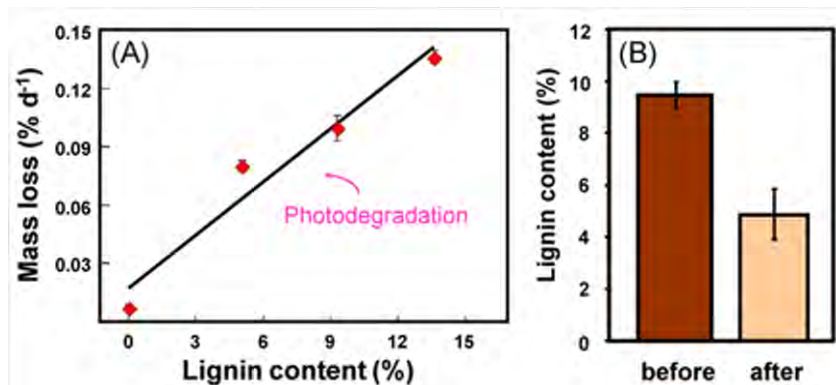


Fig. 3-4. Photodegradation reduces the lignin (biologically recalcitrant) fraction of plant litter. (A) When artificial cellulose-lignin substrates were exposed to sunlight for a period of one month during the summer in Buenos Aires (34 °S), the rate of photodegradation increased with original lignin content in the exposed material. This is explained by the fact that lignin is an effective absorber of solar radiation over a wide range of wavelengths. (B) Lignin content decreased after photodegradation, which is predicted to render the material more labile to biological degradation catalyzed by microbial enzymes. The bars indicate lignin content before and after a period of exposure to sunlight. Adapted from Austin and Ballaré.⁵

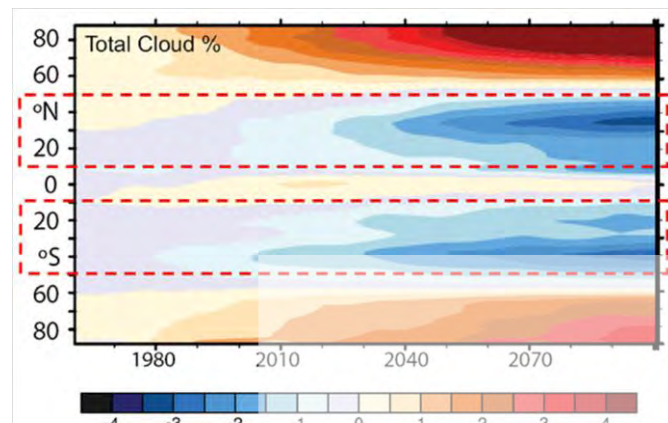


Fig. 3-5. Modeled trends for total cloud cover (% change 1960-2100 –see colour scale at the bottom of the graph) as a function of latitude. Boxed areas highlight low and mid-latitudes, where models predict reduced cloud cover. Adapted from Trenberth and Fasullo.¹⁴²

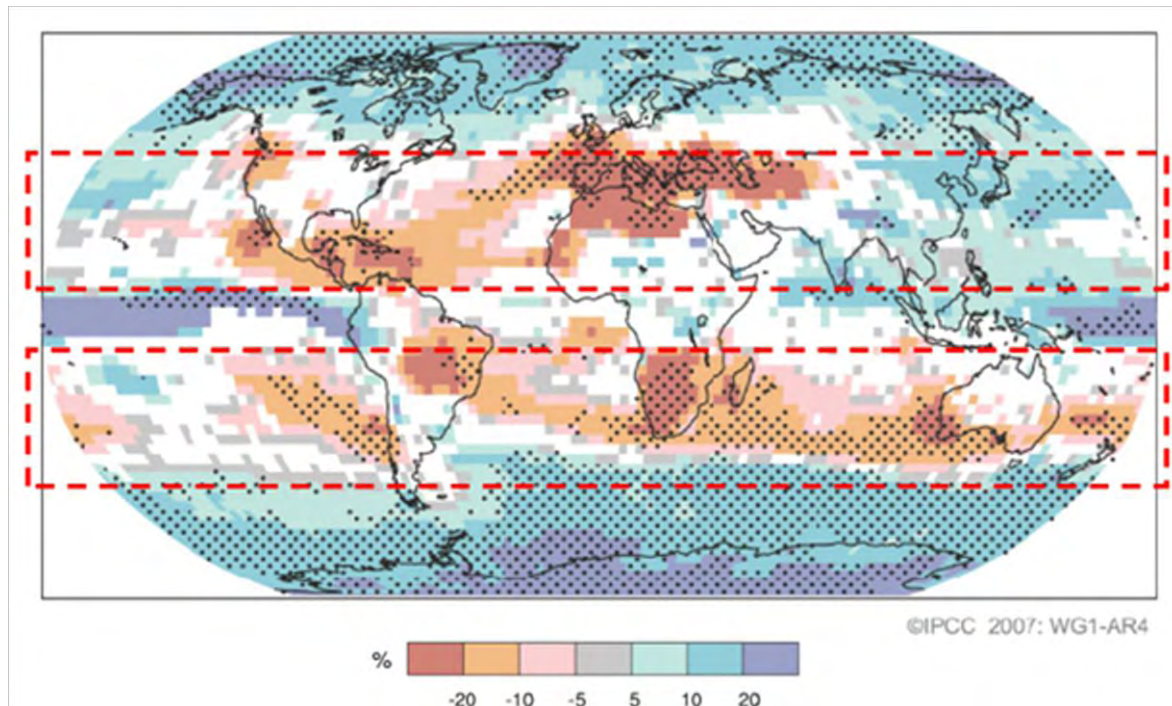


Fig. 3-6. Modelled trends for precipitation (% change between the periods 2090–2099 and 1980–1999; see colour scale at the bottom of the map). Values are multi-model averages based on the SRES A1B scenario for June to August. White areas are where less than 66% of the models agree in the sign of the change and stippled areas are where more than 90% of the models agree in the sign of the change. Boxed areas highlight mid-latitudes, where models predict reduced precipitation. Adapted from IPCC.⁶²

sider the biological effects of such combinations. Ideally, factorial studies should be used to evaluate the influences of simultaneous changes in various factors (e.g., increased prevalence of drought, higher temperatures, more available nitrogen and increased UV radiation). Information from such studies is also required to apportion correctly the effects of combined factors. For example, increased incident UV-B radiation (as a result of ozone depletion) is correlated with the Southern Annular Mode, indicative of atmospheric variability, and with increasing wind at coastal Antarctic sites in the summer.^{121, 140} This can make it difficult to attribute changes in growth rate observed in Antarctic mosses specifically to the negative effects of UV-B radiation or to desiccation from drying winds, although the results clearly show an impact of the ozone hole on the dominant moss flora.^{46, 144}

The following examples from recent studies of factor combinations discuss how other changes in climate enhance or ameliorate effects of UV radiation. Given the paucity of such interaction studies, a comprehensive meta-analysis, as discussed earlier for plant growth, is not possible.

UV radiation and precipitation

Changes in precipitation patterns and increased evaporative loss due to increased temperature are likely to occur as a result of climate change in many regions.^{53, 62, 110} Reduced water availability in terrestrial ecosystems is one of the few environmental factors that clearly interacts with UV-B radiation; past reports highlight numerous studies demonstrating reduced UV sensitivity in higher plants under water stress.³⁰ Recent studies of single plant species under controlled conditions have also shown some of the ways in which cross-tolerance to drought and UV-B radiation might occur. When grown under moderate UV-B levels, *Arabidopsis* plants were more tolerant to a 12-day drought treatment than plants grown without UV-B, as

indicated by two-fold higher photosynthetic rates, and higher relative water contents.¹¹³ In a study of poplar tree cuttings, exposure to enhanced UV-B radiation significantly decreased plant growth and photosynthesis under well-watered conditions, but these effects were obscured by drought, which by itself caused a more drastic growth reduction.⁴⁵ Two studies^{35, 49} which combined high doses of UV-B radiation and water deprivation showed that, overall, UV-B and water stress reduced growth considerably, but less than would be predicted from the additive effects of both stressors. While these results could reflect increased resilience to UV-B in higher plants pre-treated by water deprivation, the apparent interaction may simply indicate that the comparatively subtle effects of UV-B radiation are overwhelmed by those of reduced water availability (e.g., reduced growth, or leaf expansion).

Most of these interaction studies have focused on higher plants (especially cultivated species) that were grown under well-watered conditions and then subsequently exposed to drought treatments. At the other end of the scale, in regions where water severely limits primary production, such as in arid lands, any reduction in availability of water could compromise the ability of the organisms to tolerate UV radiation. Cryptogamic communities (comprising lower plants such as mosses, lichens and algae) are common in these ecosystems. Such communities can be highly tolerant of desiccation. However, if precipitation declines further as a result of region-specific climate change (Fig. 3-6), almost all the fixed carbon would be allocated to maintenance and repair, potentially reducing the resources available for UV protection. This could critically compromise the ability of many desert organisms to survive.^{12, 39}

Studies in Antarctic mosses that related the changes in UV-B-protective pigments and accumulation of DNA photoproducts (damage) to a range of environmental factors suggest that water availability strongly influences the effects of UV-B radiation.¹⁴³ Accumulation of both UV-B-protective pigments and damage to DNA were negatively correlated with plant water content in *Bryum pseudotriquetrum*.^{46, 143} Fully desiccated Antarctic moss species can exhibit considerable resilience to high UV-B radiation; however, when the mosses are hydrated, greater DNA damage occurs at lower relative water content than in fully hydrated plants, and this is likely due to reduced ability for repair. For organisms already existing at their physiological extreme, the biological cost of UV-B protection¹³² or repair³⁹ could compromise survival, but this has yet to be shown.

Biological soil crusts, a consortium of cyanobacteria, lichens, and mosses, are an important component of many dryland ecosystems. Although they produce relatively little biomass, they can be critical in stabilizing arid land soils. Results from a study that augmented UV-B radiation over two years showed that negative effects occurred during the warmer year, when increased temperatures reduced moisture and thus the time available for active growth and carbon gain.¹² The longer periods of desiccation are presumed to have reduced the ability of these organisms to fix carbon and allocate energy to the production of UV-protective pigments and other defenses. While desert organisms can survive naturally high levels of UV radiation under current moisture conditions in extremely harsh environments, even limited climate change could shift the balance from sufficient productivity to increased morbidity.^{12, 39}

Interactions between UV radiation, elevated CO₂ and temperature

Although increased atmospheric CO₂ and temperature are important variables in climate change studies, adequately controlling these factors while simulating natural radiation (especially UV-B), is technically very challenging. As reported previously,³⁰ several studies have used sunlit controlled environment chambers to manipulate UV-B radiation, temperature and

CO₂ simultaneously.^{77, 78} While such chambers were very useful in controlling these factors, they frequently fail to reproduce field conditions due to the high UV levels employed and the omission of solar UV-A radiation from the controls. These studies report that high temperatures combined with increased UV-B radiation had detrimental effects on a range of production^{77, 116} and reproductive^{78, 158} characteristics in soybean and cotton. Higher CO₂ failed to ameliorate the negative effects in soybean.^{77, 78} In two-factor experiments using cotton, elevated CO₂ similarly failed to ameliorate the negative effects of very high doses of UV-B radiation on photosynthesis and growth.^{159, 160}

Experiments designed to evaluate simulated global warming and different UV-B levels have shown responses to both of these factors for individual species and plant communities (see, e.g., Day *et al.*⁴³; Zaller *et al.*¹⁵³). However, there is little evidence of significant interactive effects between UV-B radiation and warming.^{15, 42, 90, 133} For example, in a 2-year field experiment in a South American fen ecosystem, which combined warming of 1.2°C (air temperature) with near ambient- or reduced-solar UV-B treatments,¹⁵³ plant decomposition was generally faster under near ambient UV-B than under reduced UV-B, but was unaffected by temperature. In contrast, the number and biomass of earthworms were negatively affected by warming but unaffected by UV-B radiation. An interesting feature of that study was that the effects of both UV and warming treatments were minor compared to the effect of additional rainfall in one of the years, which doubled plant biomass compared to the drier year. This highlights both the importance of long-term studies, which can control inter-annual variation in weather conditions, as well as the difficulties associated with designing experiments that fully consider multiple and interacting climate factors. Some evidence for significant interactive effects comes from studies with plants from Antarctic Peninsula tundra communities. Day *et al.*⁴² used plastic film coverings (to increase air temperatures by 1.2°C) and this was combined with three UV treatments (near ambient UV-B and two reduced solar UV-B radiation levels using different filter combinations in this area of naturally elevated UV-B radiation). After two years, reproduction in the studied species (*Deschampsia antarctica* and *Colobanthus quitensis*) was accelerated by UV-B at ambient temperatures, but in the warming treatments, UV-B had no effect.

UV radiation and increased nitrogen levels

Deposition of biologically available nitrogen occurs in many locations, especially in temperate latitudes near nitrogen sources from industrial and agricultural activity. Several studies have investigated the effects of interactions between nitrogen and UV-B radiation on agricultural and forest species (see Caldwell *et al.*³⁰), but there is little evidence of consistent interactive effects. The effects tended to be species-specific. The available agricultural studies investigated the effects of nitrogenous fertilizer rather than the deposition of nitrogen from anthropogenic sources (the amounts and timing of nitrogen availability in fertilization and deposition events are usually quite different). In the study of biological soil crusts discussed above, deposition of nitrogen only alleviated UV-induced inhibition of growth in a limited number of cases.¹²

Future approaches to predicting interactive responses

While we have addressed interactions of UV-B radiation with a number of other potential combinations of environmental factors in this short synopsis, most studies, for logistic reasons, were only able to address one interaction or two, or occasionally three factors at a time. In addition, because of difficulties in manipulating multiple factors at the field plot level, many studies are performed in controlled environments. Most interaction studies address the effects of changes in the mean levels of a certain factor, rather than the interactive effects of

discrete events of extreme conditions. Thus, the challenges of predicting real-world responses with several interacting environmental factors are not trivial, especially at the ecosystem scale. While the need for this type of assessment is clear, the pathway to achieve it is not.

Mechanisms of plant responses to UV-B radiation

Elucidating the mechanisms that mediate plant responses to solar UV-B radiation is important for understanding the effects of UV-B radiation on ecological interactions (e.g., plant-herbivore interactions), and for devising strategies for manipulating and possibly exploiting plant sensitivity to UV radiation in species of economic interest.

One of the major obstacles to our understanding of how UV-B radiation is perceived by plants is that the identity of the primary UV-B photoreceptor/s is not well defined. Data derived from a variety of sources, as well as work done on animals, indicate that damage to DNA and activation of receptors on the surface of the cell may trigger some of the responses to UV-B radiation in plant cells.^{30, 68, 136} However, evidence derived from physiological, molecular, and genetic studies indicate that other mechanisms of UV-B perception are present in plant cells.^{30, 68, 146} There are several lines of evidence suggesting that plants have specific photoreceptors for UV-B radiation, analogous to the photoreceptors involved in the perception of visible light and far-red radiation (phytochromes, cryptochromes and phototropins).^{30, 68, 146}

Studies in the reference plant, *Arabidopsis thaliana*, have demonstrated that the protein encoded by *UV RESISTANT LOCUS 8 (UVR8)* controls the expression of numerous genes involved in acclimation to and protection against UV-B radiation. The genes regulated by UVR8 include genes involved in the biosynthesis of flavonoids (protective phenolic sunscreens), the gene encoding a cyclobutane pyrimidine dimer (CPD) photolyase (*UVR2*, which is essential for repair of UV-B-induced DNA damage), and genes connected with protection against oxidative stress and photooxidative damage²⁵. Significant advances have been made in the last few years in the identification of additional components involved in this UV-B-specific signaling pathway. These components include the E3 ligase CONSTITUTIVE PHOTOMORPHOGENESIS 1 (COP1)¹⁰⁷ and the bZIP transcription factors ELONGATED HYPOCOTYL 5 (HY5),^{25, 145} and HY5 HOMOLOG (HYH).²⁷ The UVR8 protein accumulates in the nucleus in response to UV-B radiation where it binds to chromatin in the region of the *HY5* gene promoter, orchestrating the expression of UV-protective genes^{38, 72}. COP1 is required for UV-B-stimulated *HY5* gene activation in light-grown seedlings.¹⁰⁷ Furthermore, recent work has demonstrated that UV-B radiation promotes the direct interaction between the UVR8 and COP1 proteins in the nucleus, and that this interaction is a very early step in UV-B signaling.⁴⁸ In experiments carried out in solar simulators, mutants defective in UVR8 or COP1 show increased sensitivity to UV-B radiation which is consistent with the idea that the UVR8-COP1 pathway plays a key role in activating protective mechanisms under natural conditions.⁴⁸

Whereas the importance of the UV-B-specific UVR8-COP1 pathway in acclimation to UV-B radiation is now well-recognized, the photobiological mechanisms that lead to its activation upon UV-B exposure are unclear. Based on kinetic considerations and the results of genetic screenings (which have failed to find signaling components acting upstream of UVR8), Brown *et al.*²⁶ and Favory *et al.*⁴⁸ have advanced the intriguing possibility that UVR8 itself could act as a UV-B photoreceptor. This interesting hypothesis warrants further investigation.

Neither of the responses that have received quantitative analysis in this assessment (namely growth and herbivory inhibition by solar UV-B radiation, Figs. 1A and 2), have so far been linked explicitly with the UVR8-COP1 pathway. Since the UVR8-COP1 pathway controls the activation of protection and acclimation responses, such as expression of genes involved in DNA repair, it could be predicted that variation among genotypes in the activation of this pathway may lead to differences in their sensitivity to changes in UV-B radiation (slope of Fig. 3-1A), because UV-B-induced inhibition of growth in the field is often correlated with accumulation of DNA damage.^{54, 122} In fact, recent work showed that the inhibitory effects of UV-B radiation on plant growth were more pronounced in mutants that fail to activate the UVR8-COP1 pathway, and also revealed that this pathway is involved in the control of several features that are important for leaf development.¹⁵¹ The connections between UVR8-COP1 activation and the UV-B-induced changes in plant secondary chemistry that determine differences in herbivory patterns (Fig. 3-2, and see section on canopy arthropods) remain to be explored.

Improved understanding of the molecular mechanisms of plant responses to UV-B radiation can be useful in facilitating attempts to enhance UV-B tolerance in crops. Ambient levels of UV-B radiation can diminish crop yield in sensitive varieties;⁹¹ even though these effects are relatively small, they can be economically significant. Recent work on *Arabidopsis* indicates that it is possible to increase the capacity to repair UV-B-induced DNA damage by manipulating the expression of *UVR2* using biotechnology.⁷¹ This technology could be transferred to sensitive plants of economic interest in order to reduce the negative effects of solar UV-B radiation. In addition, as discussed in this assessment, solar UV-B radiation induces plants to accumulate secondary metabolites that play important roles as anti-herbivore defenses (see section on Consumers and decomposers) and alters the levels of chemical compounds that are pharmacologically active or nutritionally valuable (as discussed by Jensen *et al.*)⁶⁶. Therefore, a better understanding of the mechanisms of UV-B perception and signaling may be useful for the production of crop varieties that are more resistant to insect pests (and therefore less dependent on the use of synthetic pesticides) or have improved nutritional value for human consumption.

Technical issues in conducting and evaluating UV-B radiation research

In this section we very briefly address some technical issues in the implementation of biological experiments with UV radiation. Obviously, researchers in the field must make compromises, but appreciation of the limitations of such research is important, as illustrated by the examples presented below.

The analysis of results of multiple experiments shows sizable variation in plant responses to UV-B-manipulation treatments. This is indicated by the scatter of data points in Fig. 3-1A and by the graphically displayed variance in the meta-analysis of Searles *et al.*¹²⁹ Similar broad ranges of responses are seen in experiments with exclusion and/or reduction in UV radiation.^{102, 127} While it is clear that different species (or even varieties) of plants have greatly different sensitivities to UV-B radiation, differences in experimental techniques, as described below, may also have contributed to the variation observed among experiments.

Methodological issues in UV supplementation and exclusion/reduction experiments require careful attention. Filtered UV-B lamps do not have a spectral output that matches that of sunlight, with or without ozone depletion.^{31, 32} Biological Spectral Weighting Functions (BSWF) are therefore used for calculating “biologically effective” UV and relating this to depletion of stratospheric ozone (see Fig. 1-7 in Chapter 1). These BSWFs are dimensionless

factors that represent the relative effectiveness of the different wavelengths in influencing a particular biological response.³² There are many issues involved in choosing the appropriate BSWF for a particular experiment, and there are many potential sources of error.³¹ These potential errors are much greater in greenhouse and controlled-environment studies than in experiments conducted outdoors.^{31, 109} There have been only a few attempts to evaluate the appropriateness of different BSWFs in field environments.^{33, 80, 122}

Experiments employing the reduction or removal of solar UV with various filter materials would appear more straightforward than experiments with UV supplements from lamps, but there are still many complications that need to be addressed, especially to allow comparisons among experiments. Ideally, measurements of solar UV radiation should also be made in association with these experiments.¹²⁷

Subtle effects caused by small differences in shading can also be problematic. To suspend filters and/or lamps above plants used in experiments, various structures have been devised which inevitably cast shade on the plants to various degrees. However, the effect of even small differences in shading among different UV radiation treatments can be appreciable.⁵¹ Other issues can occur in UV exclusion/reduction experiments such as those due to small differences in visible radiation and alterations of other environmental conditions, such as precipitation and wind exposure.⁵⁰

The measurement of UV radiation in field UV lamp supplementation experiments presents many challenges, and simple UV dosimeter measurements supply very limited information. Spectral irradiance data are necessary to calculate BSWF-weighted irradiance. Furthermore, measurements of UV spectral irradiance in experimental settings need to be well documented.

Our understanding of biological responses to UV radiation has improved greatly in the past 5 to 10 years. Similar advances in the physical measurements with appropriate instrumentation, calibration and measurement protocols are needed.

General conclusions

In the coming decades, terrestrial ecosystems will be exposed to further changes in UV irradiance resulting from changes in stratospheric ozone, climate (e.g., altered cloud cover, snow cover, etc.), and land use and agricultural practices (e.g., deforestation, afforestation, changes in crop density, etc.). Predicting the effects of these changes is challenging, given the diversity of ecosystems that are likely to be affected, the paucity of biological response studies, and the need for models that integrate biological knowledge to estimate changes in ecosystem functioning. Also, a number of uncertainties remain regarding the basic mechanisms of plant responses to UV radiation and the experimental approaches that are most suitable to evaluate plant and ecosystem responses under field conditions. However, based on the evidence discussed in this assessment, we can make some inferences on the processes that are more likely to be affected by changes in solar UV radiation.

(i) Current information derived from field studies indicates that the effects of UV-B radiation on the aboveground biomass of terrestrial plants are relatively small. A synthesis of results from a host of comparable studies suggests that, because the Montreal Protocol has been successful in limiting ozone depletion, the reduction in plant growth caused by increased UV-B radiation in areas affected by ozone decline since 1980 is unlikely to have exceeded 6% (Fig. 3-1).^{9, 102, 129} However, caution must be taken with this generalization because variation in susceptibility to UV-B radiation among plant species has been documented

in several studies. In addition, while effects on plant growth may be small, long-term effects of these reductions may be important, particularly for potential carbon sequestration. Below-ground changes as a result of UV exposure above the soil surface also may result in complex interactions for plants, the soil microenvironment and soil microorganisms.

(ii) Sizable effects of changes in UV-B radiation on plant consumption by herbivores and other organisms may have occurred during the last three decades, and are likely to occur in the future in response to predicted variation in the levels of UV radiation. This may be inferred from short-term studies showing large effects of UV-B manipulations on plant interactions with herbivores and microorganisms (see, e.g., Fig. 3-2). However, the long-term consequences of these effects have not been explicitly investigated. From a practical point of view, the knowledge gained on the mechanisms that mediate the effects of UV-B radiation on plant secondary chemistry and plant-herbivore interactions may be used in the design of cropping systems that take advantage of natural plant defenses against herbivores and deliver plant products of increased nutritional value.

(iii) Changes in UV radiation resulting from climate change (e.g., reduced cloud cover and/or vegetative cover in response to increased aridity) or changes in land use patterns may have more important consequences on terrestrial ecosystems than those that have resulted from ozone depletion. This is because the variations in solar radiation caused by climate and land use change: (a) will affect a greater range of ecosystems than those affected by ozone depletion; and (b) will not be restricted solely to the UV-B component of solar radiation. There are several biological and physical processes in terrestrial ecosystems that are not particularly sensitive to UV-B but which are strongly affected by UV-A radiation. Moreover, as discussed in this assessment, interactions between multiple global change drivers and UV radiation are not well understood.

iv) One example of a process that is effectively driven by solar UV-A radiation is the physical degradation of plant litter. Increased photodegradation, in response to reduced cloudiness or reduced canopy cover, will lead to increased carbon release to the atmosphere. In addition, because photodegradation primarily affects the lignin fraction of plant litter, which usually limits microbial decomposition, more photodegradation is also predicted to facilitate biological degradation, thereby increasing carbon release to the atmosphere.

Acknowledgments

The authors wish to thank Drs Jelte Rozema for discussions on the analysis of the data presented in Fig. 3-1, Jay Herman for sharing the data included in Fig. 3-1B before publication, and Amy Austin for helpful comments on the text.

References

- 1 Andrady A, Aucamp PJ, Bais AF, Ballaré CL, Björn LO, Bornman JF, Caldwell M, Cullen AP, Erickson DJ, de Gruijl FR, Häder DP, Ilyas M, Kulandaivelu G, Kumar HD, Longstreth J, McKenzie RL, Norval M, Paul N, Redhwi HH, Smith RC, Solomon KR, Sulzberger B, Takizawa Y, Tang XY, Teramura AH, Torikai A, van der Leun JC, Wilson SR, Worrest RC and Zepp RG, 2010, Environmental effects of ozone depletion and its interactions with climate change: progress report, 2009, *Photochem. Photobiol. Sci.*, **9**, 275-294.
- 2 Andrady A, Aucamp PJ, Bais AF, Ballaré CL, Björn LO, Bornman JF, Caldwell M, Cullen AP, Erickson DJ, Degruijl FR, Häder DP, Ilyas M, Kulandaivelu G, Kumar

- HD, Longstreth J, McKenzie RL, Norval M, Paul N, Redhwi HH, Smith RC, Solomon KR, Sulzberger B, Takizawa Y, Tang X, Teramura AH, Torikai A, van der Leun JC, Wilson SR, Worrest RC and Zepp RG, 2008, Environmental effects of ozone depletion and its interactions with climate change: Progress report, 2007, *Photochem. Photobiol. Sci.*, **7**, 15-27.
- 3 Andrady A, Aucamp PJ, Bais AF, Ballaré CL, Björn LO, Bornman JF, Caldwell M, Cullen AP, Erickson DJ, Degruil FR, Häder DP, Ilyas M, Kulandaivelu G, Kumar HD, Longstreth J, McKenzie RL, Norval M, Paul N, Redhwi HH, Smith RC, Solomon KR, Sulzberger B, Takizawa Y, Tang X, Teramura AH, Torikai A, van der Leun JC, Wilson SR, Worrest RC and Zepp RG, 2009, Environmental effects of ozone depletion and its interactions with climate change: Progress report 2008, *Photochem. Photobiol. Sci.*, **8**, 13-22.
 - 4 Austin AT, Araujo PI and Leva PE, 2009, Interaction of position, litter type and pulsed water events on decomposition of grasses from the semiarid Patagonian steppe, *Ecol.*, **90**, 2642-2647.
 - 5 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.
 - 6 Austin AT and Vivanco L, 2006, Plant litter decomposition in a semiarid ecosystem controlled by photodegradation, *Nature*, **442**, 555-558.
 - 7 Bais AF, Butchart N, Eyring V, Fahey DW, Kinnison DE, Langematz U, Mayer B, Portmann RW, Rozanov E, Braesicke P, Charlton-Perez AJ, Chubarova NY, Diaz SB, Gillett NP, Giorgetta MA, Komala K, Lefevre F, McLandress C, Perlwitz J, Peter T and Shibata K, 2011, Future Ozone and its Impact on Surface UV Scientific Assessment of Ozone Depletion: 2010, UNEP SAP Report No., Nairobi,
 - 8 Balint-Kurti P, Simmons SJ, Blum JE, Ballaré CL and Stapleton AE, 2010, Maize leaf epiphytic bacteria diversity patterns are genetically correlated with resistance to fungal pathogen infection, *Mol. Plant Microbe Interact.*, **23**, 473-484.
 - 9 Ballaré CL, Rousseaux CM, Searles PS, Zaller JG, Giordano CV, Robson MT, Caldwell MM, Sala OE and Scopel AL, 2001, Impacts of solar ultraviolet-B radiation on terrestrial ecosystems of Tierra del Fuego (southern Argentina) An overview of recent progress, *J. Photochem. Photobiol. A.*, **62**, 67-77.
 - 10 Ballaré CL, Scopel AL, Stapleton AE and Yanovsky MJ, 1996, Solar ultraviolet-B radiation affects seedling emergence, DNA integrity, plant morphology, growth rate, and attractiveness to herbivore insects in *Datura ferox*, *Plant Physiol.*, **112**, 161-170.
 - 11 Bassman JH, 2004, Ecosystem consequences of enhanced solar ultraviolet radiation: Secondary plant metabolites as mediators of multiple trophic interactions in terrestrial plant communities, *Photochem. Photobiol.*, **79**, 382-398.
 - 12 Belnap J, Phillips SL, Flint S, Money J and Caldwell M, 2008, Global change and biological soil crusts: effects of ultraviolet augmentation under altered precipitation regimes and nitrogen additions, *Glob. Change Biol.*, **14**, 670-686.
 - 13 Bergvinson DJ, Arnason JT, Hamilton RI, Tachibana S and Towers GHN, 1994, Putative role of photodimerized phenolic-acids in maize resistance to *Ostrinia nubilalis* (Lepidoptera, Pyralidae), *Environ. Entomol.*, **23**, 1516-1523.
 - 14 Bidart-Bouzat MG and Imeh-Nathaniel A, 2008, Global change effects on plant chemical defenses against insect herbivores, *J. Integr. Plant Biol.*, **50**, 1339-1354.
 - 15 Bjerke JW, Zielke M and Solheim B, 2003, Long-term impacts of simulated climatic change on secondary metabolism, thallus structure and nitrogen fixation activity in two cyanolichens from the Arctic, *New. Phytol.*, **159**, 361-367.

- 16 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.
- 17 Bokhorst S, Bjerke JW, Bowles FW, Melillo J, Callaghan TV and Phoenix GK, 2008, Impacts of extreme winter warming in the sub-Arctic: growing season responses of dwarf shrub heathland, *Glob. Change Biol.*, **14**, 2603-2612.
- 18 Bokhorst SF, Bjerke JW, Tommervik H, Callaghan TV and Phoenix GK, 2009, Winter warming events damage sub-Arctic vegetation: consistent evidence from an experimental manipulation and a natural event, *J. Ecol.*, **97**, 1408-1415.
- 19 Bonan GB, 2008, Forests and climate change: Forcings, feedbacks, and the climate benefits of forests, *Science.*, **320**, 1444-1449.
- 20 Bothwell ML, Sherbot DMJ and Pollock CM, 1994, Ecosystem responses to solar ultraviolet-B radiation: influence of trophic-level interactions, *Science.*, **265**, 97-100.
- 21 Brandt L, King J, Hobbie S, Milchunas D and Sinsabaugh R, 2010, The role of photodegradation in surface litter decomposition across a grassland ecosystem precipitation gradient, *Ecosystems*, **13**, 765-781.
- 22 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.
- 23 Brandt LA, King JY and Milchunas DG, 2007, Effects of ultraviolet radiation on litter decomposition depend on precipitation and litter chemistry in a shortgrass steppe ecosystem, *Glob. Change Biol.*, **13**, 2193-2205.
- 24 Brosché M, Schuler MA, Kalbina I, Connor L and Strid A, 2002, Gene regulation by low level UV-B radiation: Identification by DNA array analysis, *Photochem. Photobiol. Sci.*, **1**, 656-664.
- 25 Brown BA, Cloix C, Jiang GH, Kaiserli E, Herzyk P, Kliebenstein DJ and Jenkins GI, 2005, A UV-B-specific signaling component orchestrates plant UV protection, *Proc. Nat. Acad. Sci. USA.*, **102**, 18225-18230.
- 26 Brown BA, Headland LR and Jenkins GI, 2009, UV-B action spectrum for UVR8-mediated HY5 transcript accumulation in Arabidopsis, *Photochem. Photobiol.*, **85**, 1147-1155.
- 27 Brown BA and Jenkins GI, 2008, UV-B signaling pathways with different fluence-rate response profiles are distinguished in mature Arabidopsis leaf tissue by requirement for UVR8, HY5, and HYH, *Plant Physiol.*, **146**, 576-588.
- 28 Caldwell MM, 1971, Solar UV Irradiation and the Growth and Development of Higher Plants, in *Photophysiology, Current Topics in Photobiology and Photochemistry*, Vol. VI ed.: Giese AC, Academic Press:, New York, N.Y., USA; London, England, pp. 131-177.
- 29 Caldwell MM, Ballaré CL, Bornman JF, Flint SD, Björn LO, Teramura AH, Kulandaivelu G and Tevini M, 2003, Terrestrial ecosystems increased solar ultraviolet radiation and interactions with other climatic change factors, *Photochem. Photobiol. Sci.*, **2**, 29-38.
- 30 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.
- 31 Caldwell MM, Camp LB, Warner CW and Flint SD, 1986, Action spectra and their key role in assessing biological consequences of solar UV-B radiation change, in *Stratospheric ozone reduction, solar ultraviolet radiation and plant life* eds.: Worrest RC and Caldwell MM, Springer, Berlin, pp. 87-111.

- 32 Caldwell MM and Flint SD, 1997, Uses of biological spectral weighting functions and the need of scaling for the ozone reduction problem, *Plant Ecol.*, **128**, 66-76.
- 33 Caldwell MM and Flint SD, 2006, Use and Evaluation of Biological Spectral UV Weighting Functions for the Ozone Reduction Issue, in *Environmental UV radiation: Impact on ecosystems and human health and predictive models* eds.: Ghatti F, Checcucci G and Bornman JF, Springer-Verlag, Dordrecht, The Netherlands, pp. 71-84.
- 34 Caputo C, Rutitzky M and Ballaré CL, 2006, Solar ultraviolet-B radiation alters the attractiveness of *Arabidopsis* plants to diamondback moths (*Plutella xylostella* L): Impacts on oviposition and involvement of the jasmonic acid pathway, *Oecologia*, **149**, 81-90.
- 35 Cechin I, Corniani N, Fumis TD and Cataneo AC, 2008, Ultraviolet-B and water stress effects on growth, gas exchange and oxidative stress in sunflower plants, *Rad. Environ. Phys.*, **47**, 405-413.
- 36 Chapin FS, Matson PA and Mooney HA, 2002, *Principles of Terrestrial Ecosystem Ecology*, Springer, New York.
- 37 Clé C, Hill LM, Niggeweg R, Martin CR, Guisez Y, Prinsen E and Jansen MAK, 2008, Modulation of chlorogenic acid biosynthesis in *Solanum lycopersicum*; consequences for phenolic accumulation and UV-tolerance, *Phytochem.*, **69**, 2149-2156.
- 38 Cloix C and Jenkins GI, 2008, Interaction of the *Arabidopsis* UV-B-specific signaling component UVR8 with chromatin, *Molecular Plant*, **1**, 118-128.
- 39 Cockell CS, McKay CP, Warren-Rhodes K and Horneck G, 2008, Ultraviolet radiation-induced limitation to epilithic microbial growth in and deserts - Dosimetric experiments in the hyperarid core of the Atacama Desert, *J. Photochem. Photobiol. B.*, **90**, 79-87.
- 40 Convey P, Pugh PJA, Jackson C, Murray AW, Ruhland CT, Xiong FS and Day TA, 2002, Response of antarctic terrestrial microarthropods to long-term climate manipulations, *Ecol.*, **83**, 3130-3140.
- 41 Correia CM, Areal ELV, Torres-Pereira MS and Torres-Pereira JMG, 1999, Intraspecific variation in sensitivity to ultraviolet-B radiation in maize grown under field conditions - II Physiological and biochemical aspects, *Field. Crops. Res.*, **62**, 97-105.
- 42 Day TA, Ruhland CT, Grobe CW and Xiong F, 1999, Growth and reproduction of Antarctic vascular plants in response to warming and UV radiation reductions in the field, *Oecologia*, **119**, 24-35.
- 43 Day TA, Ruhland CT and Xiong FS, 2008, Warming increases aboveground plant biomass and C stocks in vascular-plant-dominated Antarctic tundra, *Glob. Change Biol.*, **14**, 1827-1843.
- 44 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.
- 45 Duan BL, Xuan ZY, Zhang XL, Korpelainen H and Li CY, 2008, Interactions between drought, ABA application and supplemental UV-B in *Populus yunnanensis*, *Physiol. Plant.*, **134**, 257-269.
- 46 Dunn JL and Robinson SA, 2006, Ultraviolet B screening potential is higher in two cosmopolitan moss species than in a co-occurring Antarctic endemic moss: implications of continuing ozone depletion, *Glob. Change Biol.*, **12**, 2282-2296.
- 47 Elliger CA, Wong Y, Chan BG and Waiss Jr AC, 1981, Growth inhibitors in tomato (*Lycopersicon*) to tomato fruitworm (*Heliothis zea*), *J. Chem. Ecol.*, **7**, 753-758.

- 48 Favory JJ, Stec A, Gruber H, Rizzini L, Oravec A, Funk M, Albert A, Cloix C, Jenkins GI, Oakeley EJ, Seidlitz HK, Nagy F and Ulm R, 2009, Interaction of COP1 and UVR8 regulates UV-B-induced photomorphogenesis and stress acclimation in *Arabidopsis*, *EMBO J.*, **28**, 591-601.
- 49 Feng HY, Li SW, Xue LG, An LZ and Wang XF, 2007, The interactive effects of enhanced UV-B radiation and soil drought on spring wheat, *S. A. J. Bot.*, **73**, 429-434.
- 50 Flint SD, Ryel RJ and Caldwell MM, 2003, Ecosystem UV-B experiments in terrestrial communities: a review of recent findings and methodologies, *Agric. Forest Meteorol.*, **120**, 177-189.
- 51 Flint SD, Ryel RJ, Hudelson TJ and Caldwell MM, 2009, Serious complications in experiments in which UV doses are effected by using different lamp heights, *J. Photochem. Photobiol. B.*, **97**, 48-53.
- 52 Foggo A, Higgins S, Wargent JJ and Coleman RA, 2007, Tri-trophic consequences of UV-B exposure: Plants, herbivores and parasitoids, *Oecologia*, **154**, 505-512.
- 53 Ganguly AR, Steinhäuser K, Erickson DJ, Branstetter M, Parish ES, Singh N, Drake JB and Buja L, 2009, Higher trends but larger uncertainty and geographic variability in 21st century temperature and heat waves, *Proc. Nat. Acad. Sci. USA.*, **106**, 15555-15559.
- 54 Giordano CV, Galatro A, Puntarulo S and Ballaré CL, 2004, The inhibitory effects of UV-B radiation (280-315 nm) on *Gunnera magellanica* growth correlate with increased DNA damage but not with oxidative damage to lipids, *Plant Cell Environ.*, **27**, 1415-1423.
- 55 Gunasekera TS and Paul ND, 2007, Ecological impact of solar ultraviolet-B (UV-B : 320-290 nm) radiation on *Corynebacterium aquaticum* and *Xanthomonas* sp colonization on tea phyllosphere in relation to blister blight disease incidence in the field, *Lett. Appl. Microbiol.*, **44**, 513-519.
- 56 Han BA, Kats LB, Pommerening RC, Ferrer RP, Murry-Ewers M and Blaustein AR, 2007, Behavioral avoidance of ultraviolet-B radiation by two species of neotropical poison-dart frogs, *Biotropica*, **39**, 433-435.
- 57 Hari P, Raivonen M, Vesala T, Munger JW, Pilegaard K and Kulmala M, 2003, Atmospheric science - Ultraviolet light and leaf emission of NO_x, *Nature*, **422**, 134-134.
- 58 Hatcher PE and Paul ND, 1994, The effect of elevated UV-B radiation on herbivory of pea by *Autographa gamma*, *Entomol. Exp. Appl.*, **71**, 227-233.
- 59 Herman JR, 2010, Global increase in UV irradiance during the past 30 years (1979-2008) estimated from satellite data, *J. Geophys. Res.*, **115**, D04203.
- 60 Herman JR, 2010, Use of an improved RAF to estimate the effect of total ozone changes on action spectrum weighted irradiances and an instrument response function, *J. Geophys. Res.*, **115**, D23119
- 61 Hoffland E, Dicke M, Van Tintelen W, Dijkman H and Van Beusichem ML, 2000, Nitrogen availability and defense of tomato against two-spotted spider mite, *J. Chem. Ecol.*, **26**, 2697-2711.
- 62 IPCC, 2007, *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, U.K.
- 63 Izaguirre MM, Mazza CA, Biondini M, Baldwin IT and Ballaré CL, 2006, Remote sensing of future competitors: Impacts on plants defenses, *Proc. Nat. Acad. Sci. USA.*, **103**, 7170-7174.

- 64 Izaguirre MM, Mazza CA, Svatos A, Baldwin IT and Ballaré CL, 2007, Solar ultraviolet-B radiation and insect herbivory trigger partially overlapping phenolic responses in *Nicotiana attenuata* and *Nicotiana longiflora*, *Ann. Bot.*, **99**, 103-109.
- 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 Jansen MAK, Hectors K, O'Brien NM, Guisez Y and Potters G, 2008, Plant stress and human health: Do human consumers benefit from UV-B acclimated crops?, *Plant Sci.*, **175**, 449-458.
- 67 Jansen MAK, Le Martret B and Koornneef M, 2010, Variations in constitutive and inducible UV-B tolerance; dissecting photosystem II protection in *Arabidopsis thaliana* accessions, *Physiol. Plant.*, **138**, 22-34.
- 68 Jenkins GI, 2009, Signal transduction in responses to UV-B radiation, *Annu. Rev. Plant Biol.*, **60**, 407-431.
- 69 Johnson D, Campbell CD, Lee JA, Callaghan TV and Gwynn-Jones D, 2002, Arctic microorganisms respond more to elevated UV-B radiation than CO₂, *Nature*, **416**, 82-83.
- 70 Kadivar H and Stapleton AE, 2003, Ultraviolet radiation alters maize phyllosphere bacterial diversity, *Micro. Ecol.*, **45**, 353-361.
- 71 Kaiser G, Kleiner O, Beisswenger C and Batschauer A, 2009, Increased DNA repair in *Arabidopsis* plants overexpressing CPD photolyase, *Planta*, **230**, 505-515.
- 72 Kaiserli E and Jenkins GI, 2007, UV-B promotes rapid nuclear translocation of the *Arabidopsis* UV-B-specific signaling component UVR8 and activates its function in the nucleus, *Plant Cell*, **19**, 2662-2673.
- 73 Kalbin G, Hidema J, Brosché M, Kumagai T, Bornman JF and Strid A, 2001, UV-B-induced DNA damage and expression of defence genes under UV-B stress: tissue-specific molecular marker analysis in leaves, *Plant. Cell. Environ.*, **24**, 983-990.
- 74 Kalbina I and Strid A, 2006, Supplementary ultraviolet-B irradiation reveals differences in stress responses between *Arabidopsis thaliana* ecotypes, *Plant. Cell. Environ.*, **29**, 754-763.
- 75 Keppler F, Hamilton JTG, Brass M and Rockmann T, 2006, Methane emissions from terrestrial plants under aerobic conditions, *Nature*, **439**, 187-191.
- 76 Kilian J, Whitehead D, Horak J, Wanke D, Weinl S, Batistic O, D'Angelo C, Bornberg-Bauer E, Kudla J and Harter K, 2007, The AtGenExpress global stress expression data set: protocols, evaluation and model data analysis of UV-B light, drought and cold stress responses, *Plant J.*, **50**, 347-363.
- 77 Koti S, Reddy KR, Kakani VG, Zhao D and Gao W, 2007, Effects of carbon dioxide, temperature and ultraviolet-B radiation and their interactions on soybean (*Glycine max* L.) growth and development, *Environ. Exp. Bot.*, **60**, 1-10.
- 78 Koti S, Reddy KR, Reddy VR, Kakani VG and Zhao D, 2005, Interactive effects of carbon dioxide, temperature, and ultraviolet-B radiation on soybean (*Glycine max* L.) flower and pollen morphology, pollen production, germination, and tube lengths, *J. Exp. Bot.*, **56**, 725-736.
- 79 Kotilainen T, Haimi J, Tegelberg R, Julkunen-Tiitto R, Vapaavuori E and Aphalo PJ, 2009, Solar ultraviolet radiation alters alder and birch litter chemistry that in turn affects decomposers and soil respiration, *Oecologia*, **161**, 719-728.
- 80 Kotilainen T, Venalainen T, Tegelberg R, Lindfors A, Julkunen-Tiitto R, Sutinen S, O'Hara RB and Aphalo PJ, 2009, Assessment of UV biological spectral weighting

- functions for phenolic metabolites and growth responses in silver birch seedlings, *Photochem. Photobiol.*, **85**, 1346-1355.
- 81 Kuhlmann F and Müller C, 2009, Development-dependent effects of UV radiation exposure on broccoli plants and interactions with herbivorous insects, *Environ. Exp. Bot.*, **66**, 61-68.
- 82 Kuhlmann F and Müller C, 2010, UV-B impact on aphid performance mediated by plant quality and plant changes induced by aphids, *Plant Biol.*, **12**, 676-684.
- 83 Lavola A, Julkunen-Tiitto R, Roininen H and Aphalo P, 1998, Host-plant preference of an insect herbivore mediated by UV-B and CO₂ in relation to plant secondary metabolites, *Biochem. Syst. Ecol.*, **26**, 1-12.
- 84 Leitner M, Boland W and Mithöfer A, 2005, Direct and indirect defences induced by piercing-sucking and chewing herbivores in *Medicago truncatula*, *New. Phytol.*, **167**, 597-606.
- 85 Li F-R, Peng S-L, Chen B-M and Hou Y-P, 2010, A meta-analysis of the responses of woody and herbaceous plants to elevated ultraviolet-B radiation, *Acta Oecol.*, **36**, 1-9.
- 86 Li J, Lim MLM, Zhang Z, Liu Q, Chen FL and Li D, 2008, Sexual dichromatism and male colour morph in ultraviolet-B reflectance in two populations of the jumping spider *Phintella vittata* (Araneae: Salticidae) from tropical China, *Biol. J. Linn. Soc.*, **94**, 7-20.
- 87 Li J, Zhang Z, Liu F, Liu Q, Gan W, Chen J, Lim MLM and Li D, 2008, UVB-based mate-choice cues used by females of the jumping spider *Phintella vittata*, *Curr. Biol.*, **18**, 699-703.
- 88 Lindow SE and Brandl MT, 2003, Microbiology of the phyllosphere, *Appl. Environ. Microbiol.*, **69**, 1875-1883.
- 89 Lindroth RL, Hofmann RW, Campbell BD, McNabb WC and Hunt DY, 2000, Population differences in *Trifolium repens* L response to ultraviolet-B radiation: Foliar chemistry and consequences for two lepidopteran herbivores, *Oecologia*, **122**, 20-28.
- 90 Lud D, Huiskes AHL, Moerdijk TCW and Rozema J, 2001, The effects of altered levels of UV-B radiation on an Antarctic grass and lichen, *Plant Ecol.*, **154**, 87-99.
- 91 Mazza CA, Battista D, Zima AM, Szwarberg-Bracchitta M, Giordano CV, Acevedo A, Scopel AL and Ballaré CL, 1999, The effects of solar ultraviolet-B radiation on the growth and yield of barley are accompanied by increased DNA damage and antioxidant responses, *Plant Cell Environ.*, **22**, 61-70.
- 92 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.
- 93 Mazza CA, Izaguirre MM, Zavala J, Scopel AL and Ballaré CL, 2002, Insect perception of ambient ultraviolet-B radiation, *Ecol. Lett.*, **5**, 722-726.
- 94 Mazza CA, Zavala J, Scopel AL and Ballaré CL, 1999, Perception of solar UVB radiation by phytophagous insects: Behavioral responses and ecosystem implications, *Proc. Nat. Acad. Sci. USA.*, **96**, 980-985.
- 95 McCloud ES and Berenbaum MR, 1994, Stratospheric ozone depletion and plant-insect interactions: effects of UVB radiation on foliage quality of *Citrus jambhiri* for *Trichoplusia ni*, *J. Chem. Ecol.*, **20**, 525-539.
- 96 McKenzie RL, Aucamp PJ, Bais AF, Björn LO and Ilyas M, 2007, Changes in biologically-active ultraviolet radiation reaching the Earth's surface, *Photochem. Photobiol. Sci.*, **6**, 218-231.

- 97 McKenzie RL, Aucamp PJ, Bais AF, Björn LO, Ilyas M and Madronich S, 2011, Ozone depletion and climate change: impacts on UV radiation, *Photochem. Photobiol. Sci.*, **10**, DOI: 10.1039/c1030pp90034f.
- 98 McLeod AR, Fry SC, Loake GJ, Messenger DJ, Reay DS, Smith KA and Yun BW, 2008, Ultraviolet radiation drives methane emissions from terrestrial plant pectins, *New. Phytol.*, **180**, 124-132.
- 99 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.
- 100 Misra P, Pandey A, Tiwari M, Chandrashekar K, Sidhu OP, Asif MH, Chakrabarty D, Singh PK, Trivedi PK, Nath P and Tuli R, 2010, Modulation of transcriptome and metabolome of tobacco by Arabidopsis transcription factor, AtMYB12, leads to insect resistance, *Plant Physiol.*, **152**, 2258-2268.
- 101 Mittler R, 2006, Abiotic stress, the field environment and stress combination, *Trends Plant Sci.*, **11**, 15-19.
- 102 Newsham KK and Robinson SA, 2009, Responses of plants in polar regions to UVB exposure: a meta-analysis, *Glob. Change Biol.*, **15**, 2574-2589.
- 103 Nisbet RER, Fisher R, Nimmo RH, Bendall DS, Crill PM, Gallego-Sala AV, Hornibrook ERC, Lopez-Juez E, Lowry D, Nisbet PBR, Shuckburgh EF, Srisantharajah S, Howe CJ and Nisbet EG, 2009, Emission of methane from plants, *Proc. R. Soc. B. Biol. Sci.*, **276**, 1347-1354.
- 104 Ohtsuka K and Osakabe M, 2009, Deleterious effects of UV-B radiation on herbivorous spider mites: they can avoid it by remaining on lower leaf surfaces, *Environ. Entomol.*, **38**, 920-929.
- 105 Olsson LC, Veit M, Weissenböck G and Bornman JF, 1998, Differential flavonoid response to enhanced UV-B radiation in *Brassica napus*, *Phytochem.*, **49**, 1021-1028.
- 106 Onzo A, Sabelis MW and Hanna R, 2010, Effects of ultraviolet radiation on predatory mites and the role of refuges in plant structures, *Environ. Entomol.*, **39**, 695-701.
- 107 Oravecz A, Baumann A, Mate Z, Brzezinska A, Molinier J, Oakeley EJ, Adam E, Schafer E, Nagy F and Ulm R, 2006, CONSTITUTIVELY PHOTOMORPHOGENIC1 is required for the UV-B response in Arabidopsis, *Plant Cell*, **18**, 1975-1990.
- 108 Pancotto VA, Sala OE, Cabello M, Lopez NI, Robson TM, Ballaré CL, Caldwell MM and Scopel AL, 2003, Solar UV-B decreases decomposition in herbaceous plant litter in Tierra del Fuego, Argentina: potential role of an altered decomposer community, *Glob. Change Biol.*, **9**, 1465-1474.
- 109 Paul ND, Jacobson RJ, Taylor A, Wargent JJ and Moore JP, 2005, The use of wavelength-selective plastic cladding materials in horticulture: Understanding of crop and fungal responses through the assessment of biological spectral weighting functions, *Photochem. Photobiol.*, **81**, 1052-1060.
- 110 Phillips OL, Aragao L, Lewis SL, Fisher JB, Lloyd J, Lopez-Gonzalez G, Malhi Y, Monteagudo A, Peacock J, Quesada CA, van der Heijden G, Almeida S, Amaral I, Arroyo L, Aymard G, Baker TR, Banki O, Blanc L, Bonal D, Brando P, Chave J, de Oliveira ACA, Cardozo ND, Czimczik CI, Feldpausch TR, Freitas MA, Gloor E, Higuchi N, Jimenez E, Lloyd G, Meir P, Mendoza C, Morel A, Neill DA, Nepstad D, Patino S, Penuela MC, Prieto A, Ramirez F, Schwarz M, Silva J, Silveira M, Thomas AS, ter Steege H, Stropp J, Vasquez R, Zelazowski P, Davila EA, Andelman S, Andrade A, Chao KJ, Erwin T, Di Fiore A, Honorio E, Keeling H, Killeen TJ, Laurance WF, Cruz AP, Pitman NCA, Vargas PN, Ramirez-Angulo H, Rudas A,

- Salamao R, Silva N, Terborgh J and Torres-Lezama A, 2009, Drought sensitivity of the Amazon rainforest, *Science*, **323**, 1344-1347.
- 111 Phoenix GK, Gwynn-Jones D, Callaghan TV, Sleep D and Lee JA, 2001, Effects of global change on a sub-Arctic heath: effects of enhanced UV-B radiation and increased summer precipitation, *J. Ecol.*, **89**, 256-267.
- 112 Pieterse CMJ, Leon-Reyes A, Van der Ent S and Van Wees SCM, 2009, Networking by small-molecule hormones in plant immunity, *Nature Chemical Biology*, **5**, 308-316.
- 113 Poulson ME, Boeger MRT and Donahue RA, 2006, Response of photosynthesis to high light and drought for *Arabidopsis thaliana* grown under a UV-B enhanced light regime, *Photosyn. Res.*, **90**, 79-90.
- 114 Raivonen M, Bonn B, Sanz MJ, Vesala T, Kulmala M and Hari P, 2006, UV-induced NO_y emissions from Scots pine: Could they originate from photolysis of deposited HNO₃?, *Atmos. Environ.*, **40**, 6201-6213.
- 115 Ravishankara AR, Daniel JS and Portmann RW, 2009, Nitrous oxide (N₂O): The dominant ozone-depleting substance emitted in the 21st century, *Science*, **326**, 123-125.
- 116 Reddy KR, Kakani VG, Zhao D, Koti S and Gao W, 2004, Interactive effects of ultraviolet-B radiation and temperature on cotton physiology, growth, development and hyperspectral reflectance, *Photochem. Photobiol.*, **79**, 416-427.
- 117 Rinnan R, Keinänen MM, Kasurinen A, Asikainen J, Kekki TK, Holopainen T, Røpoulsen H, Mikkelsen TN and Michelsen A, 2005, Ambient ultraviolet radiation in the Arctic reduces root biomass and alters microbial community composition but has no effects on microbial biomass, *Glob. Change Biol.*, **11**, 564-574.
- 118 Rinnan R, Nerg AM, Ahtoniemi P, Suokanerva H, Holopainen T, Kyro E and Baath E, 2008, Plant-mediated effects of elevated ultraviolet-B radiation on peat microbial communities of a subarctic mire, *Glob. Change Biol.*, **14**, 925-937.
- 119 Roberts MR and Paul ND, 2006, Seduced by the dark side: Integrating molecular and ecological perspectives on defence against pests and pathogens, *New. Phytol.*, **170**, 677-699.
- 120 Robson TM, Pancotto VA, Scopel AL, Flint SD and Caldwell MM, 2005, Solar UV-B influences microfaunal community composition in a Tierra del Fuego peatland, *Soil Biol. Biochem.*, **37**, 2205-2215.
- 121 Roscoe HK and Haigh JD, 2007, Influences of ozone depletion, the solar cycle and the QBO on the Southern Annular Mode, *Q. J. Roy. Meteor. Soc.*, **133**, 1855-1864.
- 122 Rousseaux MC, Ballaré CL, Giordano CV, Scopel AL, Zima AM, Szwarcberg-Bracchitta M, Searles PS, Caldwell MM and Diaz SB, 1999, Ozone depletion and UVB radiation: Impact on plant DNA damage in southern South America, *Proc. Natl. Acad. Sci.*, **96**, 15310-15315.
- 123 Rousseaux MC, Ballaré CL, Scopel AL, Searles PS and Caldwell MM, 1998, Solar ultraviolet-B radiation affects plant-insect interactions in a natural ecosystem of Tierra del Fuego (Southern Argentina), *Oecologia*, **116**, 528-535.
- 124 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.
- 125 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.

- 126 Ryan KG, Markham KR, Bloor SJ, Bradley JM, Mitchell KA and Jordan BR, 1998, UVB radiation induced increase in Quercetin : Kaempferol ratio in wild-type and transgenic lines of *Petunia*, *Photochem. Photobiol.*, **68**, 323-330.
- 127 Ryel RJ, Flint SD and Barnes PW, 2010, Solar UV-B Radiation and Global Dimming: Effects on Plant Growth and UV-shielding, in *UV Radiation in Global Climate Change: Measurements, Modeling and Effects on Ecosystems* eds.: Gao W, Schmoldt DL and Slusser JR, Springer and Capital Press, pp. 370-394.
- 128 Schlesinger WH, 1997, *Biogeochemistry: An Analysis of Global Change*, Academic Press, San Diego.
- 129 Searles PS, Flint SD and Caldwell MM, 2001, A meta analysis of plant field studies simulating stratospheric ozone depletion, *Oecologia*, **127**, 1-10.
- 130 Searles PS, Kropp BR, Flint SD and Caldwell MM, 2001, Influence of solar UV-B radiation on peatland microbial communities of southern Argentina, *New. Phytol.*, **152**, 213-221.
- 131 Snell KRS, Convey P and Newsham KK, 2007, Metabolic recovery of the Antarctic liverwort *Cephaloziella varians* during spring snowmelt, *Polar Biol.*, **30**, 1115-1122.
- 132 Snell KRS, Kokubun T, Griffiths H, Convey P, Hodgson DA and Newsham KK, 2009, Quantifying the metabolic cost to an Antarctic liverwort of responding to an abrupt increase in UVB radiation exposure, *Glob. Change Biol.*, **15**, 2563-2573.
- 133 Sonesson M, Carlsson BA, Callaghan TV, Halling S, Bjorn LO, Bertgren M and Johanson U, 2002, Growth of two peat-forming mosses in subarctic mires: species interactions and effects of simulated climate change, *Oikos*, **99**, 151-160.
- 134 Stamp NE and Osier TL, 1998, Response of five insect herbivores to multiple allelochemicals under fluctuating temperatures, *Entomol. Exp. Appl.*, **88**, 81-96.
- 135 Stapleton AE and Simmons SJ, 2006, Plant control of phyllosphere diversity: Genotype interactions with ultraviolet-B radiation, in *Microbial Ecology of Aerial Plant Surfaces* eds.: Iacobellis NS, Collmer A, Hutcheson SW, Mansfield JW, Morris CE, J. M, Schaad NW, Stead DE, Surico G and Ullrich M, Kluwer Academic CAB International, Dordrecht, The Netherlands, pp. 223-239.
- 136 Stratmann J, 2003, Ultraviolet-B radiation co-opts defense signaling pathways, *Trends Plant Sci.*, **8**, 526-533.
- 137 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.
- 138 Swift MJ, Heal OW and Anderson JM, 1979, *Decomposition in Terrestrial Ecosystems*, University of California Press, Berkeley.
- 139 Tattini M, Guidi L, Morassi-Bonzi L, Pinelli P, Remorini D, Degl'Innocenti E, Giordano C, Massai R and Agati G, 2004, Differential accumulation of flavonoids and hydroxycinnamates in leaves of *Ligustrum vulgare* under excess light and drought stress, *New. Phytol.*, **163**, 547-561.
- 140 Thompson DWJ and Solomon S, 2002, Interpretation of recent Southern Hemisphere climate change, *Science*, **296**, 895-899.
- 141 Torabinejad J and Caldwell MM, 2000, Inheritance of UV-B tolerance in seven ecotypes of *Arabidopsis thaliana* L Heynh and their F-1 hybrids, *J. Hered.*, **91**, 228-233.
- 142 Trenberth KE and Fasullo JT, 2009, Global warming due to increasing absorbed solar radiation, *Geophys. Res. Lett.*, **36**, L07706.
- 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 JD and Robinson SA, 2009, Accumulation of DNA damage in Antarctic mosses: correlations with ultraviolet-B radiation, temperature and turf water content vary among species, *Glob. Change Biol.*, **15**, 319-329.
- 145 Ulm R, Baumann A, Oravecz A, Mate Z, Adam E, Oakeley EJ, Schaefer E and Nagy F, 2004, Genome-wide analysis of gene expression reveals function of the bZIP transcription factor HY5 in the UV-B response of *Arabidopsis*, *Proc. Natl. Acad. Sci.*, **101**, 1397-1402.
- 146 Ulm R and Nagy F, 2005, Signalling and gene regulation in response to ultraviolet light, *Curr. Opin. Plant Biol.*, **8**, 477-482.
- 147 Vigano I, van Weelden H, Holzinger R, Keppler F, McLeod A and Rockmann T, 2008, Effect of UV radiation and temperature on the emission of methane from plant biomass and structural components, *Biogeosci.*, **5**, 937-947.
- 148 Volynchik S, Plotkin M, Bergman DJ and Ishay JS, 2008, Hornet flight activity and its correlation with UVB radiation, temperature and relative humidity, *Photochem. Photobiol.*, **84**, 81-85.
- 149 Wang ZP, Gullledge J, Zheng JQ, Liu W, Li LH and Han XG, 2009, Physical injury stimulates aerobic methane emissions from terrestrial plants, *Biogeosci.*, **6**, 615-621.
- 150 Wang ZP, Song Y, Gullledge J, Yu Q, Liu HS and Han XG, 2009, China's grazed temperate grasslands are a net source of atmospheric methane, *Atmos. Environ.*, **43**, 2148-2153.
- 151 Wargent JJ, Gegas VC, Jenkins GI, Doonan JH and Paul ND, 2009, UVR8 in *Arabidopsis thaliana* regulates multiple aspects of cellular differentiation during leaf development in response to ultraviolet B radiation, *New. Phytol.*, **183**, 315-326.
- 152 Yao Y, Xuan Z, He Y, Lutts S, Korpelainen H and Li C, 2007, Principal component analysis of intraspecific responses of tartary buckwheat to UV-B radiation under field conditions, *Environ. Exp. Bot.*, **61**, 237-245.
- 153 Zaller JG, Caldwell MM, Flint SD, Ballaré CL, Scopel AL and Sala OE, 2009, Solar UVB and warming affect decomposition and earthworms in a fen ecosystem in Tierra del Fuego, Argentina, *Glob. Change Biol.*, **15**, 2493-2502.
- 154 Zaller JG, Caldwell MM, Flint SD, Scopel AL, Sala OE and Ballaré CL, 2002, Solar UV-B radiation affects below-ground parameters in a fen ecosystem in Tierra del Fuego, Argentina: implications of stratospheric ozone depletion, *Glob. Change Biol.*, **8**, 867-871.
- 155 Zavala JA, Casteel CL, DeLucia EH and Berenbaum MR, 2008, Anthropogenic increase in carbon dioxide compromises plant defense against invasive insects, *Proc. Nat. Acad. Sci. USA.*, **105**, 5129-5133.
- 156 Zavala JA and Ravetta DA, 2002, The effect of solar UV-B radiation on terpenes and biomass production in *Grindelia chilensis* (Asteraceae), a woody perennial of Patagonia, Argentina, *Plant Ecol.*, **161**, 185-191.
- 157 Zavala JA, Scopel AL and Ballaré CL, 2001, Effects of ambient UV-B radiation on soybean crops: Impact on leaf herbivory by *Anticarsia gemmatilis*, *Plant Ecol.*, **156**, 121-130.
- 158 Zhao D, Reddy KR, Kakani VG, Koti S and Gao W, 2005, Physiological causes of cotton fruit abscission under conditions of high temperature and enhanced ultraviolet-B radiation, *Physiol. Plant.*, **124**, 189-199.
- 159 Zhao D, Reddy KR, Kakani VG, Mohammed AR, Read JJ and Gao W, 2004, Leaf and canopy photosynthetic characteristics of cotton (*Gossypium hirsutum*) under elevated CO₂ concentration and UV-B radiation, *J. Plant. Physiol.*, **161**, 581-590.
- 160 Zhao D, Reddy KR, Kakani VG, Read JJ and Sullivan JH, 2003, Growth and physiological responses of cotton (*Gossypium hirsutum* L) to elevated carbon dioxide

and ultraviolet-B radiation under controlled environmental conditions, *Plant. Cell. Environ.*, **26**, 771-782.

Chapter 4. Effects of UV radiation on aquatic ecosystems and interactions with climate change

D.-P. Häder^a, E. W. Helbling^b, C. E. Williamson^c, and R. C. Worrest^d

^a*Neue Str. 9, 91096 Möhrendorf, Germany*

^b*Estación de Fotobiología Playa Unión & CONICET, Casilla de Correo N° 15, (9103) Rawson, Chubut, Argentina*

^c*Department of Zoology, 158 Pearson Hall, Miami University of Ohio, Oxford, Ohio 45056, USA*

^d*CIESIN Fellow, Columbia University, 190 Turnbull Road, New Hartford, Connecticut 06057, USA*

Summary

The health of freshwater and marine ecosystems is critical to life on Earth. The impact of solar UV-B radiation is one potential stress factor that can have a negative impact on the health of certain species within these ecosystems. Although there is a paucity of data and information regarding the effect of UV-B radiation on total ecosystem structure and function, several recent studies have addressed the effects on various species within each trophic level. Climate change, acid deposition, and changes in other anthropogenic stressors such as pollutants, alter UV exposure levels in inland and coastal marine waters. These factors potentially have important consequences for a variety of aquatic organisms including waterborne human pathogens. Recent results have demonstrated the negative impacts of exposure to UV-B radiation on primary producers, including effects on cyanobacteria, phytoplankton, macroalgae and aquatic plants. UV-B radiation is an environmental stressor for many aquatic consumers, including zooplankton, crustaceans, amphibians, fish, and corals. Many aquatic producers and consumers rely on avoidance strategies, repair mechanisms and the synthesis of UV-absorbing substances for protection. However, there has been relatively little information generated regarding the impact of solar UV-B radiation on species composition within natural ecosystems or on the interaction of organisms between trophic levels within those ecosystems. There remains the question as to whether a decrease in population size of the more sensitive primary producers would be compensated for by an increase in the population size of more tolerant species, and therefore whether there would be a net negative impact on the absorption of atmospheric carbon dioxide by these ecosystems. Another question is whether there would be a significant impact on the quantity and quality of nutrients cycling through the food web, including the generation of food proteins for humans. Interactive effects of UV radiation with changes in other stressors, including climate change and pollutants, are likely to be particularly important.

Introduction

The important scientific results on the effects of solar UV radiation published during the past four years are assessed for aquatic ecosystems. In total, aquatic ecosystems (1) absorb a similar amount of atmospheric carbon dioxide as terrestrial ecosystems, (2) produce half of the biomass on our planet,⁸⁴ (3) are a major source for human food supply and drinking water, and (4) are economically important for pharmaceutical and chemical industries.^{25, 55, 132, 136, 142, 171, 228, 257, 275, 287}

Solar UV radiation can damage aquatic organisms and decrease the productivity of aquatic ecosystems. These effects of UV radiation may reduce the photosynthetic uptake of atmospheric carbon dioxide and affect species diversity, ecosystem stability,

trophic interactions, and global biogeochemical cycles. The negative effects of UV radiation may be augmented by other environmental changes,^{96, 122} including global climate change⁷ and pollution that result in vast “dead zones”,¹⁶⁵ which collectively turn “estuaries and even parts of the oceans into barren wastelands”.⁴⁹ Many bacteria, plants and animals cope with UV stress with adaptive responses.^{53, 92, 139, 245}

We briefly assess current knowledge on factors controlling the penetration of solar UV radiation into the water column, as well as protective mechanisms of aquatic organisms against solar UV radiation (Fig. 4-1). This is followed by a more in-depth assessment of the impacts of UV radiation on different components of aquatic ecosystems, including bacteria, cyanobacteria, phytoplankton, seaweeds (macroalgae), and consumers (zooplankton, amphibians, fish, corals and other animals). The interactive effects of UV radiation with pollutants and changing oceanic pH are also discussed.

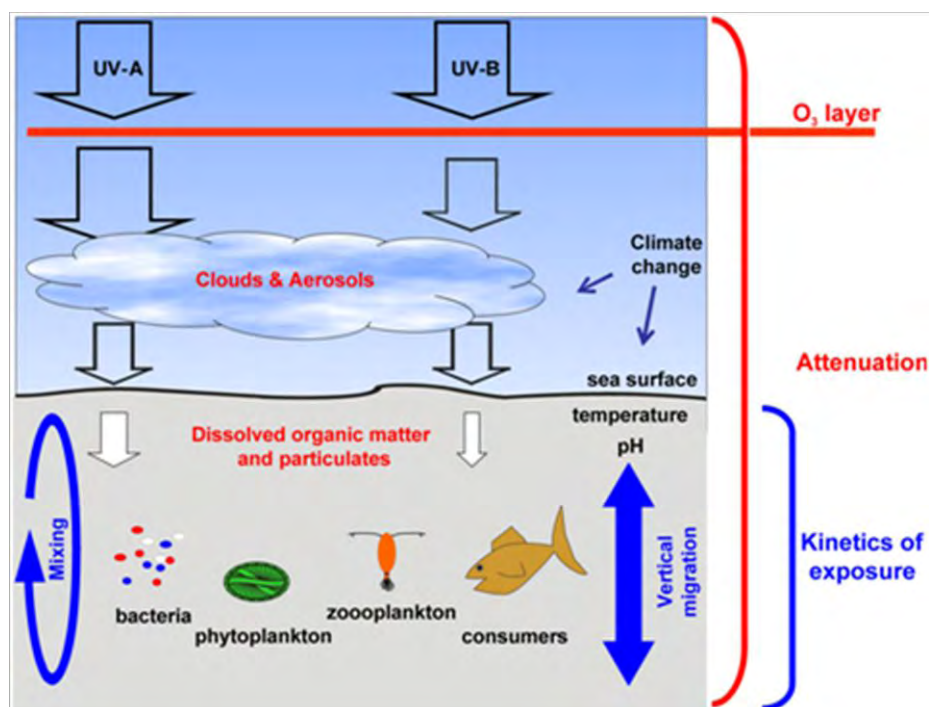


Fig. 4-1. Main factors affecting the quantity and quality of UV radiation received by aquatic organisms. Modified from Gonçalves et al.⁷⁹

UV radiation in the water column and climate-change effects

Transmission into natural waters

The transmission of solar UV radiation into the water column depends on variables in the atmosphere and in the water that affect the amount of UV radiation and wavelength distribution.^{85, 227} Water transparency to UV depends on the optical properties of the water itself,²⁸ dissolved material, phytoplankton concentration, and the density of suspended particles.^{31, 231} Coloured dissolved organic matter (CDOM) is a major factor controlling optical characteristics of freshwater and coastal habitats, thus reducing UV exposures of organisms in the water. It is generated through microbial degradation of organic material from macroalgae and plankton as well as terrestrial plants.^{107, 110} Quality and quantity of CDOM thus vary seasonally due to variations in these aquatic processes and rainfall events.^{97, 243} CDOM plays direct and indirect roles in biogeochemical cycles (Chapter 5).

Some of the most UV-transparent waters are systems with extremely low CDOM concentrations such as the hyper-oligotrophic waters of the South Pacific Gyre where diffuse attenuation coefficients indicate that 1% of incident surface UV radiation (at 325 nm) reaches as deep as 84 m.²⁴⁹ In some of the clearest lakes 1% of UV (at 320 nm) penetrates as deep as

27 m (Lake Tahoe, California-Nevada, USA),²⁰⁹ or 62 m (Crater Lake, Oregon, USA).⁹⁵ Due to their high elevation and location above the treeline, alpine lakes have very little CDOM and also higher levels of incident UV, giving them some of the highest overall UV exposure levels in the world, with important implications for species composition (Fig. 4-2).²⁰⁹

Solar UV radiation causes photo-degradation of CDOM,^{56, 256, 286} this being a key process in the carbon cycle.^{8, 264} The breakdown of larger molecules into smaller fragments stimulates bacterial activity and can alter the species composition of bacterioplankton,¹⁹⁰ while degradation of organic matter from several aquatic plants releases nutrients such as phosphorus and iron.^{19, 167, 218} The photo-degradation of CDOM increases transmission of solar UV radiation in the water column, potentially enhancing deleterious effects on aquatic organisms.⁵⁶ In freshwater lakes, measurements of CDOM absorption can be used as a proxy for UV transmission and prediction of water quality, as was done in the shallow Lake Taihu, China, an important drinking water resource.²⁸⁸ In Lake Tahoe in California-Nevada, strong inshore-offshore gradients and seasonal changes in transparency to UV-A (380 nm) radiation provide a more sensitive indicator of environmental change than variations in visible light transparency.²⁰⁹ Water samples taken at different locations in the Bering Sea and exposed to solar UV radiation at controlled temperatures showed an 18-55% decrease in CDOM at some stations.³² At other stations, up to a 16-fold increase in CDOM absorption was observed and attributed to decreases in the ability of microbes to degrade CDOM derived from algal blooms. Experiments with freshwater samples from Antarctica and North America have shown that UV-induced production of singlet oxygen by CDOM contributes to degradation of dissolved free amino acids.²⁷

Climate change and UV radiation in the water column

Climate change and other stressors have important effects on the underwater UV radiation through a variety of mechanisms including changes in UV transparency and mixing depth of the surface waters. The consequent changes in UV exposure have important implications for processes ranging from UV inactivation of water-borne human pathogens to carbon cycling. Some of the major consequences of climate change effects on aquatic ecosystems are chang-

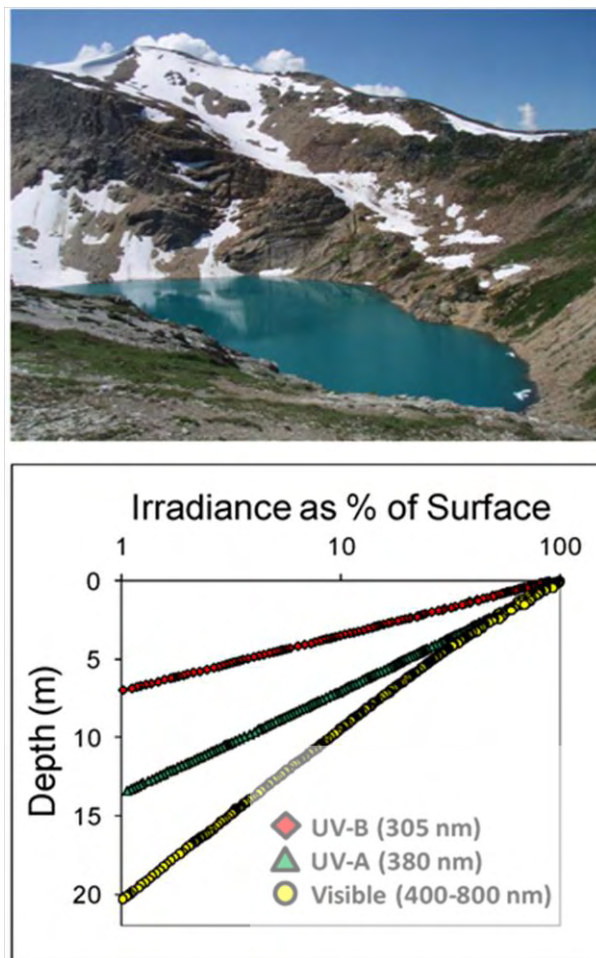


Fig. 4-2. Profiles of UV-B, UV-A radiation, and visible light penetration in Sunlite Lake, an alpine lake in the Canadian Rocky Mountains. The high elevation of alpine lakes leads to high incident UV radiation, while the low levels of DOM in alpine lakes lead to high UV transparency of the waters. The result is that aquatic organisms are exposed to higher levels of damaging UV radiation in alpine lakes than in any other aquatic ecosystem.

ing temperature, precipitation and ice melting. In some regions warmer air temperatures and reduced precipitation are predicted by climate models, while in other regions the opposite is expected.¹¹⁴ Both of these will affect the depth of the surface mixed layer.¹¹⁶ Shallower surface mixing depths have the potential to increase UV exposure of aquatic organisms that live in the upper layers.

Over the past two decades, concentrations of DOM have doubled in inland waters across major portions of north-eastern North America and Europe.^{54, 59, 163} The reasons for this appear to be related largely to reductions in acid deposition,^{54, 163} but climate may also play an important role.^{241, 267} One major concern is that increased DOM concentrations will reduce the natural levels of solar UV that are important for inactivating human pathogens such as *Cryptosporidium*^{43, 131, 272} and Chapter 2.

Optical properties in polar freshwater and marine systems are further modulated by snow and ice cover as well as by dissolved and particulate material from runoff during melting.²¹⁶ Climate-driven decreases in the duration of ice cover have been observed in polar marine waters.^{238, 242, 263} These conditions are predicted to undergo large changes due to climate change in the future. A model based on several environmental factors, such as concentrations of DOM, weather conditions, and water acidification, indicated that the dominant effects of climate change on the organisms of the upper water layers of small lakes operate through processes that affect water transparency.^{128, 183} The number of days above freezing is also an important predictor of concentration of DOM.²⁶⁷ Very limited information is available on the balance between the interactive effects of climate-driven changes in temperature, precipitation, and quality and quantity of DOM, information that is necessary to decipher the net effects of climate change on UV exposure in aquatic ecosystems.

Protective mechanisms of aquatic organisms against UV radiation

All photosynthetic aquatic organisms are restricted to the sunlit upper layers of the water column where they are simultaneously exposed to solar visible and ultraviolet radiation. But many of the consumers in aquatic habitats are also found in this zone and will face the same environmental stresses. In addition to the current elevated levels of solar UV-B radiation in some regions, several aspects of global climate change may increase the exposure and impose additional stresses on these organisms.

During evolution, aquatic organisms have developed a variety of protective strategies against solar UV stress. Motile biomass producers and consumers avoid excessive radiation by vertical migration. Sessile (attached) organisms rely on selection of habitat to limit solar exposure. Effective DNA repair systems eliminate DNA lesions encountered during high solar UV irradiation. Different taxonomic groups have developed a number of photoprotective substances such as melanins, mycosporines, mycosporine-like amino acids (MAAs), scytonemin, carotenoids, phycobiliproteins and several other UV-absorbing compounds of yet unknown chemical structure.¹³²

Protection by UV-absorbing mycosporine-like amino acids (MAAs)

MAAs are the most common UV-screens in many marine and freshwater organisms.²²³⁻²²⁵ They are small (<400 Dalton), intracellular, water-soluble compounds.⁸⁴ They absorb in the UV-A and UV-B range (between 309 and 362 nm) and are characterized by high molar extinction coefficients, photostability and resistance to many abiotic environmental factors. These substances seem to have evolved in cyanobacteria and are also synthesized by many phytoplankton groups and seaweeds (macroalgae). They are also found in animals as a result

of being taken up through their diets. Nonetheless, a recent study identified the genes encoding enzymes for MAA biosynthesis in the starlet sea anemone *Nematostella vectensis*, indicating that some animals may be capable of MAA synthesis or modification.²³⁹ Another option to obtain UV protection is to host MAA-producing symbionts as found in the marine algal-bearing ciliate (*Maristentor dinoferus*) isolated from coral reefs.²³² Corals are other examples which obtain MAAs from their photosynthetic symbionts.³ In most corals, concentrations of MAAs vary seasonally and there is a negative correlation between MAA concentration and depth.^{21, 251}

While the precise mechanisms of MAA biosynthesis are still not completely understood, recently several groups clarified the early stages of biosynthesis and identified the genes involved in the pathway in cyanobacteria and green and red algae.^{195, 222} MAA synthesis requires the availability of sufficient nitrogen in the environment.⁶³ Therefore, environmental factors reducing the concentration of nitrogen in water will compromise the capability of the organisms to protect themselves against solar UV radiation. Recent research has continued to clarify the biochemical pathway and molecular structure of the important UV-absorbing pigments.^{42, 133} In addition to their role as UV-absorbing pigments, MAAs have other physiological functions such as osmotic regulation and scavenging of reactive oxygen species (ROS), which can contribute to adaptation strategies.^{40, 175}

Changing environmental conditions due to global climate change (such as osmotic stress, salt stress, temperature) affect the biosynthesis of MAAs in several groups of aquatic organisms.²²¹ Desiccation plays a key role in the economically important *Porphyra* (nori) in maintaining high concentrations of MAAs,¹¹⁷ thus allowing this seaweed to compete in the intertidal zone exposed to high levels of UV radiation. In diatoms, in contrast to many other aquatic organisms, MAAs are largely bound to the silica cell wall.¹¹³ Therefore MAAs are found in sediments and can be used as markers for previous MAA concentrations in marine organisms.

Protection by other UV-absorbing pigments

The UV-absorbing scytonemin is exclusively synthesized by cyanobacteria.¹⁹⁸ It is a dimeric, lipid-soluble pigment deposited in the extracellular sheaths of the cells.²²⁰ Like MAAs, synthesis of scytonemin requires the availability of nitrogen.⁶³ Periodic desiccation augments its productivity.⁶² In *Nostoc punctiforme* the response of a specific region in the genome associated with scytonemin synthesis was found to be activated (up-regulated) by exposure to UV radiation.^{234, 235} Other UV-absorbing/screening compounds in marine organisms include 3-hydroxykynurenine, sporopollenin, melanin and fluorescent pigments.⁸⁶

Effects of UV-B radiation on aquatic bacteria

Bacteria, being decomposers, occupy a key position in the microbial loop of aquatic ecosystems, breaking down and mineralizing organic matter of decaying plants and animals. They form a link to higher trophic levels and are the main users of DOM. Water transparency strongly depends on the density of bacterial populations, and simultaneously phototransformation of DOM influences species distribution and bacteria concentrations in both freshwater and marine waters.^{1, 185} Passive screening pigments are not effective in bacteria, because of their small size, which would require the concentration of these screening compounds to be excessively high to provide sufficient absorption. Therefore many aquatic bacteria are severely damaged by solar UV-B radiation at the molecular, cellular and population levels. Surface samples of heterotrophic bacteria collected during the BIOSCOPE cruise in the South East

Pacific documented highest inhibition rates in bacterial productivity at noon time corresponding to the highest levels of solar UV-B radiation.²⁵⁹

Possible strategies to mitigate UV-B radiation damage include high rates of reproduction and effective repair mechanisms.^{179, 290} Immunoassay techniques applied to bacterioplankton samples collected off the coast of Chile (36° S) during the austral spring showed damaged DNA evidenced by a high induction of cyclobutane pyrimidine dimers (CPD) after exposure to surface solar radiation.^{101, 102} Bacteria in surface water samples showed a more effective photorepair mechanism than subsurface assemblages. Residual, chronic DNA damage was detected at the end of the experiment, and thus CPDs accumulated with time.

Bacteria with the highest UV-B tolerances found to date are from remote, high-altitude Andean lakes between 4200 and 4600 m above sea level.^{50, 283} Different species have different sensitivities with respect to UV radiation.^{4, 125} For solar (UV-A and UV-B) radiation and actively growing cells, the Gram-positive *Microbacterium maritopicum* was three times more resistant than the Gram-negative *Vibrio natriegens*.²⁷⁰ These results indicate that increased exposure to solar UV-B radiation may affect bacterial assemblages, which may have consequences for higher trophic levels in aquatic ecosystems. It may also affect population densities of human pathogenic bacteria (see Chapter 2).

Consequences for cyanobacteria of elevated solar UV radiation and global climate change

Photosynthetic cyanobacteria are ubiquitous in freshwater and marine habitats from polar regions to the equator (Fig. 4-3). They are major biomass producers in the oceans and wetlands and responsible for the conversion of atmospheric nitrogen into nitrate and other compounds used by phytoplankton. Cyanobacteria are believed to have been the first photosynthetic organisms to produce oxygen 2.5–2.7 billion years ago. The enrichment of photosynthetically produced oxygen in the atmosphere over millions of years ultimately led to the development of the ozone (O₃) layer in the stratosphere.¹²² Obviously, early ancestors of modern cyanobacteria were well adapted to high levels of solar UV-B and even UV-C radiation (below 280 nm) before the development of the ozone layer⁴¹ and this could explain why some specialized cyanobacteria are capable of surviving in extreme habitats characterized by



Fig. 4-3. Typical assemblages of cyanobacteria with other algae in aquatic habitats. Cyanobacteria are major biomass producers in freshwater and marine habitats. They are also important nitrogen fixers for aquatic habitats. Even though they synthesize protective pigments and use other mitigating strategies they are affected by solar UV-B radiation. Courtesy R. P. Sinha.

very high levels of UV-B radiation today.^{188, 189}

In contrast, current solar UV-B radiation inhibits photosynthetic activity in most cyanobacteria.²²⁴ One main target in photosynthesis is the D1 protein in the photosynthetic electron transport chain within the reaction center of photosystem II.²¹⁹ The damaged D1 proteins are replaced by newly synthesized molecules.³⁸ Furthermore, the phycobilin antenna pigments, responsible for collecting solar energy, are dismantled.²²⁶

Solar UV radiation also modifies the morphological structure of filamentous cyanobacteria (*Arthrospira*) which is interpreted as a protection against solar radiation.^{73, 147} This morphological alteration is prevented at elevated temperatures.^{70 149} In *Anabaena*, solar UV radiation also inhibited the development of heterocysts, which are responsible for fixation of atmospheric nitrogen.^{72, 146}

Cyanobacteria are protected from solar UV-B radiation by production of a number of UV-absorbing substances (see section on protective mechanisms above).²⁸⁵ Other mitigating strategies include avoidance, colony and mat formation, scavenging of reactive oxygen species (ROS), and repair of UV-induced damage.²²⁰ In addition, cyanobacteria regulate their position in the water column through buoyancy, by producing gas vesicles.¹⁵⁰ When grown only under visible radiation, the filaments of *Arthrospira* maintained their buoyancy, whereas they migrated downwards when UV radiation (280 – 400 nm) was added. Higher temperatures caused by global climate change may compromise this avoidance strategy under excessive solar UV-B radiation, e.g. by decreasing the depth of the upper mixed layer.

In addition to direct cellular damage, solar UV-B radiation can impair cyanobacteria by producing ROS,²² against which the organisms protect themselves by the synthesis of antioxidants.⁹⁸ *Nodularia* are dominant cyanobacteria in massive blooms in the Baltic Sea during high levels of solar radiation and stable stratification. The ability to fix nitrogen, tolerance to phosphorus starvation and increased MAA production, demonstrated in an outdoor experiment, may contribute to the competitive advantage over other phytoplankton during blooms.¹⁶¹

Effects of UV radiation on phytoplankton communities

Phytoplankton are one of the main producers in marine systems, synthesizing organic matter via photosynthesis and accounting for about half of the production of organic matter on Earth. They absorb large amounts of atmospheric carbon dioxide, some of which sinks to the deep sea floor (see discussion of the “biological pump” in Chapter 5). Specific effects of UV radiation (particularly UV-B) on DNA,¹⁵⁹ carbonic anhydrase,²⁷⁶ fatty acid composition²⁷⁴ and metabolic processes, e.g., photosynthesis,²⁶² and calcification⁸² of phytoplankton organisms have been reported.

Specificity of UV radiation effects

The responses of phytoplankton to solar UV radiation exposure have an important component of species-specificity,^{140, 274} thus having an impact not only on biodiversity but also on the food web. However, part of the responses and the acclimation potential to light stress, for both PAR (photosynthetically active radiation, 400-700 nm) and UV radiation, are dependent on the previous light history regime imposed on the cells. On the one hand, the light history depends on various climate change factors, such as the changing depth of the upper mixed layer, the water transparency, etc., while acclimation would also depend on temperature. For example, some species are photoinhibited under high UV radiation when previously acclimated to low light, but are then capable of reaching high photoprotection levels when accli-

mated to moderate-high light. The acclimation mechanisms include interspecific changes in the xanthophyll cycle activity,^{51, 258} in MAAs concentration¹⁶² or in superoxide dismutase activity.¹¹⁵

When exposed to UV radiation, some diatoms (i.e., *Skeletonema costatum*) were very sensitive and did not survive for more than three days, whereas others (e.g., *Amphora coffeaeformis* and *Odontella aurita*) were able to acclimate to UV stress, although through different processes.⁶⁴ Differential acclimation of species in relation to their habitat can occur during the spring bloom in some coastal areas.⁵¹ The acclimation mechanisms, however, are also affected by UV radiation (e.g. affecting the xanthophyll cycle), thus reducing the photoprotective capacity.⁸⁶ In addition, different species use different mechanisms. For example, while one species acclimated relatively fast (3–5 days) to solar UV radiation by synthesizing UV-absorbing compounds,⁶⁸ another species accelerated or upgraded repair processes for UV-induced damage.⁸¹ The concentration of CO₂ seems to have a role in conditioning the sensitivity of a diatom (*Thalassiosira pseudonana*) as this species was more sensitive to UV radiation when acclimated to high CO₂ than under atmospheric CO₂ levels. Previous acclimation to UV radiation, however, partially counteracted the increased sensitivity observed under elevated CO₂ conditions.^{229, 230}

Comparative studies on the swimming behaviour (avoidance strategy) of some phytoplankton species also demonstrated a high variability among species. While some species were insensitive to UV radiation and accumulated near the surface, others were very sensitive to UV-B radiation, decreasing the swimming speed and percentage of motile cells after 2–3 h of exposure to solar radiation. In addition, cells migrate deep in the water column when irradiances are high (local noon).^{196, 197} Climate change issues, such as the decreasing depth of the upper mixed layer may change the swimming behaviour as cells may not be able to migrate deep in the water column thus favouring UV-resistant species.

Effects on natural phytoplankton communities

Working with specific cultures, as mentioned above, is important to understand the differential sensitivity and underlying mechanisms for the impacts of UV-B radiation. However, the extrapolation from laboratory results to natural conditions is not direct or simple, and thus working *in situ* and with natural assemblages is preferable. Latitudinal studies have highlighted the variability of phytoplankton responses to solar UV radiation. Studies conducted in the Antarctic showed that open-ocean phytoplankton were more sensitive to UV radiation than coastal assemblages, the latter having higher rates of repair.⁶⁶ The effects of UV radiation were transient and growth of Antarctic benthic diatoms was generally unaffected, suggesting little or no UV radiation impact.²⁷⁸ One contrasting study, however, suggested that the effects of ozone depletion on primary production of Antarctic phytoplankton, in ice-covered and open waters, might not be negative but instead could enhance primary production.⁸⁷ UV radiation induced photoinhibition of natural post-bloom phytoplankton diatom-dominated assemblages from temperate latitudes of Patagonia. The inhibition, however, decreased when samples were dominated by chlorophytes that are potentially a better quality food for grazers.²⁶² Tropical phytoplankton assemblages from a coastal site of the South China Sea were significantly inhibited by UV radiation (mostly by UV-B) during sunny days. However, during cloudy days, while small cells (pico- and nanoplankton <20 µm) were still inhibited by UV radiation, larger cells (microplankton >20 µm) used UV-A radiation as a source of energy for photosynthesis.⁶⁹ Since climate change would affect cloud cover, this would have a different impact on phytoplankton depending on their size with potential negative implications for the food web.

The importance of small-size cell structure was highlighted in studies carried out in deep ultraoligotrophic lakes in the Andean-Patagonian region where UV-B radiation had a low contribution to photosynthetic inhibition.³⁶ In temperate and tropical environments, artificially added UV-B radiation had a greater inhibitory effect on the synthesis of D1 protein than on the D1 degradation process itself, thus affecting the synthesis/degradation balance. In addition, the net damage rate of D1 was faster in tropical communities, most likely due to the effects of high light and water temperature.³⁰

Estuarine diatoms had a higher and more flexible capacity for photoprotection than oceanic and coastal species, and when exposed to excess light they had less photoinhibition, and thus an adaptive advantage.¹⁴¹ Tidal dynamics and physical forcing had important effects on the distribution and photosynthesis dynamics of estuarine phytoplankton. Mixing conditions during low tide, together with relatively high concentrations of DOM and particulate material, result in partial protection for phytoplankton against solar radiation stress.¹⁰⁰ Since both stratification and DOM are affected by climate change (see above), it is not yet clear how the circulation and thus the response of phytoplankton will be affected in estuaries.

Solar radiation affects stoichiometry causing deviations from the carbon:nitrogen:phosphorus (C:N:P) ratio (the Redfield ratio) in phytoplankton, thus changing food quality in aquatic food-webs, as well as affecting biogeochemical cycling.¹⁰⁴ High levels of PAR increase C:P ratios in Arctic marine and freshwater phytoplankton species which would likely lower food quality for herbivores. In contrast, exposure to UV radiation reduced cellular C:P (and N:P) ratios in phytoplankton.¹⁰⁴ It was suggested that the low C:P ratios in living and dead particles (seston) in the water column are the outcome of an adaptive strategy of algae in environments with high UV radiation exposure and extreme nutrient limitation.³⁷ Natural plankton communities maintained in mesocosm enclosure experiments (initial CO₂ concentrations of 350, 700 and 1,050 ppm) consumed up to 39% more dissolved inorganic carbon at increased CO₂ levels, whereas nutrient uptake remained the same. The stoichiometry of carbon to nitrogen uptake increased from low CO₂ to high CO₂, and this excess carbon consumption was associated with higher loss of organic carbon from the upper layer of the stratified mesocosms.¹⁹⁹ While the increase in CO₂ concentration would decrease the food quality available for grazers, exposure to UV radiation would tend to counteract this by reducing carbon fixation. Different regions would be affected differently and the balance between these two contrasting effects is still unknown.

Effects of vertical mixing

Studies of the combined effects of vertical mixing and UV radiation have gained increased interest, as mixing affects the radiation field (i.e., it produces a fluctuating radiation regime) under which cells are exposed. In addition, increased temperature, as a result of climate change, will affect the stratification of the water column thereby decreasing the upper mixed layer depth, thus affecting mixing and increasing exposure of cells to solar radiation. Fast changing exposure experiments showed significant inter-specific differences in photosynthesis when phytoplankton cells circulated within a simulated upper mixed layer. While one species (*Dunaliella salina*) was affected by both high and low solar irradiances, another (*Thalassiosira weissflogii*) was inhibited only by high solar irradiances. *Heterocapsa triquetra* showed the least variability and benefited from fluctuating radiation regimes.¹⁶ No DNA damage (as measured by accumulation of cyclobutane pyrimidine dimers) was detected in a comparison of three dinoflagellate species (*Heterocapsa triquetra*, *Gymnodinium chlorophorum* and *Prorocentrum micans*) exposed to solar radiation under static and mixing conditions during the austral spring.⁹⁹ However, a significant inhibition of photosynthesis was observed in static samples of the three species. Increasing mixing speed increased UV-induced inhibi-

tion of carbon fixation in *G. chlorophorum* and *H. triquetra*, but not in *P. micans*. Most of the loss in carbon fixation in *G. chlorophorum* was due to UV-B radiation, while in *H. triquetra* it was due to UV-A radiation. Simulated vertical mixing resulted in more inhibition of photosynthesis by UV radiation as compared to static samples of coastal phytoplankton from the English Channel.¹¹⁹ Studies carried out with phytoplankton from a tropical, shallow lake in southern China, showed that cells had lower photosynthetic quantum yields under static conditions than under *in situ* conditions in the lake at the same time of the day. During stratified conditions, no impact of UV radiation could be detected *in situ* as compared with the static samples. Increasing vertical mixing not only counteracted the impact of UV radiation but also stimulated photosynthesis.²⁶¹ Growth of subpolar phytoplankton under static and mixed conditions was inhibited by UV-B radiation at the beginning of the experiment (flagellate dominated assemblages) but not after several days of exposure (diatom dominated assemblages). While synthesis of MAAs was the strategy of cells to cope with UV radiation in the fixed-depth experiments, changes in species composition towards more tolerant ones was observed under mixing conditions.¹⁰³ Variable mixing conditions together with grazing greatly influenced the algal losses in a freshwater lake.²⁵⁰

Long-term effects - mesocosm studies

As opposed to short-term experiments (<1 day), long-term experiments using large volumes of samples (mesocosms) provide insight into processes (e.g., acclimation, changes in species composition, etc.) that need several days to take effect and are often not observed in short-term experiments. Overall, long-term studies point to differential selection of species and food quality, towards UV-tolerant cells. These changes play a critical role that might affect the food chain, although the impact depends on the particular environment considered, thus varying geographically.

Mesocosm studies with phytoplankton from the Gulf of St. Lawrence (Canada), using solar and enhanced UV-B radiation, did not find any effect on phytoplankton biomass or cell concentrations. Bacterial abundances, on the other hand, increased in the enhanced UV-B radiation treatment, due to a reduction of grazing ciliates (*Strombidinium* sp., *Prorodon ovum* and *Tintinnopsis* sp.).⁵⁷ Similarly, Antarctic phytoplankton biomass was not reduced by UV radiation, but the species composition was modulated by grazers in the absence of UV radiation.²⁸⁰ At two markedly different sites, a temperate (Canada) and a tropical (Brazil) site, there was no effect of increases in UV-B radiation on phytoplankton. Attenuation of solar radiation, vertical mixing, and nutrient concentration were the main factors that determined the photoprotection strategies used by the phytoplankton assemblages in these coastal environments.¹⁶² Experiments carried out with phytoplankton from temperate, tropical, and subantarctic sites showed minor changes in phytoplankton biomass due to the UV-B radiation; however, changes were significant in UV-B enhanced treatments corresponding to 30% ozone depletion.²¹¹ With high nutrient concentration, phytoplankton photosynthesis was not inhibited by enhanced UV-B radiation, but when nutrients became limiting the sensitivity increased (i.e., resulting in net photodamage of photosynthesis reaction centres). Supplemental UV-B radiation also resulted in low abundance of 1,5-bisphosphate carboxylase/oxygenase (RUBISCO, an enzyme involved in carbon fixation during photosynthesis), and increased photoinhibition as compared to the phytoplankton exposed to surface ambient irradiance.²⁹ In temperate regions of the South Atlantic the observed changes in species composition were mainly due to nutrient availability, and to a lesser extent to solar UV radiation.¹⁵³ Studies conducted in a high-mountain lake in the Sierra Nevada (Spain) suggested that the UV radiation and total phosphorus interactive effect would favour a few UV-tolerant rapidly-growing species.⁴⁸ Significant interactive effects of UV radiation and nutri-

ents and UV radiation and DOM were found on phytoplankton when working with natural assemblages from Lake Giles (USA). The differential sensitivity to UV radiation of some species (*Synura* sp. and *Chroomonas* sp.) suggests that changing environmental factors between spring and summer promoted differences in the relative importance of UV radiation in changing phytoplankton community structure.²¹⁷ Arctic fjord mesocosm studies suggested that UV-B radiation had the effect of changing the relative biomass proportions of flagellates (i.e., nanoflagellates and choanoflagellates).²⁶⁶

Productivity of seaweeds under elevated UV radiation levels and global climate change

Seaweeds (macroalgae) are major biomass producers in all oceans from the tropics to polar marine habitats. They provide shelter and food for fish, crustaceans and many other animals, and perform other vital ecosystem functions.²⁴ In addition, they are exploited for a wide range of products for industry, such as gelling agents, as human foods and a source for vitamins, minerals and phytopharmaca, e.g. as antioxidants.^{80, 123, 279} *Sargassum* is a potent source of CDOM since it floats on the ocean surface which maximizes its exposure to solar UV.

Even though not immediately endangered by current levels of solar UV-B radiation, the combination with other stress factors such as global warming, increased storm frequencies and pollution, may impact macroalgal canopies, with far-reaching consequences for aquatic grazers and other members of these habitats.

In contrast to phytoplankton, macroalgae are attached to the substratum and therefore cannot escape excessive UV radiation by vertical migration. PAR, and especially UV-B radiation, is major factors in determining the depth of growth, thus controlling the vertical zonation. In the intertidal zone UV-tolerant macroalgae are exposed to extreme variations in temperature, salinity and exposure to solar radiation.²⁰ Sensitive species are generally limited to greater depths or shaded habitats. Transplantation experiments showed that deep-water, UV-sensitive species do not tolerate being exposed at or close to the water surface.⁹¹ In intertidal species, DNA damage by UV radiation is lower and repair of DNA damage more efficient than in deep water species.^{205, 206, 269} Field experiments on macroalgal communities on King George Island, Antarctica, demonstrated that increased solar UV-B radiation due to stratospheric ozone depletion may affect the zonation, composition and diversity of Antarctic intertidal seaweeds.²⁸¹ Vertical zonation is also determined by species-specific sensitivity of early life stages to solar UV-B radiation.

Most macroalgae undergo life cycles with delicate juvenile developmental stages, which are specifically prone to damage by solar UV-B radiation.²⁰¹ Spore germination and attachment of young plants of *Laminaria japonica* were found to be impaired by even low UV-B radiation doses.¹⁴⁸ Also, the early developmental stages of commercially important red and green algae were found to be affected by high levels of solar UV-B radiation.^{117, 168} Higher temperatures, such as those expected to result from global climate change, augment UV-B-related damage of early developmental stages.⁶⁵

One of the major targets of solar UV radiation is the photosynthetic apparatus. Oxygen production, electron transport and quantum yield are affected in red, green and brown algae.^{89, 118, 203} In seaweeds, the photosynthetic complexes are reorganized for adaptation to the diurnally changing UV stress.^{2, 74}

DNA is another target of solar UV-B radiation.²⁰⁷ DNA damage is a function of geographical position, depth of growth, water transparency, UV-absorbing pigments and thallus thickness.²⁰⁴

Macroalgae have developed a number of protective strategies against solar UV-B radiation. In addition to habitat selection, they produce a range of UV-absorbing pigments. While many red algae synthesize MAAs,^{143, 279} in brown algae, alginates and phenolic compounds such as phlorotannins provide protection from solar UV radiation.^{202, 214} The brown alga, *Sargassum*, uses the carotenoid fucoxanthin for protection from UV-B radiation.²⁸¹ In addition, these organisms use repair mechanisms to mitigate DNA damage.²⁰⁷

Responses of aquatic plants and mosses in freshwater ecosystems to enhanced solar UV-B radiation

Aquatic higher plants and mosses are major biomass producers in freshwater ecosystems and are exposed to UV-B radiation stress. Solar UV radiation impairs photosynthesis as well as respiration in some aquatic plants (e.g., *Ceratophyllum*).⁷⁷ Experiments with simulated solar UV radiation on aquatic plants, collected in New Zealand from different South Island lakes with different transparencies, indicated that photosynthetic yield was decreased by UV-B radiation stress.⁹⁰ However, surprisingly, in some species the photosynthetic yield was decreased more when UV-B radiation was filtered out of the spectrum. This observation was confirmed by field studies. One possible explanation is that short wavelength radiation may induce recovery processes.

UV-absorption spectra of extracts from a number of mosses and liverworts were analysed from Tierra del Fuego (Argentina).¹⁷⁶ The detected substances were identified as phenolic derivatives, which may be either screening pigments or antioxidants. Those in liverworts were more pronounced than those in mosses.

Physiological responses to solar UV-B radiation have been studied over three years in the aquatic liverwort, *Jungermannia*, growing in mountain streams in Northern Spain. Among the variables measured, the photosynthetic quantum yield (decreased) and the level of UV-absorbing compounds (increased) seemed to be the most responsive to enhanced UV-B radiation.¹⁵⁸ In autumn, newly developed shoots produce significantly higher concentrations of the UV-absorbing pigments than in winter or spring. The best correlation was found between the main UV-absorbing substance (p-coumaroylmalic acid) and UV-B radiation stress, reflecting seasonal changes. Because of the high concentrations of the UV-absorbing pigments, hardly any UV damage was detected on vitality, photosynthetic quantum efficiency or chlorophyll concentration, indicating that this liverwort is tolerant to UV radiation.⁹ Researchers also tried to correlate the concentration of the UV-absorbing hydroxycinnamic acid derivatives with historic UV radiation levels from 1850 to 2006 using 135 herbarium samples of *Jungermannia* from Northern Europe.¹⁷⁸ Both UV absorbance and UV irradiance were positively correlated with the collection year. Because of this high correlation, hydroxycinnamic acid derivatives in this aquatic liverwort have been suggested as potential bioindicators of enhanced solar UV radiation.⁹

Effects on aquatic consumers of UV radiation and interactions with climate change

The important role of UV radiation as an environmental stressor has been demonstrated in many aquatic animals with a particular focus on zooplankton, amphibians, fish, and corals. A recent meta-analysis revealed negative effects of ambient UV-B radiation on growth and survival of a wide range of aquatic organisms (not just animals) and concluded that synergisms among multiple stressors are particularly important in the face of global environmental change.¹⁴ There is also some evidence that although UV radiation is generally perceived as

damaging, certain levels of solar UV radiation exposure may be beneficial to some consumers.²⁷² Here we assess results from recent work on UV radiation effects on animals with a particular emphasis on the sublethal and interactive effects of UV with other environmental variables.

Zooplankton

Zooplankton provide a key link in aquatic food webs in lakes and oceans. Their feeding on phytoplankton can alter the transparency of water and simultaneously acts as a conduit of primary productivity to higher levels in the food web including most fish. Some zooplankton such as copepods are also important vectors of human parasites and pathogens.¹⁹⁴ With ozone depletion still a persistent problem at higher latitudes for the coming decades, (see Chapter 1) the potentially damaging effects of UV radiation on zooplankton remain a central concern. A recent paper reviews the different strategies that zooplankton use to cope with UV radiation including photoprotection, photorepair, and behavioural avoidance, and suggests that in general zooplankton are well adapted to existing UV radiation levels.^{92, 154} Most of the recent UV work with zooplankton has been on freshwater species, but there have been several studies on marine species as well. The primary findings suggest that UV radiation has the potential to cause damage to some zooplankton through both direct and indirect effects, but many species have effective defences, and a few UV-tolerant copepods may even benefit from moderate UV radiation exposure. This makes it unlikely that the levels of UV radiation predicted for the coming decades will have direct, large-scale negative impacts on zooplankton in natural waters. The interactive effects of UV radiation with other stressors, including climate change, leave greater cause for concern as they are poorly understood and may have important effects on the role of zooplankton in aquatic ecosystems.

Direct effects of UV on marine zooplankton include reduced survival of UV-exposed larval krill and copepods from Antarctic waters.¹² Indirect effects of UV include production of fewer eggs and more deformed larvae in marine copepods when they are fed UV-exposed versus unexposed diatoms.¹³⁴ Freshwater zooplankton are similarly susceptible to UV radiation damage, and sensitivity varies with species, life history stage, and temperature. Field experiments in alpine lakes at 8° and 12°C found a significant negative effect of ambient UV radiation on juvenile survival and the reproductive state of female copepods at the colder temperature only.⁴⁵ Adult survival was not influenced by UV at either temperature. Laboratory experiments with the widespread and abundant freshwater (cladoceran) *Daphnia* also demonstrated a greater sensitivity of juveniles as well as lower reproduction of UV-exposed survivors later in life¹⁰⁹ and cumulative multigenerational effects.¹⁰⁸ This is an important result: rather than prior, sublethal exposure to UV-B radiation conferring an adaptive advantage to *Daphnia*, it actually magnified the negative effects of UV-B radiation over time. Variable responses to UV radiation by different *Daphnia* species may contribute to the contrasting results. Other sublethal effects of UV radiation include significant changes in respiration rates,⁶⁰ decreased susceptibility to metal toxicity, increased sensitivity to flouoroanthene (a polycyclic aromatic hydrocarbon, PAH) and the antibiotic sulfathiazole in *Daphnia*,¹³⁰ inhibition of acetylcholinesterases²³⁶ and increased production of constitutive heat shock (stress) proteins in copepods.²⁴⁸ In some of the more UV-tolerant copepods, low levels of UV exposure may actually be beneficial, enhancing survival and reproduction,⁴⁴ a result consistent with the positive association of diaptomid copepods with high UV environments in alpine lakes.¹²⁹

Freshwater zooplankton can also reduce the threat of UV radiation damage through behavioural avoidance, which is generally stronger in cladocerans such as *Daphnia* than in copepods.^{61, 93, 112} The behavioural response of *Daphnia* to UV radiation, however, is uninflu-

enced by prior exposure to the radiation.⁷⁸ Field studies in lakes with¹²⁹ and without²⁸² visual predators suggest that UV radiation plays a role in the daytime vertical distribution of some, but not all zooplankton. While cladocerans show stronger behavioural avoidance of UV, copepods use photoprotection to a greater extent.⁹⁴ Some freshwater protozoans¹⁵¹ and the larvae of coral¹⁹² depend heavily on photorepair of their DNA damage.

Zooplankton also reduce UV radiation damage with photoprotective compounds including carotenoids, MAAs, and the antioxidant enzymes catalase (CAT) and glutathione-S-transferase (GST). MAAs have been reported in krill,²⁰⁰ rotifers¹⁷⁰ and freshwater²³³ and marine²³² ciliates that contain endosymbiotic algae. Symbiotic *Chlorella* in the ciliate *Paramecium bursaria* contain no MAAs, but still confer some UV protection to this ciliate.²⁴⁴ Several factors have been found to influence the concentrations of photoprotective compounds in zooplankton including ambient UV radiation exposure levels,^{111, 247} temperature,⁷⁵ and visual predators.^{111, 247} UV radiation exposure levels in the field were not related to the activity of CAT and GST in two freshwater crustaceans,²³⁷ but low ratios of phosphorus to carbon in algal food and UV exposure in laboratory experiments reduce levels of these antioxidant enzymes.¹¹

UV influences the interactions of zooplankton with other components of aquatic ecosystems. For example, seasonal increases in UV transparency (UV “clear-water phases”) appear to be induced by photobleaching of DOM by UV radiation and to a lesser extent by zooplankton grazing.²⁷¹ UV radiation can also increase feeding rates of planktivorous fish on zooplankton,¹⁴⁴ increase degradation rates of chemicals released by predators that induce defences in their zooplankton prey,²⁴⁰ and contribute to photosensitization of toxic compounds.²⁶⁵ Susceptibility to UV radiation of some insect larvae (*Chaoborus*) is species specific.¹⁶⁴

One of the most striking relationships recently observed between UV radiation and zooplankton is the strong reduction in the species diversity of zooplankton in shallower lakes with high UV transparency in Patagonia. Only a single species of highly UV-tolerant copepod persists in fishless lakes with high UV radiation (on average the water column has of UV levels over 10% of incident sunlight measured at 320 nm UV).¹⁵⁴ The interactive effects of climate, as well as pH-driven changes in DOM and hence UV transparency of aquatic ecosystems, may be particularly important to the reproduction, survival, and development of early life history stages of even more UV-tolerant copepod species.⁴⁵ Modelling suggests that photoinhibition by UV radiation can contribute to destabilization of plankton communities.¹⁰⁹

Amphibians

In recent years there has been an active debate as to the relative importance of UV radiation in widespread declines and malformations in amphibians. The most recent data suggest that a combination of behavioural responses by egg-laying females, physiological tolerance of embryos, reduced water clarity related to DOM concentrations, and timing of oviposition make it unlikely that UV radiation is an important factor for lethal effects in nature.^{180, 181} A recent review of the effects of UV-B radiation on amphibian development and metamorphosis emphasizes the importance of looking at sub-lethal effects rather than just mortality.⁴⁷ These sublethal effects may in turn lead to ecologically important trade-offs in the growth and reproduction of amphibians due to reductions in the ability to exploit optimal thermal habitats or food resources, or minimize exposure to predation. In other cases exposure to UV radiation may increase resistance to some toxic compounds. Complex interactions between UV radiation and other environmental variables seem to be the rule rather than the exception.

One of the sublethal effects is the behavioural avoidance of UV radiation. Field surveys and experiments revealed no avoidance of UV-B radiation by three species of anuran tadpoles,¹⁵ but some behavioural avoidance of UV-B in poison dart frogs.⁸⁸ Laboratory experiments show that prior exposure to UV radiation increases UV tolerance in larval and juvenile salamanders and that there is high resistance to damage by natural levels of UV radiation.³⁵ Similarly, a combination of low water transparency to UV radiation as well as to UV-protective compounds in the jelly of egg masses suggest several species of amphibian embryos in Patagonia are not susceptible to UV damage in nature.¹⁸⁶ This same study reported no significant effect of UV radiation on survival, but an elevated incidence of malformations with UV-B exposure when comparing natural and elevated levels of UV-B radiation. Laboratory experiments comparing UV-B tolerance of frog eggs from populations at different elevations (333-2450 m) revealed that UV-B induced a shorter larval body length, with the effect being strongest in eggs collected from low elevations.¹⁵⁶ Field studies of the boreal toad in Glacier National Park, Montana, USA indicate that UV-B exposure does not limit distribution, and breeding was actually higher in high UV radiation habitats.¹⁰⁶

UV radiation has important interactive effects with other environmental stressors, including delayed development rates in frog tadpoles when exposed to UV-B radiation and environmentally realistic concentrations of 4-*tert*-octylphenol, an estrogenic microbial decomposition product of widely used industrial surfactants,⁴⁶ and a seven-fold increase in lethality of UV-B radiation when toad tadpoles were exposed in the presence of nitrite.¹⁵² There is also some evidence that prior exposure to UV radiation may confer resistance to the interactive effects of UV radiation and toxic compounds, a phenomenon known as co-tolerance. For example, higher levels of UV-B tolerance of tadpoles may confer resistance to the PAH benzo[a]pyrene due to similar genotoxic defences against these two stressors.¹⁵⁷ Higher genetic diversity was also found to confer increased resistance to UV-B-induced mortality and deformity in larvae of wood frogs exposed to natural sunlight with and without UV-B.²⁶⁸ Frog larvae exposed to artificial UV-B radiation in the laboratory had lower growth rates and more deformities than unexposed larvae, and there was some evidence that they were more susceptible to predation.²⁰⁸ No synergistic effects of UV-B radiation were observed when three species of anurans were exposed to UV-B radiation and the fungus, *Batrachochytrium dendrobatidi*, which causes chytridiomycosis (an infectious disease).⁷⁶ Simultaneous exposure of frog tadpoles (prey) to UV-B radiation from fluorescent lamps and predatory chemical cues significantly increased mortality, and suppressed the predator-induced phenotypic changes that protect against predation.⁵

Fish

As with many animals, the early life history stages of fish tend to be the most sensitive to UV radiation damage. Enhanced UV-B radiation can reduce growth rates and immune function in juvenile Atlantic salmon,¹²⁰ and increase cataract-causing trematodes (parasitic flatworms) in juvenile rainbow trout.¹⁵⁵ The ability to detect and avoid UV radiation exhibited by some juvenile fish such as Coho salmon in outdoor flumes¹⁰⁵ as well as juvenile black sea bream in laboratory experiments⁶⁷ suggest avoidance of UV radiation may reduce the negative effects of UV radiation in nature. Similarly, though the potential for UV radiation damage in the shallow-nesting bluegill sunfish is high, nest locations under the shade of trees or other structures or at deeper depths reduce the actual impact of UV radiation at the population level.¹⁷³ Larval mortality of bluegill is highest early in the spawning season with $\geq 10\%$ mortality in over a third of the nests.¹⁷² Adult fish may also be sensitive to UV radiation damage as indicated by laboratory exposures of adult African catfish to UV-A (366 nm) that resulted in a wide array of biochemical and tissue damages.²¹⁵ This study is of particular interest because

UV-A radiation may also be beneficial in causing repair of DNA damage through photoenzymatic repair (PER), and the importance and extent of PER differs among freshwater fish species and with UV radiation exposure level.^{160, 174} In clear cold-water lakes high UV radiation transparency may reduce invasions by exotic warm water fish species.²⁵⁴

Corals

A recent review of the effects of solar UV radiation on corals suggests that solar UV is, and has been an important ecological and evolutionary force in coral reefs for a long time, that UV radiation effects are limited to shallower reefs, and that the interactive effects of UV radiation and other stressors need consideration.¹³ UV radiation damage in the coral-algal symbiosis can include persistent decreases in photosynthetic efficiency after several days of exposure to UV radiation from lamps in the laboratory,⁵⁸ and decreases in growth rates in field experiments.²⁵² Corals have several key defences to reduce UV-radiation damage. Some recent experiments demonstrated that the UV-absorbing properties of coral skeletons can significantly reduce DNA damage in overlying tissues.¹⁹³ Advances have also been made in assessing the factors that control UV radiation exposure levels in coral reefs. Spatial and temporal variations in CDOM have been demonstrated to be important in regulating the UV radiation exposure levels of corals in the Florida Keys (USA) and Dry Tortugas (USA).²⁸⁴ A combination of remote sensing and radiative transfer modelling has also been used to estimate UV radiation exposure in coral reefs to help assess the role of UV radiation in coral bleaching.¹⁸

Other Aquatic Animals

Recent laboratory studies on the effects of UV radiation on several species of sea urchins have demonstrated structural and DNA damage to spermatozoa,¹⁹¹ developmental abnormalities,²⁶ and reduced PER rates in embryos at lower temperatures.¹³⁸ The lack of temperature compensation in PER may in part explain the results of a recent *in situ* experiment that found that embryos of an Antarctic urchin were more sensitive to DNA damage and developmental abnormalities than three other species from lower latitudes.¹³⁷

Other animals for which UV radiation effects have been examined include amphipods, gastropods, and biological control agents, some of which are relevant to human disease ecology. When some amphipods are exposed to elevated levels of UV radiation they show an increase in antioxidant capacity¹³⁵ and respiration rates.¹⁶⁹ UV radiation exposure in experimental field studies led to reduced survival of two intertidal mudflat snails.²¹³ Laboratory studies of juveniles of the snail that is the intermediate host of the human parasite *Shistosoma mansoni* showed that UV-B radiation from fluorescent lamps with an emission peak of 315 nm inhibited feeding behaviour, led to abnormal growths on the headfoot, and increased mortality.²¹² UV-B radiation from artificial lamps with an emission peak of 315 nm inhibited the effectiveness of two strains of *Bacillus sphaericus* used in biological control of mosquito larvae, suggesting that these bacteria need to be used with a photoprotectant, to be maximally effective in the field where solar radiation is high.⁸³ Human pathogens such as the oocysts of *Cryptosporidium parvum* may be susceptible to UV radiation damage, suggesting that decreases in UV transparency of surface drinking water supplies may favor persistence of this parasite.⁴³ Recent doubling of DOM concentrations in aquatic ecosystems in many parts of Europe and eastern North America^{54, 59, 163} may thus reduce UV radiation exposure levels and create surface water environments more favourable to UV-sensitive human pathogens such as *Cryptosporidium*.²⁷²

Interactions with pollutants and pH

Organisms in freshwater and coastal habitats are exposed to a number of environmental stress factors including anthropogenic contaminants from terrestrial drainage, ice melting and maritime traffic (see related discussions in Chapter 5). These stresses may have additive or synergistic effects with enhanced solar UV-B radiation challenging growth, reproduction and physiological functions of key members of these aquatic habitats.¹⁸⁴ While many toxicological studies have been conducted in the laboratory, field experiments demonstrated the complexity and the difficulty in determining the impact of multiple stressors on aquatic ecosystems.¹⁸⁴

Interactive reactions with pollutants

Heavy metals, such as cadmium (Cd), are major stress factors for cyanobacteria, phytoplankton and consumers.^{10, 289} Simultaneous application of Cd and UV-B radiation caused a more than 10-fold increase in α -tocopherol, which functions as an antioxidant in cyanobacteria.²³ In an aquatic liverwort, DNA damage, caused by UV-B radiation, was augmented in the presence of Cd.¹⁷⁷ This was attributed to the inhibition of DNA enzymatic repair mechanisms by the heavy metal. Also benthic communities in a natural stream in the Rocky Mountains (USA) are affected by heavy metal pollution; UV-B radiation had greater impact on the metal-polluted sites than on non-polluted ones.¹²⁴ In freshwater habitats, copper (Cu) and other transition metals are often complexed with DOM. Since the latter is photochemically unstable, solar UV radiation has indirect effects on Cu complexation.³³ Irradiation at intensities similar to sunlight decreased Cu complexation in a river, suggesting that increased UV radiation might result in higher Cu toxicity. Increasing Cu concentrations due to photooxidation of DOM resulted in increased mortality of larval fathead minnows.³³ Benthic communities from a metal-polluted stream were tolerant of metals, but were more sensitive to UV-B radiation than communities from a reference stream.³⁹ Experiments with freshwater periphyton indicated that cyanobacteria dominated under high-UV radiation, while diatoms dominated in low-UV radiation treatment. Although the high-UV community had higher tolerance to UV radiation and co-tolerance to cadmium (Cd), they had a fivefold reduction in the pigment, chlorophyll *a*, suggesting that acclimatisation had high metabolic costs.¹⁶⁶

Photodemethylation by solar radiation is regarded as the most important biogeochemical sink of methylmercury.¹⁴⁵ Dissolved gaseous mercury is released from mercury compounds in the water under photolytic action driven by solar radiation. Removal of UV from the radiation reduced the process by an order of magnitude. In Juam Reservoir, Korea, dissolved gaseous mercury concentrations correlated with UV-A and UV-B irradiances and consequently were higher in spring and summer than in fall and winter.¹⁸² In a temperate lake in Eastern Pennsylvania (USA) emission of gaseous mercury increased during periods of mixing in spring and autumn and was triggered by solar radiation.²⁷³

Degradation products of petroleum compounds were shown to be toxic for a number of test organisms including bacterioplankton.¹²¹ Simultaneously, UV irradiation inhibits microbial degradation of petroleum products. Water-soluble crude oil fractions and UV-B radiation were found to have synergistic detrimental effects on a field-collected microplankton assemblage from Ushuaia Bay, Southern Argentina.¹⁸⁴ Picoplankton appeared to be more affected than nanoplankton, which is attributed to their smaller size. The combination of the water-soluble fraction of crude oil and enhanced UV-B radiation exposure resulted in an exacerbation of these individual effects, demonstrating a synergistic effect of both stresses. In Arctic shallow-water marine habitats, phototoxic effects affect algae and bacteria due to the presence of pyrene, a component of crude oil in the sediments.¹⁸⁷ The water-soluble fraction of crude oil is not toxic and may even be beneficial by increasing bacterial activity, but be-

comes highly toxic under exposure to solar UV-B radiation.²¹² Toxicity of polycyclic aromatic hydrocarbons to a broad range of invertebrates, marine and freshwater fish may increase by a factor between 2 and 1000 when sediments are exposed to UV radiation.¹⁷

Interactions with increasing CO₂ concentrations

Acidification of lakes and marine habitats is a major stress factor closely related to climate change and augments exposure of aquatic organisms to solar UV-B radiation.¹²⁷ In the north-eastern Ontario lakes acid deposition is linked with atmospheric sulphur and metal emissions.¹²⁶ Experimental acidification and recovery of a small lake confirmed the changes in benthic algal communities.^{184, 255} The increasingly important role of inland aquatic ecosystems as a reservoir of organic carbon and thus an important link in the carbon cycle have been further strengthened by new studies²⁵³ and see Chapter 5)

Decreasing pH of marine waters due to increased atmospheric CO₂ concentrations affects carbonate incorporation in many calcified marine organisms and makes them more vulnerable to solar UV-B radiation. Before industrialization the CO₂ concentration in the atmosphere was about 280 ppm. This corresponded to an average pH in the oceans of about 8.2. The current 380 ppm has resulted in a decrease in pH by about 0.1, which corresponds to a 30% increase in acidity.³⁴ A pH decrease of 0.3 – 0.4 units is expected by the year 2100. This acidification compromises calcification in molluscs, phytoplankton (coccolithophoridae) and some macroalgae (e.g. *Corallina* and the *Conchocelis* stage of the Rhodophyte *Porphyra*). Calcium carbonate encrustations efficiently absorb UV radiation. At lower pH values increased transmission has been measured, exposing the organisms to higher levels of solar UV-B radiation.²⁷⁷ UV radiation significantly inhibited growth, photosynthetic oxygen evolution and calcification rates in *Corallina* at high CO₂ concentrations (1000 ppm as compared to 380 ppm).

These results indicate the synergistic effects of lower pH and enhanced solar UV-B radiation in coralline algae. In the coccolithophore, *Emiliania huxleyi*, calcification rates are diminished at lowered pH levels, which result in thinned coccoliths.⁷¹ The transmission of detrimental UV radiation was found to be significantly enhanced in enclosure experiments (mesocosms) by acidification by 0.1 pH units.

Interactive effects of UV radiation and climate change at the ecosystem level

As stated in a previous report,⁸⁴ "... the ecosystem level [is] where assessments of anthropogenic climate change and UV-related effects are interrelated and where much recent research has been directed. Several studies suggest that the influence of UV-B radiation at the ecosystem level may be more pronounced on community and trophic level structure, and hence on subsequent biogeochemical cycles, than on biomass levels *per se*" (see related discussions in Chapter 5). These effects not only have implications for marine and freshwater ecosystems, but for the economic and social systems that depend on them. Studies have investigated the effects of solar UV radiation, climate change and their possible interactions, on scales ranging from whole communities to individual organisms at the cellular, biochemical and genetic level. However, there is a paucity of data and information regarding the effects of UV-B radiation on total ecosystem structure and function. Covering new geographical locations and species, most recent studies largely confirm previous findings.⁶

As an example, the rapid warming of surface waters by 5–6 °C around the Antarctic Peninsula since 1950²³⁸ has resulted in a shift in species composition that is attributed to

deeper migration by organisms in the water column and thus further from exposure to surface UV radiation. These higher surface temperatures have led to later advance and earlier retreat of sea-ice and consequently a shorter sea-ice season.^{238, 260} The resulting potentially higher phytoplankton productivity in the area of the Antarctic Peninsula could augment carbon sequestering from the atmosphere through a shift from the invertebrates, such as krill, to an increased population of salps (free-swimming marine chordates of the subphylum Tunicata, having a translucent, somewhat flattened saclike body).²¹⁰ Besides krill and copepods (crustaceans), salps are the most important metazoans in that area involved in sequestering carbon from the atmosphere.^{52, 246} In the sequestration process, phytoplankton absorb carbon dioxide from the atmosphere via photosynthesis. Zooplankton graze on the phytoplankton, and the organic material is packaged into large fecal pellets. These pellets sink to the deep sea floor, and the embedded carbon is removed from circulation for tens of thousands of years, making the area around the Antarctic Peninsula one of the world's most important carbon sinks. In addition, due to the deep migration of the salps in the water column, they are less affected by surface UV radiation. In contrast, other studies demonstrated that any increase in UV-B irradiance would have a negative impact on Antarctic krill because of the relatively shallow descent-ascent migration pattern of their embryos and larvae.¹²

Conclusions

Numerous publications show that solar UV radiation can adversely affect aquatic organisms. The majority of these studies document significant negative impacts on individual species; yet considerable uncertainty remains with respect to assessing effects on whole ecosystems. With respect to assessing UV radiation-related effects, the influence of climate variability is often more important *via* indirect effects such as reduction in sea ice, changes in water column bio-optical characteristics and shifts in limnological or oceanographic biogeochemical conditions than through direct effects. Were it to occur, decreases in primary production would result in reduced sink capacity for atmospheric carbon dioxide, with its related effects on climate change.

Recent studies have strengthened evidence that the impact of UV-B radiation on phytoplankton is species specific. Acclimation capacity defines the species sensitivity. However, increased stratification (via thermal heating or tidal dynamics), together with changes in cloud cover, strongly modifies the light regime and response of phytoplankton. Previous acclimation also counteracts the higher sensitivity of phytoplankton observed when they grow under high CO₂ levels. The carbon uptake is higher at high CO₂ levels, but with the same nutrient uptake, thus increasing the C:N ratio and decreasing the food quality for herbivores. In contrast, exposure to UV radiation reduces cellular C:P ratios (and N:P) in phytoplankton. Therefore, exposure to CO₂ and UV radiation are causing opposite effects on food quality (i.e., phytoplankton C:N ratios). While an increase in CO₂ means a low quality food due to an increase in C uptake, exposure to UV radiation means a better quality food due to a decrease in C uptake.

While zooplankton and many other aquatic animals are often protected from the lethal effects of UV radiation by both their own defences and environmental shielding by UV-absorbing DOM, many recent studies demonstrate the importance of sublethal UV radiation effects and interactive effects of this radiation with other environmental stressors. In lakes with high UV transparency, zooplankton communities may be reduced to a single UV-tolerant species,¹⁵⁴ amphibians may be more susceptible to toxic compounds,^{46, 152} and fish spawning may be limited to shaded or otherwise low UV radiation exposure habitats.^{172, 173}

References

- 1 Abboudi M, Jeffrey WH, Ghiglione JF, Pujo-Pay M, Oriol L, Sempéré R, Charrière B and Joux F, 2008, Effects of photochemical transformations of dissolved organic matter on bacterial metabolism and diversity in three contrasting coastal sites in the northwestern Mediterranean Sea during summer, *Micro. Ecol.*, **55**, 344-357.
- 2 Aguilera J, Figueroa FL, Häder D-P and Jiménez C, 2008, Photoinhibition and photosynthetic pigment reorganisation dynamics in light/darkness cycles as photoprotective mechanisms of *Porphyra umbilicalis* against damaging effects of UV radiation, *Scientia Marina*, **72**, 87-97.
- 3 Al-Otaibi AA, Al-Sofyani A, Niaz GR and Al-Lihaibi SS, 2006, Temporal and depth variation of photoprotective mycosporine-like amino acids in soft coral species from the eastern red sea coast, *J. King Abdulaziz Univ. Mar. Sci.*, **17**, 169-180.
- 4 Alonso-Sáez L, Gasol JM, Lefort T, Hofer J and Sommaruga R, 2006, Effect of natural sunlight on bacterial activity and differential sensitivity of natural bacterioplankton groups in northwestern Mediterranean coastal waters, *Appl. Environ. Microbiol.*, **72**, 5806-5813.
- 5 Alton LA, Wilson RS and Franklin CE, 2010, Risk of predation enhances the lethal effects of UV-B in amphibians, *Glob. Change Biol.*, **16**, 538-545.
- 6 Andrady A, Aucamp PJ, Bais AF, Ballaré CL, Bjorn LO, Bornman JF, Caldwell M, Cullen AP, Erickson DJ, de Gruijl FR, Hader DP, Ilyas M, Kulandaivelu G, Kumar HD, Longstreth J, McKenzie RL, Norval M, Paul N, Redhwi HH, Smith RC, Solomon KR, Sulzberger B, Takizawa Y, Tang X, Teramura AH, Torikai A, van der Leun JC, Wilson SR, Worrest RC and Zepp RG, 2009, Environmental effects of ozone depletion and its interactions with climate change: Progress report, 2008. United Nations Environment Programme, Environmental Effects Assessment Panel, *Photochem. Photobiol. Sci.*, **8**, 13-22.
- 7 Andrady AL, Aucamp PJ, Bais AF, Ballaré CL, Bjorn LO, Bornman JF, Caldwell MM, Cullen AP, de Gruijl FR, Erickson Iii DJ, Flint SD, Häder D-P, Hamid HS, Ilyas M, Kulandaivelu G, Kumar HD, McKenzie RL, Longstreth J, Lucas RM, Noonan FP, Norval M, Paul ND, Smith RC, Solomon KR, Sulzberger B, Takizawa Y, Tang X, Torikai A, van der Leun JC, Wilson SR, Worrest RC and Zepp RG, 2007, Environmental effects of ozone depletion: 2006 assessment: interactions of ozone depletion and climate change. Executive summary, *Photochem. Photobiol. Sci.*, **6**, 212-217.
- 8 Anusha K and Asaeda T, 2008, Indirect mechanisms accelerated due to ultraviolet-B irradiation on nutrient cycling in a freshwater ecosystem, *J. Photochem. Photobiol. B.*, **93**, 1-8.
- 9 Arróniz-Crespo M, Núñez-Olivera E and Martínez-Abaigar J, 2008, Hydroxycinnamic acid derivatives in an aquatic liverwort as possible bioindicators of enhanced UV radiation, *Environ. Pollut.*, **151**, 8-16.
- 10 Arunakumara K and Zhang X, 2008, Heavy metal bioaccumulation and toxicity with special reference to microalgae, *J. Ocean Univ. China*, **7**, 60-64.
- 11 Balseiro E, Souza MS, Ressig M and Modenutti B, 2008, Living in transparent lakes: Low food P:C ratio decreases antioxidant response to ultraviolet radiation in *Daphnia*, *Limnol. Oceanogr.*, **53**, 2383-2390.
- 12 Ban S, Ohi N, Leong SCY, Takahashi KT, Riser CW and Taguchi S, 2007, Effect of solar ultraviolet radiation on survival of krill larvae and copepods in Antarctic Ocean, *Polar Biol.*, **30**, 1295-1302.

- 13 Banaszak AT and Lesser MP, 2009, Effects of solar ultraviolet radiation on coral reef organisms, *Photochem. Photobiol. Sci.*, **8**, 1276-1294.
- 14 Bancroft BA, Baker NJ and Blaustein AR, 2007, Effects of UVB radiation on marine and freshwater organisms: a synthesis through meta-analysis, *Ecol. Lett.*, **10**, 332-345.
- 15 Bancroft BA, Baker NJ, Searle CL, Garcia TS and Blaustein AR, 2008, Larval amphibians seek warm temperatures and do not avoid harmful UVB radiation, *Behav. Ecol.*, **19**, 879-886.
- 16 Barbieri ES, Villafañe VE and Helbling EW, 2006, Dynamics of oxygen production / consumption in *Dunaliella salina*, *Thalassiosira weissflogii* and *Heterocapsa triquetra* circulating within a simulated upper mixed layer, *Investig. Mar.*, **24**, 97-108.
- 17 Barron M, 2007, Sediment-associated phototoxicity to aquatic organisms, *Human Ecol. Risk Assess.*, **13**, 317-321.
- 18 Barron MG, Vivian DN, Yee SH and Santavy DL, 2009, Methods to estimate solar radiation dosimetry in coral reefs using remote sensed, modeled, and *in situ* data, *Environ. Monit. Assess.*, **151**, 445-455.
- 19 Bastidas Navarro M and Modenutti B, UVR induce optical changes and phosphorous release of lake water and macrophyte leachates in shallow Andean lakes, *J. Limnol.*, **69**, 1-8.
- 20 Becker S, Walter B and Bischof K, 2009, Freezing tolerance and photosynthetic performance of polar seaweeds at low temperatures, *Bot. Mar.*, **52**, 609-616.
- 21 Ben Yosef DZ, Kashman Y and Benayahu Y, 2006, Response of the soft coral *Heteroxenia fuscescens* to ultraviolet radiation regimes as reflected by mycosporine-like amino acid biosynthesis, *Mar. Ecol. Evolut. Perspect.*, **27**, 219-228.
- 22 Bhandari R and Sharma PK, 2007, Effect of UV-B and high visual radiation on photosynthesis in freshwater (*Nostoc spongiaeforme*) and marine (*Phormidium corium*) cyanobacteria, *Indian. J. Biochem. Biophys.*, **44**, 231-239.
- 23 Bhargava P, Atri N, Srivastava AK and Rai LC, 2007, Cadmium mitigates ultraviolet-B stress in *Anabaena doliolum*: enzymatic and non-enzymatic antioxidants, *Biologia Planta.*, **51**, 546-550.
- 24 Bischof K, Gómez I, Molis M, Hanelt D, Karsten U, Lüder U, Roleda MY, Zacher K and Wiencke C, 2006, Ultraviolet radiation shapes seaweed communities, *Reviews in Environmental Science and Biotechnology*, **5**, 141-166.
- 25 Blunt JW, Copp BR, Hu WP, Munro MHG, Northcote PT and Prinsep MR, 2007, Marine natural products, *Nat. Prod. Rep.*, **24**, 31-86.
- 26 Bonaventura R, Poma V, Russo R, Zito F and Matranga V, 2006, Effects of UV-B radiation on development and hsp70 expression in sea urchin cleavage embryos, *Mar. Biol.*, **149**, 79-86.
- 27 Boreen AL, Edlund BL, Cotner JB and McNeill K, 2008, Indirect photodegradation of dissolved free amino acids: The contribution of singlet oxygen and the differential reactivity of DOM from various sources, *Environmental Science & Technology*, **42**, 5492-5498.
- 28 Boss ES, Collier R, Larson G, Fennel K and Pegau WS, 2007, Measurements of spectral optical properties and their relation to biogeochemical variables and processes in Crater Lake, Crater Lake National Park, OR, *Hydrobiologia.*, **574**, 149-159.
- 29 Bouchard JN, Longhi ML, Roy S, Campbell DA and Ferreyra G, 2008, Interaction of nitrogen status and UVB sensitivity in a temperate phytoplankton assemblage, *J. Exp. Mar. Biol. Ecol.*, **359**, 67-76.

- 30 Bouchard JN, Roy S and Campbell DA, 2006, UVB effects on the photosystem II-D1 protein of phytoplankton and natural phytoplankton communities, *Photochem. Photobiol.*, **82**, 936-951.
- 31 Bracchini L, Dattilo AM and Hull V, 2006, The bio-optical properties of CDOM as descriptor of lake stratification, *J. Photochem. Photobiol. B.*, **85**, 145-149.
- 32 Brooks ML and Lovvorn JR, Surprising results of CDOM photooxidation in the Bering Sea: Implications for food webs, in *Ocean Sciences Meeting, March 2-7, 2008, Orlando, Florida, Session # 162*.
- 33 Brooks ML, Meyer JS and Boese CJ, 2007, Toxicity of copper to larval *Pimephales promelas* in the presence of photodegraded natural dissolved organic matter, *Can. J. Fish. Aquat. Sci.*, **64**, 391-401.
- 34 Caldeira K and Wickett ME, 2003, Anthropogenic carbon and ocean pH, *Nature*, **425**, 365.
- 35 Calfee RD, Bridges CM and Little EE, 2006, Sensitivity of two Salamander (*Ambystoma*) species to ultraviolet radiation, *J. Herpetol.*, **40**, 35-42.
- 36 Callieri C, Modenutti B, Queimaliños C, Bertoni R and Balseiro E, 2007, Production and biomass of picophytoplankton and larger autotrophs in Andean ultraoligotrophic lakes: differences in light harvesting efficiency in deep layers, *Aquat. Ecol.*, **41**, 511-523.
- 37 Carrillo P, Delgado-Molina JA, Medina-Sánchez JM, Bullejos FJ and Villar-Argaiz M, 2008, Phosphorus inputs unmask negative effects of ultraviolet radiation on algae in a high mountain lake, *Glob. Change Biol.*, **14**, 423-439.
- 38 Cheregi O, Sicora C, Kos PB, Barker M, Nixon PJ and Vass I, 2007, The role of the FtsH and Deg proteases in the repair of UV-B radiation-damaged Photosystem II in the cyanobacterium *Synechocystis* PCC 6803, *Biochimica and Biophysica Acta*, **1767**, 820-828.
- 39 Clements WH, Brooks ML, Kashian DR and Zuellig RE, 2008, Changes in dissolved organic material determine exposure of stream benthic communities to UV-B radiation and heavy metals: implications for climate change, *Glob. Change Biol.*, **14**, 2201-2214.
- 40 Coba FDL, Aguilera J, Figueroa FL, de Gálvez MV and Herrera E, 2009, Antioxidant activity of mycosporine-like amino acids isolated from three red macroalgae and one marine lichen, *J. Appl. Phycol.*, **21**, 161-169.
- 41 Cockell CS and Raven JA, 2007, Ozone and life on the Archaean Earth, *Phil.Trans.Roy.Soc.A*, **365**, 1889-1901.
- 42 Conde FR, Churio MS and Previtali CM, 2007, Experimental study of the excited-state properties and photostability of the mycosporine-like amino acid palythine in aqueous solution, *Photochem. Photobiol. Sci.*, **6**, 669-674.
- 43 Connelly SJ, Wolyniak EA, Williamson CE and Jellison KL, 2007, Artificial UV-B and solar radiation reduce *in vitro* infectivity of the human pathogen *Cryptosporidium parvum*, *Environ. Sci. Tech.*, **41**, 7101-7106.
- 44 Cooke SL and Williamson CE, 2006, Positive effects of UV radiation on a calanoid copepod in a transparent lake: do competition, predation or food availability play a role?, *J. Plankt. Res.*, **28**, 171-179.
- 45 Cooke SL, Williamson CE and Saros JE, 2006, How do temperature, dissolved organic matter and nutrients influence the response of *Leptodiptomus ashlandi* to UV radiation in a subalpine lake?, *Freshwat. Biol.*, **51**, 1827-1837.
- 46 Croteau MC, Davidson M, Duarte-Guterman P, Wade M, Popesku JT, Wiens S, Lean DRS and Trudeau VL, 2009, Assessment of thyroid system disruption in *Rana pipiens*

- tadpoles chronically exposed to UVB radiation and 4-tert-octylphenol, *Aquat. Toxicol.*, **95**, 81-92.
- 47 Croteau MC, Davidson MA, Lean DRS and Trudeau VL, 2008, Global increases in ultraviolet B radiation: Potential impacts on amphibian development and metamorphosis, *Physiol. Biochem. Zool.*, **81**, 743-761.
- 48 Delgado-Molina JA, Carrillo P, Medina-Sánchez JM, Villar-Argaiz M and Bullejos FJ, 2009, Interactive effects of phosphorus loads and ambient ultraviolet radiation on the algal community in a high-mountain lake, *J. Plankt. Res.*, **31**, 619-634.
- 49 Despommier D, 2009, The rise of vertical farms, *Sci. Am.*, **301**, 60-67.
- 50 Dib JR, Weiss A, Neumann A, Ordonez O, Estevez MC and Farias ME, 2009, Isolation of bacteria from remote high altitude Andean lakes able to grow in the presence of antibiotics, *Recent Pat. Anti-Infect. Drug Disc.*, **4**, 66-76.
- 51 Dimier C, Corato F, Tramontano F and Brunet C, 2007, Photoprotection and xanthophyll-cycle activity in three marine diatoms, *J. Phycol.*, **43**, 937-947.
- 52 Ducklow HW, Doney SC and Steinberg DK, 2009, Contributions of long-term research and time-series observations to marine ecology and biogeochemistry, *Ann. Rev. Mar. Sci.*, **1**, 279-302.
- 53 Environmental Effects Assessment Panel UNEP, 2010, Environmental effects of ozone depletion and its interactions with climate change: progress report, 2009, *Photochem Photobiol Sci.*, **9**, 275-294.
- 54 Evans CD, Chapman PJ, Clark JM, Monteith DT and Cresser MS, 2006, Alternative explanations for rising dissolved organic carbon export from organic soils, *Glob. Change Biol.*, **12**, 2044-2053.
- 55 Fattorusso E and Taglialatela-Scafati O, 2009, Marine antimalarials, *Mar. Drugs*, **7**, 130-152.
- 56 Feng S, Zhang YL and Qin BQ, 2006, Photochemical degradation of chromophoric dissolved organic matter in Meiliang Bay of Lake Taihu, *China Environ. Sci.*, **26**, 404-408.
- 57 Ferreyra GA, Mostajir B, Schloss IR, Chatila K, Ferrario ME, Sargian P, Roy S, Prod'homme J and Demers S, 2006, Ultraviolet-B radiation effects on the structure and function of lower trophic levels of the marine planktonic food web, *Photochem. Photobiol.*, **82**, 887-897.
- 58 Ferrier-Pages C, Richard C, Forcioli D, Allemand D, Pichon M and Shick JM, 2007, Effects of temperature and UV radiation increases on the photosynthetic efficiency in four scleractinian coral species, *Biol. Bull.*, **213**, 76-87.
- 59 Findlay SEG, 2005, Increased carbon transport in the Hudson River: unexpected consequence of nitrogen deposition?, *Front. Ecol. Environ.*, **3**, 133-137.
- 60 Fischer JM, Fields PA, Prybylkowski PG, Nicolai JL and Neale PJ, 2006, Sublethal exposure to UV radiation affects respiration rates of the freshwater cladoceran *Daphnia catawba*, *Photochem. Photobiol.*, **82**, 547-550.
- 61 Fischer JM, Nicolai JL, Williamson CE, Persaud AD and Lockwood RS, 2006, Effects of ultraviolet radiation on diel vertical migration of crustacean zooplankton: an *in situ* mesocosm experiment, *Hydrobiologia.*, **563**, 217-224.
- 62 Fleming ED and Castenholz RW, 2007, Effects of periodic desiccation on the synthesis of the UV-screening compound, scytonemin, in cyanobacteria, *Environ. Microbiol.*, **9**, 1448-1455.
- 63 Fleming ED and Castenholz RW, 2008, Effects of nitrogen source on the synthesis of the UV-screening compound, scytonemin, in the cyanobacterium *Nostoc punctiforme* PCC 73102, *FEMS Micro. Ecol.*, **63**, 301-308.

- 64 Fouqueray M, Mouget JL, Morant-Manceau A and Tremblin G, 2007, Dynamics of short-term acclimation to UV radiation in marine diatoms, *J. Photochem. Photobiol. B.*, **89**, 1-8.
- 65 Fredersdorf J, Müller R, Becker S, Wiencke C and Bischof K, 2009, Interactive effects of radiation, temperature and salinity on different life history stages of the Arctic kelp *Alaria esculenta* (Phaeophyceae), *Oecologia*, **160**, 483-492.
- 66 Fritz JJ, Neale PJ, Davis RF and Peloquin JA, 2008, Response of Antarctic phytoplankton to solar UVR exposure: Inhibition and recovery of photosynthesis in coastal and pelagic assemblages, *Mar. Ecol. Prog. Ser.*, **365**, 1-16.
- 67 Fukunishi Y, Masuda R and Yamashita Y, 2006, Ontogeny of tolerance to and avoidance of ultraviolet radiation in red sea bream *Pagrus major* and black sea bream *Acanthopagrus schlegeli*, *Fish. Sci.*, **72**, 356-363.
- 68 Gao K, Guan W and Helbling EW, 2007, Effects of solar ultraviolet radiation on photosynthesis of the marine red tide alga *Heterosigma akashiwo* (Raphidophyceae), *J. Photochem. Photobiol. B.*, **86**, 140-148.
- 69 Gao K, Li G, Helbling EW and Villafañe VE, 2007, Variability of UVR effects on photosynthesis of summer phytoplankton assemblages from a tropical coastal area of the South China Sea, *Photochem. Photobiol.*, **83**, 802-809.
- 70 Gao K, Li P, Watanabe T and Helbling EW, 2008, Combined effects of ultraviolet radiation and temperature on morphology, photosynthesis, and DNA of *Arthrospira (Spirulina) platensis* (Cyanophyta), *J. Phycol.*, **44**, 777-786.
- 71 Gao K, Ruan Z, Villafañe VE, Gattuso JP and Helbling EW, 2009, Ocean acidification exacerbates the effect of UV radiation on the calcifying phytoplankter *Emiliania huxleyi*, *Limnol. Oceanogr.*, **54**, 1855-1862.
- 72 Gao K, Yu H and Brown MT, 2007, Solar PAR and UV radiation affects the physiology and morphology of the cyanobacterium *Anabaena* sp. PCC 7120, *J. Photochem. Photobiol. B.*, **89**, 117-124.
- 73 Gao KS and Ma ZL, 2008, Photosynthesis and growth of *Arthrospira (Spirulina) platensis* (Cyanophyta) in response to solar UV radiation, with special reference to its minor variant, *Environ. Exp. Bot.*, **63**, 123-129.
- 74 Gao KS and Xu J, 2008, Effects of solar UV radiation on diurnal photosynthetic performance and growth of *Gracilaria lemaneiformis* (Rhodophyta), *Eur. J. Phycology*, **43**, 297-307.
- 75 Garcia PE, Perez AP, Dieguez MDC, Ferraro MA and Zagarese HE, 2008, Dual control of the levels of photoprotective compounds by ultraviolet radiation and temperature in the freshwater copepod *Boeckella antiqua*, *J. Plankt. Res.*, **30**, 817-827.
- 76 Garcia TS, Romansic JM and Blaustein AR, 2006, Survival of three species of anuran metamorphs exposed to UV-B radiation and the pathogenic fungus *Batrachochytrium dendrobatidis*, *Dis. Aquat. Org.*, **72**, 163-169.
- 77 Germ M, Mazej Z, Gaberscik A and Sedej TT, 2006, The response of *Ceratophyllum demersum* L. and *Myriophyllum spicatum* L. to reduced, ambient, and enhanced ultraviolet-B radiation, *Hydrobiologia.*, **570**, 47-51.
- 78 Gonçalves RJ, Barbieri ES, Villafañe VE and Helbling EW, 2007, Motility of *Daphnia spinulata* as affected by solar radiation throughout an annual cycle in mid-latitudes of Patagonia, *Photochem. Photobiol.*, **83**, 824-832.
- 79 Gonçalves RJ, Souza MS, Aigo J, Modenutti B, Balseiro E, Villafañe VE, Cussac V and Helbling EW, 2010, Responses of plankton and fish from temperate zones to UVR and temperature in a context of global change, *Ecología Austral*, **20**, 129-153.

- 80 González AEB, Charles MB, Mancini-Filho J and Novoa AV, 2009, Seaweeds as sources of antioxidant phytomedicines, *Rev. Cubana Plant. Medicin.*, **14**, 1-18.
- 81 Guan W and Gao K, 2008, Light histories influence the impacts of solar ultraviolet radiation on photosynthesis and growth in a marine diatom, *Skeletonema costatum*, *J. Photochem. Photobiol. B.*, **91**, 151-156.
- 82 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.
- 83 Hadapad AB, Vijayalakshmi N, Hire RS and Dongre TK, 2008, Effect of ultraviolet radiation on spore viability and mosquitocidal activity of an indigenous ISPC-8 *Bacillus sphaericus* Neide strain, *Acta Trop.*, **107**, 113-116.
- 84 Häder D-P, Kumar HD, Smith RC and Worrest RC, 2007, Effects of solar UV radiation on aquatic ecosystems and interactions with climate change, *Photochem. Photobiol. Sci.*, **6**, 267-285.
- 85 Häder D-P, Lebert M, Schuster M, del Ciampo L, Helbling EW and McKenzie R, 2007, ELDONET-a decade of monitoring solar radiation on five continents, *Photochem. Photobiol.*, **83**, 1348-1357.
- 86 Halac S, García-Mendoza E and Banaszak AT, 2009, Ultraviolet radiation reduces the photoprotective capacity of the marine diatom *Phaeodactylum tricornutum* (Bacillariophyceae, Heterokontophyta), *Photochem. Photobiol.*, **85**, 807-815.
- 87 Hamre B, Stamnes JJ, Frette, Erga SR and Stamnes K, 2008, Could stratospheric ozone depletion lead to enhanced aquatic primary production in the polar regions?, *Limnol. Oceanogr.*, **53**, 332-338.
- 88 Han BA, Kats LB, Pommerening RC, Ferrer RP, Murry-Ewers M and Blaustein AR, 2007, Behavioral avoidance of ultraviolet-B radiation by two species of neotropical poison-dart frogs, *Biotropica.*, **39**, 433-435.
- 89 Han YS, Kang SH and Han T, 2007, Photosynthesis and photoinhibition of two green macroalgae with contrasting habitats, *J. Plant Biol.*, **50**, 410-416.
- 90 Hanelt D, Hawes I and Rae R, 2006, Reduction of UV-B radiation causes an enhancement of photoinhibition in high light stressed aquatic plants from New Zealand lakes, *J. Photochem. Photobiol. B.*, **84**, 89-102.
- 91 Hanelt D, Wiencke C and Bischof K, 2007, Effects of UV radiation on seaweeds, in *Arctic Alpine Ecosystems and People in a Changing Environment, Part 3* eds.: Ørbæk JB, Kallenborn R, Tombre I, Hegseth EN, Falk-Petersen S and Hoel AH, Springer, Berlin Heidelberg, pp. 251-277.
- 92 Hansson LA and Hylander S, 2009, Effects of ultraviolet radiation on pigmentation, photoenzymatic repair, behavior, and community ecology of zooplankton, *Photochem. Photobiol. Sci.*, **8**, 1266-1275.
- 93 Hansson LA and Hylander S, 2009, Size-structured risk assessments govern *Daphnia* migration, *Proc. R. Soc. B. Biol. Sci.*, **276**, 331-336.
- 94 Hansson LA, Hylander S and Sommaruga R, 2007, Escape from UV threats in zooplankton: a cocktail of behavior and protective pigmentation, *Ecol.*, **88**, 1932-1939.
- 95 Hargreaves BR, Girdner SF, Buktenica MW, Collier RW, Urbach E and Larson GL, 2007, Ultraviolet radiation and bio-optics in Crater Lake, Oregon, *Hydrobiologia.*, **574**, 107-140.
- 96 Harrison JW and Smith REH, 2009, Effects of ultraviolet radiation on the productivity and composition of freshwater phytoplankton communities, *Photochem. Photobiol. Sci.*, **8**, 1218-1232.

- 97 Hayakawa K and Sugiyama Y, 2008, Spatial and seasonal variations in attenuation of solar ultraviolet radiation in Lake Biwa, Japan, *J. Photochem. Photobiol. B.*, **90**, 121-133.
- 98 He YY and Häder D-P, 2006, UV-B-induced oxidative stress and damage in the cyanobacterium *Anabaena* sp., in *Environmental UV Radiation: Impact on Ecosystems and Human Health and Predictive Models* eds.: Ghetti F, Checcucci G and Bornman JF, Springer, The Netherlands, p. 281.
- 99 Helbling EW, Buma AGJ, Van de Poll W, Fernández Zenoff MV and Villafañe VE, 2008, UVR-induced photosynthetic inhibition dominates over DNA damage in marine dinoflagellates exposed to fluctuating solar radiation regimes, *J. Exp. Mar. Biol. Ecol.*, **365**, 96-102.
- 100 Helbling EW, Pérez DE, Medina CD, Lagunas MG and Villafañe VE, 2010, Phytoplankton distribution and photosynthesis dynamics in the Chubut River estuary (Patagonia, Argentina) throughout tidal cycles, *Limnol. Oceanogr.*, **55**, 55-65.
- 101 Hernández KL, Quiñones RA, Daneri G, Farias ME and Helbling EW, 2007, Solar UV radiation modulates daily production and DNA damage of marine bacterioplankton from a productive upwelling zone (36 °S), Chile, *J. Exp. Mar. Biol. Ecol.*, **343**, 82-95.
- 102 Hernández KL, Quiñones RA, Daneri G and Helbling EW, 2006, Effects of solar radiation on bacterioplankton production in the upwelling system off central-southern Chile, *Mar. Ecol. Prog. Ser.*, **315**, 19-31.
- 103 Hernando M, Schloss I, Roy S and Ferreyra G, 2006, Photoacclimation to long-term ultraviolet radiation exposure of natural sub-Antarctic phytoplankton communities: fixed surface incubations versus mixed mesocosms, *Photochem. Photobiol.*, **82**, 923-935.
- 104 Hessen DO, Leu ES, Færøvig PJ and Petersen SF, 2008, Light and spectral properties as determinants of C:N:P-ratios in phytoplankton, *Deep Sea Res. Part II: Top. Stud. Oceanogr.*, **55**, 2169-2175.
- 105 Holtby LB and Bothwell ML, 2008, Effects of solar ultraviolet radiation on the behaviour of juvenile Coho salmon (*Oncorhynchus kisutch*): avoidance, feeding, and agonistic interactions, *Can. J. Fish. Aquat. Sci.*, **65**, 701-711.
- 106 Hossack BR, Diamond SA and Corn PS, 2006, Distribution of boreal toad populations in relation to estimated UV-B dose in Glacier National Park, Montana, USA, *Can. J. Zool.*, **84**, 98-107.
- 107 Hudson N, Baker A and Reynolds D, 2007, Fluorescence analysis of dissolved organic matter in natural, waste and polluted waters - a review, *River Res. Applic.*, **23**, 631-649.
- 108 Huebner JD, Loadman NL, Wiegand MD, Young DLW and Warszycki LA, 2009, The Effect of chronic exposure to artificial UVB radiation on the survival and reproduction of *Daphnia magna* across two generations, *Photochem. Photobiol.*, **85**, 374-378.
- 109 Huebner JD, Young DLW, Loadman NL, Lentz VJ and Wiegand MD, 2006, Age-dependent survival, reproduction and photorepair activity in *Daphnia magna* (Straus, 1820) after exposure to artificial ultraviolet radiation, *Photochem. Photobiol.*, **82**, 1656-1661.
- 110 Hulatt CJ, Thomas DN, Bowers DG, Norman L and Zhang C, 2007, Exudation and decomposition of chromophoric dissolved organic matter (CDOM) from some temperate macroalgae, *Estuarine, Coastal and Shelf Science*, **84**, 147-153.

- 111 Hylander S, Boeing WJ, Graneli W, Karlsson J, von Einem J, Gutseit K and Hansson LA, 2009, Complementary UV protective compounds in zooplankton, *Limnol. Oceanogr.*, **54**, 1883-1893.
- 112 Hylander S, Larsson N and Hansson LA, 2009, Zooplankton vertical migration and plasticity of pigmentation arising from simultaneous UV and predation threats, *Limnol. Oceanogr.*, **54**, 483-491.
- 113 Ingalls AE, Whitehead K and Bridoux MC, 2010, Tinted windows: The presence of the UV absorbing compounds called mycosporine-like amino acids embedded in the frustules of marine diatoms, *Geochim. Cosmochim. Acta.*, **74**, 104-115.
- 114 IPCC, 2007, Summary for Policymakers. In: *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment report of the Intergovernmental Panel on Climate Change* [Solomon, S., D. Qin, M. Manning, Z. Chen, M. Marquis, K.B Averyt, M. Tignor and H.L. Miller (eds.)]. IPCC Report No., Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 2007, pp. 1-18.
http://www.ipcc.ch/publications_and_data/ar4/wg1/en/spm.html
- 115 Janknegt PJ, van de Poll WH, Visser RJW, Rijstenbil JW and Buma AGJ, 2008, Oxidative stress responses in the marine Antarctic diatom *Chaetoceros brevis* (Bacillariophyceae) during photoacclimation, *J. Phycol.*, **44**, 957-966.
- 116 Jankowski T, Livingstone DM, Buhner H, Forster R and Niederhauser P, 2006, Consequences of the 2003 European heat wave for lake temperature profiles, thermal stability, and hypolimnetic oxygen depletion: Implications for a warmer world, *Limnol. Oceanogr.*, **51**, 815-819.
- 117 Jiang H, Gao K and Helbling EW, 2008, UV-absorbing compounds in *Porphyra haitanensis* (Rhodophyta) with special references to effects of desiccation, *J. Appl. Phycol.*, **20**, 387-395.
- 118 Jiang HX and Gao KS, 2008, Effects of UV radiation on the photosynthesis of conchocelis of *Porphyra haitanensis* (Bangiales, Rhodophyta), *Phycologia*, **47**, 241-248.
- 119 Joint I and Jordan MB, 2008, Effect of short-term exposure to UVA and UVB on potential phytoplankton production in UK coastal waters, *J. Plankt. Res.*, **30**, 199-210.
- 120 Jokinen IE, Markkula ES, Salo HM, Kuhn P, Nikoskelainen S, Arts MT and Browman HI, 2008, Exposure to increased ambient ultraviolet B radiation has negative effects on growth, condition and immune function of juvenile Atlantic salmon (*Salmo salar*), *Photochem. Photobiol.*, **84**, 1265-1271.
- 121 Karetnikova EA and Rapoport VL, 2008, Influence of UV irradiation on microbiological degradation of petroleum products, *Biol. Bull.*, **35**, 533-535.
- 122 Karsten U, 2008, Defense strategies of algae and cyanobacteria against solar ultraviolet radiation, in *Algal Chemical Ecology* ed.: Amsler CD, Springer, Berlin Heidelberg, pp. 273-296.
- 123 Karsten U, Escoubeyrou K and Charles F, 2009, The effect of re-dissolution solvents and HPLC columns on the analysis of mycosporine-like amino acids in the eulittoral macroalgae *Prasiola crista* and *Porphyra umbilicalis*, *Helgol. Mar. Res.*, **63**, 231-238.
- 124 Kashian DR, Zuellig RE, Mitchell KA and Clements WH, 2007, The cost of tolerance: sensitivity of stream benthic communities to UV-B and metals, *Ecol. Appl.*, **17**, 365-375.
- 125 Kataoka T, Hodoki Y, Suzuki K, Saito H and Higashi S, 2009, Detection of UVBR-sensitive and -tolerant bacteria in surface waters of the western North Pacific, *J. Photochem. Photobiol. B.*, **95**, 108-116.

- 126 Keller W, 2009, Limnology in northeastern Ontario: from acidification to multiple stressors, *Can. J. Fish. Aquat. Sci.*, **66**, 1189-1198.
- 127 Keller W, Yan ND, Gunn JM and Heneberry J, 2007, Recovery of acidified lakes: lessons from Sudbury, Ontario, Canada, *Water Air Soil Pollut. Focus*, **7**, 317-322.
- 128 Keller WB, Heneberry J, Leduc J, Gunn J and Yan N, 2006, Variations in epilimnion thickness in small boreal shield lakes: Relationships with transparency, weather and acidification, *Environ. Monit. Assess.*, **115**, 419-431.
- 129 Kessler K, Lockwood RS, Williamson CE and Saros JE, 2008, Vertical distribution of zooplankton in subalpine and alpine lakes: Ultraviolet radiation, fish predation, and the transparency-gradient hypothesis, *Limnol. Oceanogr.*, **53**, 2374-2382.
- 130 Kim J, Lee M, Oh S, Ku JL, Kim KH and Choi K, 2009, Acclimation to ultraviolet irradiation affects UV-B sensitivity of *Daphnia magna* to several environmental toxicants, *Chemosphere*, **77**, 1600-1608.
- 131 King BJ, Hoefel D, Daminato DP, Fanok S and Monis PT, 2008, Solar UV reduces *Cryptosporidium parvum* oocyst infectivity in environmental waters, *J. Appl. Microbiol.*, **104**, 1311-1323.
- 132 Klisch M and Häder D-P, 2008, Mycosporine-like amino acids and marine toxins - the common and the different, *Mar. Drugs*, **6**, 147-163.
- 133 Klisch M, Richter P, Puchta R, Häder D-P and Bauer W, 2007, The stereostructure of porphyrin-334: an experimental and calculational NMR investigation. Evidence for an efficient 'proton sponge', *Helv. Chim. Acta.*, **90**, 488-511.
- 134 Kouwenberg JHM and Lantoine F, 2007, Effects of ultraviolet-B stressed diatom food on the reproductive output in Mediterranean *Calanus helgolandicus* (Crustacea; Copepoda), *J. Exp. Mar. Biol. Ecol.*, **341**, 239-253.
- 135 Krapp RH, Bassinet T, Berge J, Pampanin DM and Camus L, 2009, Antioxidant responses in the polar marine sea-ice amphipod *Gammarus wilkitzkii* to natural and experimentally increased UV levels, *Aquat. Toxicol.*, **94**, 1-7.
- 136 Kwan JC, Taori K, Paul VJ and Luesch H, 2009, Lyngbyastatins 8-10, elastase inhibitors with cyclic depsipeptide scaffolds isolated from the marine cyanobacterium *Lyngbya semiplena*, *Mar. Drugs*, **7**, 528-538.
- 137 Lamare MD, Barker MF and Lesser MP, 2007, *In situ* rates of DNA damage and abnormal development in Antarctic and non-Antarctic sea urchin embryos, *Aquat. Biol.*, **1**, 21-32.
- 138 Lamare MD, Barker MF, Lesser MP and Marshall C, 2006, DNA photorepair in echinoid embryos: effects of temperature on repair rate in Antarctic and non-Antarctic species, *J. Exp. Biol.*, **209**, 5017-5028.
- 139 Langenheder S, Sobek S and Tranvik LJ, Changes in bacterial community composition along a solar radiation gradient in humic waters, *Aquat. Sci.*, **68**, 415-424.
- 140 Laurion I and Roy S, 2009, Growth and photoprotection in three dinoflagellates (including two strains of *Alexandrium tamarense*) and one diatom exposed to four weeks of natural and enhanced ultraviolet-B radiation, *J. Phycol.*, **45**, 16-33.
- 141 Lavaud J, Strzepek RF and Kroth PG, 2007, Photoprotection capacity differs among diatoms: Possible consequences on the spatial distribution of diatoms related to fluctuations in the underwater light climate, *Limnol. Oceanogr.*, **52**, 1188-1194.
- 142 Lebar MD, Heimbegner JL and Baker BJ, 2007, Cold-water marine natural products, *Nat. Prod. Rep.*, **24**, 774-797.
- 143 Lee TM and Shiu CT, 2009, Implications of mycosporine-like amino acid and antioxidant defenses in UV-B radiation tolerance for the algae species *Pterocladia capillacea* and *Gelidium amansii*, *Mar. Environ. Res.*, **67**, 8-16.

- 144 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.
- 145 Lehnherr I and Louis VLS, 2009, Importance of ultraviolet radiation in the photodemethylation of methylmercury in freshwater, *Environ. Sci. Technol.*, **43**, 5692-5698.
- 146 Lesser MP, 2008, Effects of ultraviolet radiation on productivity and nitrogen fixation in the cyanobacterium, *Anabaena* sp. (Newton's strain), *Hydrobiologia.*, **598**, 1-9.
- 147 Li P and Gao KS, 2008, Effects of solar UV and visible radiations on the spiral structure and orientation of *Arthrospira* (*Spirulina*) *platensis* (Cyanophyta), *Phycologia*, **47**, 573-579.
- 148 Liu S, Zhang QS, Wang Y, Ju Q and Tang XX, 2008, The response of the early developmental stages of *Laminaria japonica* to enhanced ultraviolet-B radiation, *Sci. China. C: Life Sci.*, **51**, 1129-1136.
- 149 Ma Z and Gao K, 2009, Photoregulation of morphological structure and its physiological relevance in the cyanobacterium *Arthrospira* (*Spirulina*) *platensis*, *Planta*, **230**, 329-337.
- 150 Ma Z and Gao K, 2009, Photosynthetically active and UV radiation act in an antagonistic way in regulating buoyancy of *Arthrospira* (*Spirulina*) *platensis* (cyanobacterium), *Environ. Exp. Bot.*, **66**, 265-269.
- 151 Macaluso AL, Mitchell DL and Sanders RW, 2009, Direct effects of UV-B radiation on the freshwater heterotrophic nanoflagellate *Paraphysomonas* sp., *Appl. Environ. Microbiol.*, **75**, 4525-4530.
- 152 Macias G, Marco A and Blaustein AR, 2007, Combined exposure to ambient UVB radiation and nitrite negatively affects survival of amphibian early life stages, *Sci. Tot. Environ.*, **385**, 55-65.
- 153 Marcoval MA, Villafañe VE and Helbling EW, 2008, Combined effects of solar ultraviolet radiation and nutrients addition on growth, biomass and taxonomic composition of coastal marine phytoplankton communities of Patagonia, *J. Photochem. Photobiol. B.*, **91**, 157-166.
- 154 Marinone MC, Marque SM, Suárez DA, del Carmen Di, guez M, Pérez P, De Los Ríos P, Soto D and Zagarese HE, 2006, UV radiation as a potential driving force for zooplankton community structure in Patagonian lakes, *Photochem. Photobiol.*, **82**, 962-971.
- 155 Markkula SE, Karvonen A, Salo H, Valtonen ET and Jokinen EI, 2007, Ultraviolet B irradiation affects resistance of rainbow trout (*Oncorhynchus mykiss*) against bacterium *Yersinia ruckeri* and trematode *Diplostomum spathaceum*, *Photochem. Photobiol.*, **83**, 1263-1269.
- 156 Marquis O and Miaud C, 2008, Variation in UV sensitivity among common frog *Rana temporaria* populations along an altitudinal gradient, *Zoology*, **111**, 309-317.
- 157 Marquis O, Miaud C, Ficetola GF, Bocher A, Mouchet F, Guittonneau S and Devaux A, 2009, Variation in genotoxic stress tolerance among frog populations exposed to UV and pollutant gradients, *Aquat. Toxicol.*, **95**, 152-161.
- 158 Martínez-Abaigar J, Núñez-Olivera E, Arróniz-Crespo M, Tomás R, Beaucourt N and Otero S, 2006, Effects of ultraviolet radiation on aquatic bryophytes, *Limnetica*, **25**, 81-94.
- 159 Meador JA, Baldwin AJ, Catala P, Jeffrey WH, Joux F, Moss JA, Pakulski JD, Stevens R and Mitchell DL, 2009, Sunlight-induced DNA damage in marine micro-organisms collected along a latitudinal gradient from 70 °N to 68 °S, *Photochem. Photobiol.*, **85**, 412-420.

- 160 Mitchell DL, Adams-Deutsch T and Olson MH, 2009, Dose dependence of DNA repair in rainbow trout (*Oncorhynchus mykiss*) larvae exposed to UV-B radiation, *Photochem. Photobiol. Sci.*, **8**, 75-81.
- 161 Mohlin M and Wulff A, 2009, Interaction effects of ambient UV radiation and nutrient limitation on the toxic cyanobacterium *Nodularia spumigena*, *Micro. Ecol.*, **57**, 675-686.
- 162 Mohovic B, Giancesella SMF, Laurion I and Roy S, 2006, Ultraviolet B-photoprotection efficiency of mesocosm-enclosed natural phytoplankton communities from different latitudes: Rimouski (Canada) and Ubatuba (Brazil), *Photochem. Photobiol.*, **82**, 952-961.
- 163 Monteith DT, Stoddard JL, Evans CD, de Wit HA, Forsius M, Høgåsen T, Wilander A, Skjelkvåle BL, Jeffries DS, Vuorenmaa J, Keller B, Kopáček J and Vesely J, 2007, Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry, *Nature*, **450**, 537-541.
- 164 Nagiller K and Sommaruga R, 2009, Differential tolerance of UV radiation between *Chaoborus* species and role of photoprotective compounds, *J. Plankt. Res.*, **31**, 503-513.
- 165 NASA, 2010, Science Focus: Dead Zones, National Aeronautics and Space Administration, http://disc.sci.gsfc.nasa.gov/oceancolor/additional/science-focus/ocean-color/dead_zones.shtml, accessed November, 2010.
- 166 Navarro E, Robinson CT and Behra R, 2008, Increased tolerance to ultraviolet radiation (UVR) and cotolerance to cadmium in UVR-acclimatized freshwater periphyton, *Limnol. Oceanogr.*, **53**, 1149-1158.
- 167 Navarro MB, Balseiro E and Modenutti B, 2009, Effect of UVR on lake water and macrophyte leachates in shallow Andean-Patagonian lakes: bacterial response to changes in optical features, *Photochem. Photobiol.*, **85**, 332-340.
- 168 Navarro NP, Mansilla A and Palacios M, 2008, UVB effects on early developmental stages of commercially important macroalgae in southern Chile, *J. Appl. Phycol.*, **20**, 897-906.
- 169 Obermuller B, Puntarulo S and Abele D, 2007, UV-tolerance and instantaneous physiological stress responses of two Antarctic amphipod species *Gondogeneia antarctica* and *Djerboa furcipes* during exposure to UV radiation, *Mar. Environ. Res.*, **64**, 267-285.
- 170 Obertegger U, Flaim G and Sommaruga R, 2008, Multifactorial nature of rotifer water layer preferences in an oligotrophic lake, *J. Plankt. Res.*, **30**, 633-643.
- 171 Olano C, Méndez C and Salas JA, 2009, Antitumor compounds from marine actinomycetes, *Mar. Drugs*, **7**, 210-248.
- 172 Olson MH, Adams-Deutsch T, Cassels KJ, Oliver AE and Mitchell DL, 2008, Patterns of ultraviolet radiation exposure in bluegill nests over the course of the spawning season, *Trans. Am. Fish. Soc.*, **137**, 1446-1454.
- 173 Olson MH, Colip MR, Gerlach JS and Mitchell DL, 2006, Quantifying ultraviolet radiation mortality risk in bluegill larvae: effects of nest location, *Ecol. Appl.*, **16**, 328-338.
- 174 Olson MH and Mitchell DL, 2006, Interspecific variation in UV defense mechanisms among temperate freshwater fishes, *Photochem. Photobiol.*, **82**, 606-610.
- 175 Oren A and Gunde-Cimerman N, 2007, Mycosporines and mycosporine-like amino acids: UV protectants or multipurpose secondary metabolites?, *FEMS Microbiol. Lett.*, **269**, 1-10.

- 176 Otero S, Cezón S, Martínez-Abaigar J and Núñez-Olivera E, 2008, Ultraviolet-absorbing capacity of aquatic bryophytes from Tierra del Fuego (Argentina), *J. Bryol.*, **30**, 290-296.
- 177 Otero S, Núñez-Olivera E, Martínez-Abaigar J, Tomás R, Arróniz-Crespo M and Beaucourt N, 2006, Effects of cadmium and enhanced UV radiation on the physiology and the concentration of UV-absorbing compounds of the aquatic liverwort *Jungermannia exsertifolia* subsp. *cordifolia*, *Photochem. Photobiol. Sci.*, **5**, 760-769.
- 178 Otero S, Núñez-Olivera E, Martínez-Abaigar J, Tomás R and Huttunen S, 2009, Retrospective bioindication of stratospheric ozone and ultraviolet radiation using hydroxycinnamic acid derivatives of herbarium samples of an aquatic liverwort, *Environ. Pollut.*, **157**, 2335-2344.
- 179 Pakulski JD, Kase JP, Meador JA and Jeffrey WH, 2008, Effect of stratospheric ozone depletion and enhanced ultraviolet radiation on marine bacteria at Palmer Station, Antarctica in the early Austral spring, *Photochem. Photobiol.*, **84**, 215-221.
- 180 Palen WJ and Schindler DE, 2010, Water clarity, maternal behavior, and physiology combine to eliminate UV radiation risk to amphibians in a montane landscape, *Proc. Nat. Acad. Sci. USA.*, **21**, 9701-9706.
- 181 Palen WJ, Williamson CE, Clauser AA and Schindler DE, 2005, Impact of UV-B exposure on amphibian embryos; linking species physiology to oviposition behavior, *Proc. R. Soc. B. Biol. Sci.*, **272**, 1227-1234.
- 182 Park JS, Oh S, Shin MY, Kim MK, Yi SM and Zoh KD, 2008, Seasonal variation in dissolved gaseous mercury and total mercury concentrations in Juam Reservoir, Korea, *Environ. Pollut.*, **154**, 12-20.
- 183 Paterson AM, Somers KM, Dillon PJ, Heneberry J, Keller WB and Ford A, 2008, Relationships between dissolved organic carbon concentrations, weather, and acidification in small Boreal Shield lakes, *Can. J. Fish. Aquat. Sci.*, **65**, 786-795.
- 184 Pelletier, Sargian P, Payet J and Demers S, 2006, Ecotoxicological effects of combined UVB and organic contaminants in coastal waters: a review, *Photochem. Photobiol.*, **82**, 981-993.
- 185 Pérez MT and Sommaruga R, 2007, Interactive effects of solar radiation and dissolved organic matter on bacterial activity and community structure, *Environ. Microbiol.*, **9**, 2200-2210.
- 186 Perotti MG and Diéguez MdC, 2006, Effect of UV-B exposure on eggs and embryos of Patagonian anurans and evidence of photoprotection, *Chemosphere*, **65**, 2063-2070.
- 187 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.
- 188 Phoenix VR, Bennett PC, Engel AS, Tyler SW and Ferris FG, 2006, Chilean high-altitude hot-spring sinters: a model system for UV screening mechanisms by early Precambrian cyanobacteria, *Geobiology*, **4**, 15-28.
- 189 Piazena H and Häder D-P, 2009, Solar UV-B and UV-A irradiance in arid high-mountain regions: Measurements on the island of Tenerife as compared to previous tropical Andes data, *J. Geophys. Res.*, **114**, G04024.
- 190 Piccini C, Conde D, Pernthaler J and Sommaruga R, 2009, Alteration of chromophoric dissolved organic matter by solar UV radiation causes rapid changes in bacterial community composition, *Photochem. Photobiol. Sci.*, **8**, 1321-1328.
- 191 Pruski AM, Nahon S, Escande ML and Charles F, 2009, Ultraviolet radiation induces structural and chromatin damage in Mediterranean sea-urchin spermatozoa, *Res. Genetic Toxicol Environ. Mutagenesis*, **673**, 67-73.

- 192 Reef R, Dunn S, Levy O, Dove S, Shemesh E, Brickner I, Leggat W and Hoegh-Guldberg O, 2009, Photoreactivation is the main repair pathway for UV-induced DNA damage in coral planulae, *J. Exp. Biol.*, **212**, 2760-2766.
- 193 Reef R, Kaniewska P and Hoegh-Guldberg O, 2009, Coral skeletons defend against ultraviolet radiation, *PLoS ONE*, **4**, e7995.
- 194 Reid JW and Williamson CE, 2009, Copepoda, in *Ecology and Classification of North American Freshwater Invertebrates*, 3rd ed. eds.: Thorp JH and Covich AP, Academic Press, Burlington, MA, USA, pp. 829-900.
- 195 Richards TA, Dacks JB, Campbell SA, Blanchard JL, Foster PG, McLeod R and Roberts CW, 2006, Evolutionary origins of the eukaryotic shikimate pathway: gene fusions, horizontal gene transfer, and endosymbiotic replacements, *Eukaryotic Cell*, **5**, 1517-1531.
- 196 Richter P, Helbling W, Streb C and Häder D-P, 2007, PAR and UV effects on vertical migration and photosynthesis in *Euglena gracilis*, *Photochem. Photobiol.*, **83**, 818-823.
- 197 Richter PR, Häder D-P, Goncalves RJ, Marcoval MA, Villafañe VE and Helbling EW, 2007, Vertical migration and motility responses in three marine phytoplankton species exposed to solar radiation, *Photochem. Photobiol.*, **83**, 810-817.
- 198 Richter PR, Sinha RP and Häder D-P, 2006, Scytonemin-rich epilithic cyanobacteria survive acetone treatment, *Curr. Trend. Microbiol.*, **2**, 13-19.
- 199 Riebesell U, Schulz KG, Bellerby RGJ, Botros M, Fritsche P, Meyerh"fer M, Neill C, Nondal G, Oschlies A, Wohlers J and Zollner E, 2007, Enhanced biological carbon consumption in a high CO₂ ocean, *Nature*, **450**, 545-548.
- 200 Riemer U, Lamare MD and Peake BM, 2007, Temporal concentrations of sunscreen compounds (mycosporine-like amino acids) in phytoplankton and in the New Zealand krill, *Nyctiphanes australis* G.O. Sars, *J. Plankt. Res.*, **29**, 1077-1086.
- 201 Roleda MY, 2009, Photosynthetic response of Arctic kelp zoospores exposed to radiation and thermal stress, *Photochem. Photobiol. Sci.*, **8**, 1302-1312.
- 202 Roleda MY, Clayton MN and Wiencke C, 2006, Screening capacity of UV-absorbing compounds in spores of Arctic Laminariales, *J. Exp. Mar. Biol. Ecol.*, **338**, 123-133.
- 203 Roleda MY, Lütz-Meindl U, Wiencke C and Lütz C, 2009, Physiological, biochemical, and ultrastructural responses of the green macroalga *Urospora penicilliformis* from Arctic Spitsbergen to UV radiation, *Protoplasma*, **243**, 105-116.
- 204 Roleda MY, Wiencke C and Hanelt D, 2006, Thallus morphology and optical characteristics affect growth and DNA damage by UV radiation in juvenile Arctic *Laminaria* sporophytes, *Planta*, **223**, 407-417.
- 205 Roleda MY, Wiencke C, Hanelt D and Bischof K, 2007, Sensitivity of the early life stages of macroalgae from the northern hemisphere to ultraviolet radiation, *Photochem. Photobiol.*, **83**, 851-862.
- 206 Roleda MY, Zacher K, Wulff A, Hanelt D and Wiencke C, 2007, Photosynthetic performance, DNA damage and repair in gametes of the endemic Antarctic brown alga *Ascoseira mirabilis* exposed to ultraviolet radiation, *Austral Ecology*, **32**, 917-926.
- 207 Roleda MY, Zacher K, Wulff A, Hanelt D and Wiencke C, 2008, Susceptibility of spores of different ploidy levels from Antarctic *Gigartina skottsbergii* (Gigartinales, Rhodophyta) to ultraviolet radiation, *Phycologia*, **47**, 361-370.
- 208 Romansic JM, Waggener AA, Bancroft BA and Blaustein AR, 2009, Influence of ultraviolet-B radiation on growth, prevalence of deformities, and susceptibility to predation in Cascades frog (*Rana cascadae*) larvae, *Hydrobiologia*, **624**, 219-233.

- 209 Rose KC, Williamson CE, Saros JE, Sommaruga R and Fischer JM, 2009, Differences in UV transparency and thermal structure between alpine and subalpine lakes: implications for organisms, *Photochem. Photobiol. Sci.*, **8**, 1244-1256.
- 210 Ross RM, Quetin LB, Martinson DG, Iannuzzi RA, Stammerjohn SE and Smith RC, 2008, Palmer LTER: Patterns of distribution of five dominant zooplankton species in the epipelagic zone west of the Antarctic Peninsula, 1993-2004, *Deep Sea Res. Part II: Top. Stud. Oceanog.*, **55**, 2086-2105.
- 211 Roy S, Mohovic B, Giancesella SMF, Schloss I, Ferrario M and Demers S, 2006, Effects of enhanced UV-B on pigment-based phytoplankton biomass and composition of mesocosm-enclosed natural marine communities from three latitudes, *Photochem. Photobiol.*, **82**, 909-922.
- 212 Ruelas DS, Karentz D and Sullivan JT, 2006, Lethal and sub-lethal effects of UVB on juvenile *Biomphalaria glabrata* (Mollusca: Pulmonata), *J. Invertebr. Pathol.*, **93**, 192-200.
- 213 Russell J and Phillips N, 2009, Species-specific vulnerability of benthic marine embryos of congeneric snails (*Haminoea* spp.) to ultraviolet radiation and other intertidal stressors, *Biol. Bull.*, **217**, 65-72.
- 214 Salgado LT, Tomazetto R, Cinelli LP, Farina M and Filho GMA, 2007, The influence of brown algae alginates on phenolic compounds capability of ultraviolet radiation absorption in vitro, *Brazil. J. Oceanog.*, **55**, 145-154.
- 215 Sayed AEDH, Ibrahim AT, Mekkiaw IAA and Mahmoud UM, 2007, Acute effects of ultraviolet-A radiation of African Catfish *Clarias gariepinus* (Burchell, 1822), *J. Photochem. Photobiol. B.*, **89**, 170-174.
- 216 Schindler DW and Smol JP, 2006, Cumulative effects of climate warming and other human activities on freshwaters of Arctic and Subarctic North America, *Ambio*, **35**, 160-168.
- 217 Scott CE, Saros JE, Williamson CE, Salm CR, Peters SC and Mitchell DL, 2009, Effects of nutrients and dissolved organic matter on the response of phytoplankton to ultraviolet radiation: experimental comparison in spring versus summer, *Hydrobiologia.*, **619**, 155-166.
- 218 Shiller AM, Duan S, van Erp P and Bianchi TS, 2006, Photo-oxidation of dissolved organic matter in river water and its effect on trace element speciation, *Limnol.Oceanogr.*, **51**, 1716-1728.
- 219 Sicora CI, Appleton SE, Brown CM, Chung J, Chandler J, Cockshutt AM, Vass I and Campbell DA, 2006, Cyanobacterial psbA families in *Anabaena* and *Synechocystis* encode trace, constitutive and UVB-induced D1 isoforms, *Biochimica and Biophysica Acta*, **1757**, 47-56.
- 220 Singh SP, Häder D-P and Sinha RP, 2010, Cyanobacteria and ultraviolet radiation (UVR) stress: Mitigation strategies, *Ageing Res. Rev.*, **9**, 79-90.
- 221 Singh SP, Klisch M, Sinha RP and Häder D-P, 2008, Effects of abiotic stressors on synthesis of the mycosporine-like amino acid shinorine in the cyanobacterium *Anabaena variabilis* PCC 7937, *Photochem. Photobiol.*, **84**, 1500-1505.
- 222 Singh SP, Klisch M, Sinha RP and Häder D-P, 2010, Genome mining of mycosporine-like amino acid (MAA) synthesizing and non-synthesizing cyanobacteria: A bioinformatics study, *Genomics*, **95**, 120-128.
- 223 Sinha RP, Keshari G, Kumari S, Singh SP, Rastogi RP and Singh KL, 2006, Screening of mycosporine-like amino acids (MAAs) in cyanobacteria, *Mod. J. Life Sci.*, **5**, 1-6.

- 224 Sinha RP, Rastogi RP, Ambasht NK and Häder D-P, 2008, Live of wetland cyanobacteria under enhancing solar UV-B radiation, *Proc. Indian. Nat. Sci. Acad.*, **78**, 53-65.
- 225 Sinha RP, Singh SP and Häder D-P, 2008, Effects of UV-B radiation on phytoplankton and macroalgae: adaptation strategies, *Proc. Indian. Nat. Sci. Acad.*, **78**, 105-116.
- 226 Six C, Joubin L, Partensky F, Holtzendorff J and Garczarek L, 2007, UV-induced phycobilisome dismantling in the marine picocyanobacterium *Synechococcus* sp. WH8102, *Photosyn. Res.*, **92**, 75-86.
- 227 Smith RC, Mobley CD and Björn LO, 2007, Underwater Light, in *Photobiology. The Science of Life and Light. Second Edition*, Springer, New York, pp. 131-138.
- 228 Smyrniotopoulos V, Vagias C and Roussis V, 2009, Sphaeroane and neodolabellane diterpenes from the red alga *Sphaerococcus coronopifolius*, *Mar. Drugs*, **7**, 184-195.
- 229 Sobrino C, Neale PJ, Phillips-Kress JD, Moeller RE and Portec JA, 2009, Elevated CO₂ increases sensitivity to ultraviolet radiation in lacustrine phytoplankton assemblages, *Limnol. Oceanogr.*, **54**, 2448-2459.
- 230 Sobrino C, Ward ML and Neale PJ, 2008, Acclimation to elevated carbon dioxide and ultraviolet radiation in the diatom *Thalassiosira pseudonana*: Effects on growth, photosynthesis, and spectral sensitivity of photoinhibition, *Limnol. Oceanogr.*, **53**, 494-505.
- 231 Sommaruga R and Augustin G, 2006, Seasonality in UV transparency of an alpine lake is associated to changes in phytoplankton biomass, *Aquat. Sci.*, **68**, 129-141.
- 232 Sommaruga R, Whitehead K, Shick JM and Lobban CS, 2006, Mycosporine-like amino acids in the zooxanthella-ciliate symbiosis *Maristentor dinoferus*, *Protist*, **157**, 185-191.
- 233 Sonntag B, Summerer M and Sommaruga R, 2007, Sources of mycosporine-like amino acids in planktonic *Chlorella* -bearing ciliates (Ciliophora), *Freshwat. Biol.*, **52**, 1476-1485.
- 234 Soule T, Garcia-Pichel F and Stout V, 2009, Gene expression patterns associated with the biosynthesis of the sunscreen scytonemin in *Nostoc punctiforme* ATCC 29133 in response to UVA radiation, *J. Bacteriol.*, **191**, 4639-4646.
- 235 Soule T, Stout V, Swingley WD, Meeks JC and Garcia-Pichel F, 2007, Molecular genetics and genomic analysis of scytonemin biosynthesis in *Nostoc punctiforme* ATCC 29133, *J. Bacteriol.*, **189**, 4465-4472.
- 236 Souza MS, Balseiro E, Laspoumaderes C and Modenutti B, 2010, Effect of ultraviolet radiation on acetylcholinesterase activity in freshwater copepods, *Photochem. Photobiol.*, **86**, 367-373.
- 237 Souza MS, Modenutti BE and Balseiro EG, 2007, Antioxidant defences in planktonic crustaceans exposed to different underwater light irradiances in Andean lakes, *Water Air Soil Pollut.*, **183**, 49-57.
- 238 Stammerjohn SE, Martinson DG, Smith RC and Iannuzzi RA, 2008, Sea ice in the western Antarctic Peninsula region: Spatio-temporal variability from ecological and climate change perspectives, *Deep Sea Res. Part II: Top. Stud. Oceanog.*, **55**, 2041-2058.
- 239 Starcevic A, Akthar S, Dunlap WC, Shick JM, Hranueli D, Cullum J and Long PF, 2008, Enzymes of the shikimic acid pathway encoded in the genome of a basal metazoan, *Nematostella vectensis*, have microbial origins, *Proc. Nat. Acad. Sci. USA.*, **105**, 2533-2537.

- 240 Sterr B and Sommaruga R, 2008, Does ultraviolet radiation alter kairomones? An
experimental test with *Chaoborus obscuripes* and *Daphnia pulex*, *J. Plankt. Res.*, **30**,
1343-1350.
- 241 Striegl RG, Aiken GR, Dornblaser MM, Raymond PA and Wickland KP, 2005, A
decrease in discharge-normalized DOC export by the Yukon River during summer
through autumn, *Geophys. Res. Lett.*, **32**, L21413.
- 242 Stroeve J and Serreze M, 2008, Arctic sea ice extent plummets in 2007, *Eos*
(*Transactions of the American Geophysical Union*), **89**, 13-20.
- 243 Suhett AL, Amado AM, Enrich-Prast A, de Assis Esteves F and Farjalla VF, 2007,
Seasonal changes of dissolved organic carbon photo-oxidation rates in a tropical
humic lagoon: the role of rainfall as a major regulator, *Can. J. Fish. Aquat. Sci.*, **64**,
1266-1272.
- 244 Summerer M, Sonntag B, Hortnagl P and Sommaruga R, 2009, Symbiotic ciliates
receive protection against UV damage from their algae: a test with *Paramecium*
bursaria and *Chlorella*, *Protist*, **160**, 233-243.
- 245 Takahashi A and Ohnishi T, 2009, Molecular mechanisms involved in adaptive
responses to radiation, UV light, and heat, *J. Rad. Res.*, **50**, 385-393.
- 246 Tanimura A, Kawaguchi S, Oka N, Nishikawa J, Toczko S, Takahashi KT, Terazaki
M, Odate T, Fukuchi M and Hosie G, 2008, Abundance and grazing impacts of krill,
salps and copepods along the 140 °E meridian in the Southern Ocean during summer,
Antarctic. Sci., **20**, 365-379.
- 247 Tartarotti B and Sommaruga R, 2006, Seasonal and ontogenetic changes of
mycosporine-like amino acids in planktonic organisms from an alpine lake,
Limnol. Oceanogr., **51**, 1530-1541.
- 248 Tartarotti B and Torres JJ, 2009, Sublethal stress: Impact of solar UV radiation on
protein synthesis in the copepod *Acartia tonsa*, *J. Exp. Mar. Biol. Ecol.*, **375**, 106-113.
- 249 Tedetti M, Sempere R, Vasilkov A, Charriere B, Nerini D, Miller WL, Kawamura K
and Raimbault P, 2007, High penetration of ultraviolet radiation in the south east
Pacific waters, *Geophys. Res. Lett.*, **34**, L126101-L126105.
- 250 Tirok K and Gaedke U, 2007, The effect of irradiance, vertical mixing and
temperature on spring phytoplankton dynamics under climate change: Long-term
observations and model analysis, *Oecologia*, **150**, 625-642.
- 251 Torregiani JH and Lesser MP, 2007, The effects of short-term exposures to ultraviolet
radiation in the Hawaiian coral *Montipora verrucosa*, *J. Exp. Mar. Biol. Ecol.*, **340**,
194-203.
- 252 Torres JL, Armstrong RA, Corredor JE and Gilbes F, 2007, Physiological responses
of *Acropora cervicornis* to increased solar irradiance, *Photochem. Photobiol.*, **83**,
839-850.
- 253 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.
- 254 Tucker AJ, Williamson CE, Rose KC, Oris JT, Connelly SJ, Olson MH and Mitchell
DL, 2010, Ultraviolet radiation affects invasibility of lake ecosystems by warmwater
fish, *Ecol.*, **91**, 882-890.
- 255 Turner MA, Findlay DL, Baulch HM, Armstrong LM, Kasian SEM, McNicol DK and
Vinebrooke RD, 2009, Heavy metal bioaccumulation and toxicity with special

- reference to microalgae Benthic algal communities: recovery from experimental acidification, *Can. J. Fish. Aquat. Sci.*, **66**, 1875-1891.
- 256 Tzortziou M, Osburn CL and Neale PJ, 2007, Photobleaching of dissolved organic material from a tidal marsh-estuarine system of the Chesapeake Bay, *Photochem. Photobiol.*, **83**, 782-792.
- 257 Usami Y, 2009, Recent synthetic studies leading to structural revisions of marine natural products, *Mar. Drugs*, **7**, 314-330.
- 258 van de Poll WH and Buma AGJ, 2009, Does ultraviolet radiation affect the xanthophyll cycle in marine phytoplankton?, *Photochem. Photobiol. Sci.*, **8**, 1295-1301.
- 259 Van Wambeke F, Tedetti M, Duhamel S and Sempéré R, 2008, Diel variability of heterotrophic bacterial production and UV doses in the South East Pacific, *Biogeosci. Discuss.*, **5**, 435-462.
- 260 Vernet M, Martinson DG, Iannuzzi R, Stammerjohn S, Kozlowski W, Sines K, Smith R and Garibottie I, 2008, Primary production within the sea-ice zone west of the Antarctic Peninsula: Sea ice, summer mixed layer, and irradiance, *Deep Sea Res. Part II: Top. Stud. Oceanogr.*, **55**, 2068-2085.
- 261 Villafañe VE, Gao K, Li P and Helbling EW, 2007, Vertical mixing within the epilimnion modulates UVR-induced photoinhibition in tropical freshwater phytoplankton from southern China, *Freshwat. Biol.*, **52**, 1260-1270.
- 262 Villafañe VE, Janknegt PJ, de Graaff M, Visser RJW, van de Poll WH, Buma AGJ and Helbling EW, 2008, UVR-induced photoinhibition of summer marine phytoplankton communities from Patagonia, *Mar. Biol.*, **154**, 1021-1029.
- 263 Wang M and Overland JE, 2009, A sea ice free summer Arctic within 30 years?, *Geophys. Res. Lett.*, **36**, L07502.
- 264 Wang X, Lou T and Xie H, 2009, Photochemical production of dissolved inorganic carbon from Suwannee river humic acid, *Chinese J. Oceanol. Limnol.*, **27**, 570-573.
- 265 Wang Y, Chen JW, Lin J, Wang Z, Bian HT, Cai XY and Hao C, 2009, Combined experimental and theoretical study on photoinduced toxicity of an anthraquinone dye intermediate to *Daphnia magna*, *Environ. Toxicol. Chem.*, **28**, 846-852.
- 266 Wängberg SA, Andreasson KIM, Gustavson K, Reinthaler T and Henriksen P, 2008, UV-B effects on microplankton communities in Kongsfjord, Svalbard - A mesocosm experiment, *J. Exp. Mar. Biol. Ecol.*, **365**, 156-163.
- 267 Weyhenmeyer GA and Karlsson J, 2009, Nonlinear response of dissolved organic carbon concentrations in boreal lakes to increasing temperatures, *Limnol. Oceanogr.*, **54**, 2513-2519.
- 268 Weyrauch SL and Grubb TC, 2006, Effects of the interaction between genetic diversity and UV-B radiation on wood frog fitness, *Conserv. Biol.*, **20**, 802-810.
- 269 Wiencke C, Roleda MY, Gruber A, Clayton MN and Bischof K, 2006, Susceptibility of zoospores to UV radiation determines upper depth distribution limit of Arctic kelps: evidence through field experiments, *J. Ecol.*, **94**, 455-463.
- 270 Williams PD, Eichstadt SL, Kokjohn TA and Martin EL, 2007, Effects of ultraviolet radiation on the Gram-positive marine bacterium *Microbacterium maritropicum*, *Curr. Microbiol.*, **55**, 1-7.
- 271 Williamson CE, De Lange HJ and Leech DM, 2007, Do zooplankton contribute to an ultraviolet clear-water phase in lakes?, *Limnol. Oceanogr.*, **52**, 662-667.
- 272 Williamson CE and Rose KC, 2010, When UV meets freshwater, *Science*, **329**, 637-639.
- 273 Wollenberg JL and Peters SC, 2009, Mercury emission from a temperate lake during autumn turnover, *Sci. Tot. Environ.*, **407**, 2909-2918.

- 274 Wong CY, Chu WL, Marchant H and Phang SM, 2007, Comparing the response of Antarctic, tropical and temperate microalgae to ultraviolet radiation (UVR) stress, *J. Appl. Phycol.*, **19**, 689-699.
- 275 Wright AD, Nielson JL, Tapiolas DM, Motti CA, Ovenden SPB, Kearns PS and Liptrot CH, 2009, Detailed NMR, including 1,1-ADEQUATE, and anticancer studies of compounds from the echinoderm *Colobometra perspinosa*, *Mar. Drugs*, **7**, 565-575.
- 276 Wu H and Gao K, 2009, Ultraviolet radiation stimulated activity of extracellular carbonic anhydrase in the marine diatom *Skeletonema costatum*, *Funct. Plant Biol.*, **36**, 137-143.
- 277 Wu HY, Zou DH and Gao KS, 2008, Impacts of increased atmospheric CO₂ concentration on photosynthesis and growth of micro- and macro-algae, *Sci. China. C: Life Sci.*, **51**, 1144-1150.
- 278 Wulff A, Zacher K, Hanelt D, Al-Handal A and Wiencke C, 2008, UV radiation - a threat to Antarctic benthic marine diatoms?, *Antarctic. Sci.*, **20**, 13-20.
- 279 Xu J and Gao KS, 2008, Growth, pigments, UV-absorbing compounds and agar yield of the economic red seaweed *Gracilaria lemaneiformis* (Rhodophyta) grown at different depths in the coastal waters of the South China Sea, *J. Appl. Phycol.*, **20**, 681-686.
- 280 Zacher K, Hanelt D, Wiencke C and Wulff A, 2007, Grazing and UV radiation effects on an Antarctic intertidal microalgal assemblage: a long-term field study, *Polar Biol.*, **30**, 1203-1212.
- 281 Zacher K, Wulff A, Molis M, Hanelt D and Wiencke C, 2007, Ultraviolet radiation and consumer effects on a field-grown intertidal macroalgal assemblage in Antarctica, *Glob. Change Biol.*, **13**, 1201-1215.
- 282 Zadereev YS and Tolomeyev AP, 2007, The vertical distribution of zooplankton in brackish meromictic lake with deep-water chlorophyll maximum, *Hydrobiologia.*, **576**, 69-82.
- 283 Zenoff VF, Siñeriz F and Farías ME, 2006, Diverse responses to UV-B radiation and repair mechanisms of bacteria isolated from high-altitude aquatic environments, *Appl. Environ. Microbiol.*, **72**, 7857-7863.
- 284 Zepp RG, Shank GC, Stabenau E, Patterson KW, Cyterski M, Fisher W, Bartels E and 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.
- 285 Zhang L, Li L and Wu Q, 2007, Protective effects of mycosporine-like amino acids of *Synechocystis* sp. PCC 6803 and their partial characterization, *J. Photochem. Photobiol. B.*, **86**, 240-245.
- 286 Zhang Y, Liu M, Qin B and Feng S, 2009, Photochemical degradation of chromophoric-dissolved organic matter exposed to simulated UV-B and natural solar radiation, *Hydrobiologia.*, **627**, 159-168.
- 287 Zhang Y, Mu J, Gu X, Zhao C, Wang X and Xie Z, 2009, A marine sulfate-reducing bacterium producing multiple antibiotics: biological and chemical investigation, *Mar. Drugs*, **7**, 341-354.
- 288 Zhang Y, Qin B, Zhu G, Zhang L and Yang L, 2007, Chromophoric dissolved organic matter (CDOM) absorption characteristics in relation to fluorescence in Lake Taihu, China, a large shallow subtropical lake, *Hydrobiologia.*, **581**, 43-52.
- 289 Zhou W, Juneau P and Qiu B, 2006, Growth and photosynthetic responses of the bloom-forming cyanobacterium *Microcystis aeruginosa* to elevated levels of cadmium, *Chemosphere*, **65**, 1738-1746.

- 290 Zhou W, Tang X, Xiao H, Wang Y and Wang R, 2009, Response of marine microalgae, heterotrophic bacteria and their relationship to enhanced UV-B radiation, *J. Ocean Univ. China*, **8**, 35-38.

Chapter 5. Effects of solar UV radiation and climate change on biogeochemical cycling: Interactions and feedbacks

R. G. Zepp,^a D. J. Erickson III,^b N. D. Paul^c and B. Sulzberger^d

^a U.S. Environmental Protection Agency, National Exposure Research Laboratory, 960 College Station Road, Athens, Georgia 30605-2700 USA

^b Computational Earth Sciences Group, Computer Science and Mathematics Division, Oak Ridge National Laboratory, MS 6016 Oak Ridge TN 37831-6016 USA;

^c Lancaster Environment Centre, Lancaster University, Lancaster LA1 4YQ, UK;

^d Swiss Federal Institution of Aquatic Science and Technology (Eawag), Überlandstrasse 133, CH-8600 Dübendorf, Switzerland.

Summary

Solar UV radiation, climate and other drivers of global change are undergoing significant changes and models forecast that these changes will continue for the remainder of this century. Here we assess the effects of solar UV radiation on biogeochemical cycles and the interactions of these effects with climate change, including feedbacks on climate. Such interactions occur in both terrestrial and aquatic ecosystems. While there is significant uncertainty in the quantification of these effects, they could accelerate the rate of atmospheric CO₂ increase and subsequent climate change beyond current predictions. The effects of predicted changes in climate and solar UV radiation on carbon cycling in terrestrial and aquatic ecosystems are expected to vary significantly between regions. The balance of positive and negative effects on terrestrial carbon cycling remains uncertain, but the interactions between UV radiation and climate change are likely to contribute to decreasing sink strength in many oceanic regions. Interactions between climate and solar UV radiation will affect cycling of elements other than carbon, and so will influence the concentration of greenhouse and ozone-depleting gases. For example, increases in oxygen-deficient regions of the ocean caused by climate change are projected to enhance the emissions of nitrous oxide, an important greenhouse and ozone-depleting gas. Future changes in UV-induced transformations of aquatic and terrestrial contaminants could have both beneficial and adverse effects. Taken in total, it is clear that the future changes in UV radiation coupled with human-caused global change will have large impacts on biogeochemical cycles at local, regional and global scales.

Introduction

The transport and transformation of substances in the environment, through living organisms, water, land, and the atmosphere are known collectively as biogeochemical cycles. The elements that participate in these cycles exist in a range of forms that can be altered not only by Earth's chemical, physical and geological processes but also by the activities of living organisms. In turn, biogeochemical cycles control the availability of chemical elements to organisms, whether as nutrients or toxins, and so exert major effects on life on Earth. There are extensive feedbacks and interactions between biogeochemical cycles, UV radiation and various elements of climate change. These effects involve both the UV-A part of solar UV radiation (315-400 nm), which is weakly affected by stratospheric ozone, as well as the UV-B (280-315 nm) spectral region, which is strongly affected by ozone. Thus, discussions here

include the biogeochemical effects that are influenced by the entire solar UV spectrum (280-400 nm). UV radiation interacts with a myriad of processes that influence the emission, exchange, transport and removal of trace gases and particulates in the atmosphere and ocean. The overall aim of the Environmental Effects Assessment Panel is to consider the effects of changes in stratospheric ozone and their interaction with climate change. Biogeochemical cycling is clearly at the heart of such interactions in both terrestrial and aquatic ecosystems, largely because carbon cycling drives many of the feedbacks within the climate system. The wide extent of these interactions is summarized in Table 5-1, which is based on results presented in this and previous UNEP reports.^{231, 232} Biogeochemical cycles in terrestrial and aquatic ecosystems play a significant role in determining the rate and extent of changes in atmospheric CO₂, other trace gases and particulates. Changes in exposure of ecosystems to UV radiation influence their ability to remove some fraction of the human-derived CO₂ that is emitted into the atmosphere.

Table 5-1. Summary of selected direct and indirect effects of solar UV radiation on biogeochemical cycles, based on this and previous reports.^{231, 232} Several of these direct and indirect effects may operate concurrently on the biogeochemical system.

Element	Environmental compartment	Impact on biogeochemical cycling
Carbon	Terrestrial Eco-systems	1. Impact on plant growth, morphology and photosynthesis, and interactions between species, and community composition
		2. Enhances emissions of CH ₄ and CO
		3. Impacts on litter composition and decomposition and organic matter decomposition
	Aquatic ecosys-tems	1. Impact on photosynthesis and organic carbon production, including coloured dissolved organic matter (CDOM).
		2. Impact on organic matter degradation and turnover with effects on CO ₂ and CO production and microbial lability of DOM
	Atmosphere	3. Impact on spectral properties of water column
1. Impact on ecosystem-atmosphere exchange of trace C gases, e.g. CO ₂ , CO, CH ₄		
		2. Effects on atmospheric chemistry, e.g. on reactions involving OH and ozone
Nitrogen	Terrestrial Eco-systems	1. Effects on nitrogen fixation
		2. Impacts on nitrification, N ₂ O and NO _x emissions
		3. Effects on litter composition and decomposition
		4. Release of inorganic N through degradation of organic matter with resulting impacts on soil fertility, CH ₄ /CO sinks
	Aquatic ecosys-tems	1. Impact on ammonification of dissolved organic N
		2. Effects on nitrogen fixation
		3. Increased hypoxia with increased nitrous oxide emissions from ocean
	Atmosphere	4. Effects on CDOM production and UV attenuation
		1. Impact on ecosystem-atmosphere exchange of trace N gases.
		2. Effects on atmospheric chemistry, e.g. on reactions involving OH and ozone

Element	Environmental compartment	Impact on biogeochemical cycling
Sulfur	Terrestrial Eco-systems	1. Uptake and release of DMS and COS by vegetation.
	Aquatic ecosystems	1. Uptake and release of DMS, DMSO, COS and S precursors by aquatic organisms 2. Effect on biological production and consumption of DMSP 3. Photooxidation of DMS and organosulfur compounds to COS.
	Atmosphere	1. Impact on ecosystem-atmosphere exchange of S gases, e.g. DMS, COS 2. Impact on conversion of DMS and other S compounds to aerosols/cloud condensation nuclei
Phosphorus and metals	Terrestrial ecosystems	1. Perturbation of P cycling in plant rhizosphere 2. Degradation of organic matter and with resulting impacts on soil fertility.
	Aquatic ecosystems	1. Effects on biological availability of metal nutrients, e.g. Fe, Cu, Mn, and metal pollutants, e.g. Hg 2. Formation of ROS by Fe reactions
	Atmosphere	1. Indirect impacts on ecosystem-atmosphere exchange of trace gases via changes in nutrient availability
Oxygen	Terrestrial Eco-systems	1. Effects on O ₂ uptake during litter decomposition
	Aquatic ecosystems	1. Effects on O ₂ production by photosynthesis of and O ₂ consumption by DOC oxidation 2. Effects on formation and degradation of H ₂ O ₂ and other ROS, e.g. HO ₂ and OH
	Atmosphere	1. Effects on ecosystem-atmosphere exchange and chemical oxidation processes
Halogens	Terrestrial ecosystems	1. Production of organohalogens
	Aquatic ecosystems	1. Effects on biogenic production and consumption of organohalogens
	Atmosphere	1. Decomposition of methyl halides, sea salt derived particles and CFC substitutes

It is clear that many factors will lead to changes in solar UV radiation reaching Earth's surface (Chapter 1). To briefly summarize, after a period of several decades when depletion of stratospheric ozone led to increases in UV-B radiation, the remainder of this century is expected to be a period of ozone recovery with the concentration of ozone in some regions greater than present in 1980. As a result, by the end of the century UV-B irradiances likely will be at or below those measured prior to the onset of ozone depletion, by around 5-15% in the mid-latitudes and perhaps up to 20% at high and polar latitudes. The tropics will be little affected by these changes in ozone. In addition, UV exposure in the biosphere will be affected by changes in cloud and aerosols. The current assessment of the effects of climate change on cloudiness highlights the large variation in change in different locations (Chapter 1). At low latitudes, cloud cover is predicted to decrease, which should result in increases in UV radiation compared to the present. At high latitudes, cloud cover is predicted to increase substantially (up to 4% compared with the 1950-2000 mean see Chapter 1), which will further enhance the decrease in UV-B radiation due to increases in stratospheric ozone. The projected decreases in UV-B radiation are larger in high latitude regions of the southern hemisphere than in the northern hemisphere.

This Chapter assesses the state of knowledge of the responses of global biogeochemical cycles to interactions between changes in UV radiation and other co-occurring environmental changes in climate, land use, and atmospheric CO₂. These interactions are varied and complex. Many interactions occur through the effects of different elements of environmental

change on living organisms. These effects and their consequences for biodiversity and the functioning of terrestrial and aquatic ecosystems, have been assessed by others (see Chapters 3 and 4). Here we will consider how the changes in individual organisms and ecosystems considered by these other authors affect biogeochemical cycling, and also how changes in cycling may feed back to the biology of organisms and ecosystems. We will also consider interactions of element cycling with environmental changes that are mediated through chemical, photochemical and physical processes in aquatic and terrestrial ecosystems. One focus will be the assessment of effects of these changes in aquatic and terrestrial biogeochemistry on the atmospheric concentrations of trace gases and aerosols that influence the radiative balance and chemistry of the atmosphere. Particular emphasis is put on the advances in understanding of these interactions that have occurred since the last quadrennial assessment.²³² Later in this assessment we address future changes in biogeochemical cycles that may occur in response to projected changes in climate and stratospheric ozone.

The key role of carbon in regulating climate through the atmospheric concentration of carbon dioxide (CO₂) places the carbon cycle at the heart of any consideration of biogeochemical cycles in the context of environmental change. The degree to which any factor influences the energy balance of the Earth-atmosphere system, and hence climate, can be expressed in terms of radiative forcing (RF).⁷⁰ The increasing concentration of CO₂ in the atmosphere is a major driver for human-induced climate change, with the most recent IPCC report⁷⁰ estimating its RF as $1.66 \pm 0.17 \text{ W m}^{-2}$, far higher than any other factor (Table 5-2). Radiative forcing can also be used to assess the effect of other changes affected by altered biogeochemical cycling. For example, methane is also a potent greenhouse gas (Table 5-2) and carbon monoxide and volatile organic compounds exert indirect effects on radiative forcing through their effects on chemical processes that influence ozone, aerosol and cloud properties in the troposphere (Table 5-2). There is increasing evidence that aerosols and clouds play a multi-faceted role in the interactions of biogeochemical cycles with changes in climate and ozone. Changes in the properties and distribution of clouds and aerosols are likely to result in changes in UV radiation reaching the Earth's surface that for many parts of the globe are at least as great as those caused by ozone recovery (Chapter 1). However, the effects of such changes in UV radiation on the components of biogeochemical cycling remain poorly understood.

Table 5-2. Links between biogeochemical cycling, climate and stratospheric ozone changes, expressed as the radiative forcing of different factors. Radiative forcing is the degree to which any factor influences the energy balance of the Earth-atmosphere system, and hence climate and the values here are derived from the most recent IPCC report.⁷⁰ Note that the inherent time scales of the different links vary significantly.

Element of change	IPCC ⁷⁰ estimate of radiative forcing (W m ⁻²)	Links with stratospheric ozone change and changing UV radiation
Carbon dioxide (CO ₂)	$+1.66 \pm 0.17$	Directly affected by the effects of changing UV radiation on the balance of carbon uptake and loss from terrestrial and aquatic ecosystems
Methane (CH ₄)	$+0.48 \pm 0.05$	Production from plants may be driven by exposure to UV radiation and main sink in troposphere involves reaction with OH radicals that are produced by UV-induced reactions
Tropospheric ozone (O ₃)	$+0.35$	Tropospheric chemistry influenced directly by UV radiation, and by concentrations of VOCs and NO _x , which are affected by UV radiation (Chapter 6).
Montreal Protocol gases	$+0.32 \pm 0.03$	Now declining due to implementation of the Montreal Protocol (Chapter 1). Naturally-produced halogen compounds from ter-

Element of change	IPCC ⁷⁰ estimate of radiative forcing (W m ⁻²)	Links with stratospheric ozone change and changing UV radiation
Nitrous oxide (N ₂ O)	+0.16 ± 0.02	restrial and aquatic ecosystems may be affected by climate change. Both a greenhouse gas and precursor to N species that deplete stratospheric ozone.
Carbon monoxide	+0.04	Indirectly affects climate by modulating the OH concentrations in the atmosphere and thus concentrations of methane, ozone and other GHGs
Stratospheric ozone (O ₃)	-0.05 ± 0.10	See Chapter 1.
Total aerosols	-0.5 ± 0.4	Affected indirectly by changing UV radiation through effects on volatile organic compounds (VOCs), dimethylsulphide (DMS) and other trace gases (see Chapter 1).
Clouds	-0.7	Affected indirectly by changing UV radiation through effects on volatile organic compounds (VOCs), dimethylsulphide (DMS) and other trace gases (see Chapter 1).

Solar UV radiation may also affect the nitrogen and sulphur cycles that can directly affect climate through changes in concentrations of atmospheric trace gases such as nitrous oxide, NO_x (NO plus NO₂) and dimethylsulphide (DMS). NO_x and DMS influence atmospheric chemistry and cloud formation, and hence radiative forcing (See Table 5-2). Changes in the concentration of NO_x and halogenated compounds have a specific relevance to this assessment, since these compounds have the potential to deplete atmospheric ozone, and their production by both terrestrial and aquatic systems is influenced by climate change and by UV radiation itself (Chapter 1). Nitrous oxide is not only an important greenhouse gas but it also plays a dominant role in chemical reactions that deplete stratospheric ozone.¹⁶⁶ The cycles of many metals have widespread biological importance as they can act as essential nutrients or significant toxins depending on their chemical form and availability, and are affected by UV radiation.

This Chapter specifically addresses and highlights the emerging understanding of the complex interplay between the physical, biological and chemical ramifications of climate change, with co-occurring increases in greenhouse gases, shifting patterns of atmospheric ozone concentrations and UV radiation changes in the atmosphere and Earth's surface.

Combined effects of changes in solar UV radiation and climate on the carbon cycle

Of the ~10 petagrams (Pg) of carbon per year (number based on 2008, 1 Pg = 10¹⁵ g) that are emitted into the atmosphere by human activities (fossil fuel burning, land-use change), ca 30% are taken up by terrestrial ecosystems, 25% by the ocean, and the remaining 45% (often referred to as the "airborne fraction") accumulates in the atmosphere.^{31, 70, 107, 112} Ecosystems are net CO₂ sinks on a global average but some regions are net CO₂ sinks and others net sources.^{69, 84, 162} A recent analysis indicates that the airborne fraction has likely increased from 40% to 45% during the past 50 years¹¹² due to reductions in terrestrial and oceanic sinks caused by climate change, stratospheric ozone depletion and other environmental changes.^{41, 113, 160, 201, 202} Decreasing sink strengths of terrestrial and aquatic ecosystems cause positive feedbacks that amplify the growth of atmospheric CO₂ and accelerate future climate warming.^{41, 75, 124, 125, 235} For example, fire was found to be a primary disturbance that changes terrestrial ecosystems from carbon sinks to sources.⁷

Terrestrial ecosystems

In terrestrial ecosystems, carbon fixed by plants may be sequestered in timber or long-lived soil components such as peat. Such carbon sequestration is a significant element of the global carbon budget, and may be affected by various elements of climate change, and by direct interventions to mitigate climate change, such as afforestation. UV-B radiation has the potential to affect many aspects of the growth, development and function of terrestrial ecosystems. The magnitude of such effects varies between species, and these variable effects have been shown to cause local changes in the species-composition of terrestrial ecosystems, especially at high latitudes.^{30, 232} UV radiation can also affect the decomposer organisms that control carbon release from plant litter (dead organic material that falls to the ground) and soils. Decomposition is controlled by many climate-sensitive physical and biological parameters. Among the most important are temperature, soil moisture and the chemistry of the plant litter. UV-B exposure affects the chemistry of living leaves and these changes are often inherited by litter, although effects are highly species specific and this is reflected in changes in decomposition. However, given (i) the expected slow recovery in stratospheric ozone (Chapter 1) and magnitude of the effects of increases in UV-B radiation even in high latitude terrestrial ecosystems and (ii) the contribution of these high latitude terrestrial ecosystems to global carbon uptake, it is unlikely that these direct effects of stratospheric ozone recovery will have a significant effect on global carbon fixation. However, changes in UV exposure mediated by responses to climate change may result in far more widespread effects. For example, UV-induced photodegradation of above-ground plant litter is important in arid terrestrial ecosystems (see Chapter 3 and refs^{5, 25, 91, 232}) and is likely to become a much more significant global pathway for terrestrial organic matter decomposition in the future. Photochemical production of trace gases such as methane and carbon monoxide may also increase in such systems.

Stratospheric ozone, cloud, and factors such as aerosols and surface albedo (Chapter 1) affect UV irradiance incident on terrestrial ecosystems, but changes in ecosystems due to climate change and altered land use will further affect penetration of UV radiation into vegetation and to the soil surface. The balance of evidence from climate models is that soil moisture will decline in most parts of the globe as a result of changes in both precipitation and evaporation.⁶⁸ The effects of these future changes in climate on the vegetation cover of specific regions remains somewhat controversial. However, for most low-mid latitude systems, the most likely changes in plant communities, such as declines in woodland or reduced vegetation cover (Fig. 5-1), are expected to result in increased penetration of solar UV radiation into and through the canopy. Changes in land use and management can also lead to increased UV penetration to the ground, for example, increased grazing,⁷⁹ felling of woodland,⁹⁸ and shrub invasion in arid systems.²⁰³ More open ecosystems can also enhance soil surface temperatures and this enhancement can stimulate soil to atmosphere movement of nitrogen and presumably loss of productivity in the affected ecosystems.¹²⁹ In addition, the prediction of increased aridity over large areas at low latitudes is expected to enhance the contribution of direct photochemical effects of UV radiation to carbon and nutrient cycling (see above). By contrast, at northern high latitudes, projected gains in forest, woodland and shrub communities (Fig. 5-1) will reduce UV penetration into and through the canopy.

A further factor that will alter UV exposure in terrestrial ecosystems is the changing geographical distribution of those ecosystems that will result from climate change. Current models project major changes in global ecosystems in response to climatic and social changes,^{7, 35, 40-42, 120, 174} and one such change is that vegetation zones will move towards the poles as temperatures increase. As vegetation zones shift from their current range of distribution towards the poles, they will experience the lower mean annual UV doses

associated with lower solar elevation. This latitudinal shift, like that of ozone depletion, is more pronounced at shorter wavelengths and as a result, the effect of changes towards the poles will be greater for responses with action spectra that are more strongly biased towards shorter wavelengths (Chapter 1).

In summary, at low-mid latitudes in terrestrial systems, projected changes in stratospheric ozone are small, but predicted decreases in cloud, increased aridity and reduced cover are all expected to lead to increased UV irradiances within canopies and at the soil surface. By contrast, at high latitudes recovery of stratospheric ozone, decreased albedo, increased cloud, increased vegetation cover and shifts in biomes towards the poles will all lead to negative trends in UV irradiances for organisms within canopies and at the soil surface. Changes in UV-B radiation both positive and negative can result in significant changes in terrestrial ecosystems, including direct effects on plant growth and biomass (Chapter 3). Current climate

change models predict increases in carbon sequestration by terrestrial ecosystems at northern high latitudes and decreases at low latitudes, and our assessment is that the combined effects of multiple environmental changes on solar UV radiation would be to amplify these predicted changes. However, the magnitude of these changes remains uncertain.

Aquatic ecosystems

Carbon capture by primary producers in the ocean followed by downward flux of the resulting dead algal material provides an important route for carbon sequestration in the oceans referred to as the biological pump.¹⁹⁵ The effects of exposure to UV radiation on primary producers in lakes and the ocean interact with climate-induced damage of primary producers^{12, 72, 86, 113, 115, 133, 185, 233} to reduce CO₂ uptake by the ocean. The exposure of primary producers to the damaging solar UV-B radiation depends on the penetration depth of UV-B radiation into water bodies, which is mainly controlled by the concentration and optical properties of coloured dissolved organic matter (CDOM).^{86, 221, 232, 233}

CDOM is the sunlight-absorbing component of dissolved organic matter (DOM). The presence of CDOM alters the spectrum of radiation penetrating into the water column, in effect decreasing the radiation amplification factor for DNA damage with increasing depth

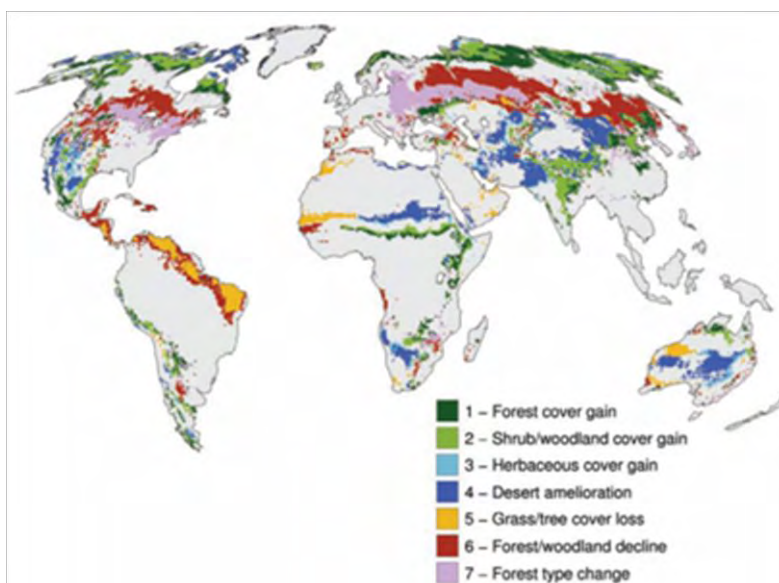


Fig. 5-1. Projected appreciable changes in terrestrial ecosystems by 2100 relative to 2000 as simulated by the Dynamic Global Vegetation / Lund-Potsdam-Jena Model (DGVM LPJ) for two Special Report Emission Scenarios forcing two climate models: (a) Hadley Centre Coupled Model-Version 3 (HadCM3 A2), (b) 5th generation ECAM general circulation model from the Max Planck Institute for Meteorology (ECHAM5 B1). LPJ is a dynamic global simulation model of vegetation biogeography and vegetation/soil biogeochemistry. The simulations assume continued greenhouse gas emissions and land-use change trends at or above current rates. Changes are considered appreciable and are only shown if they exceed 20% of the area of a simulated grid cell (Figure 4.3 of Fischlin et al.⁶⁸).

(Fig. 5-2). However, CDOM is subject to photobleaching,^{37, 38, 44, 45, 82, 89, 90, 139, 140, 148, 155, 161, 171, 177, 199, 210, 221, 233, 234} a process that occurs particularly efficiently in stratified systems.^{37, 44, 148, 199, 232, 233} The increase in CDOM concentrations with increasing latitude (Fig. 5-3) is consistent with decreased rates of photobleaching as surface UV irradiance decreases.^{148, 199} Moreover, the observed vertical distributions of CDOM in the open ocean result from a balance between biogeochemical processes (autochthonous production and solar bleaching) and the overturning circulation.¹⁴⁸ CDOM can be used as a unique tracer for evaluating changes in biogeochemistry and the overturning circulation, similar to dissolved oxygen, with the additional feature that it can be quantified from satellite observation.¹⁴⁸

Analyses of contemporary net fluxes of CO₂ in the ocean indicate that the tropics are net sources of CO₂ to the atmosphere, and both the temperate and circumpolar regions, especially the Southern Ocean, are net sinks.⁸⁴ There is a small net CO₂ sink in the Southern Ocean (south of 44°S) where a substantial outgassing of natural CO₂ almost completely offsets a strong uptake of anthropogenic CO₂. These patterns are in part due to latitudinal changes in net primary productivity.

The patterns of CO₂ fluxes are influenced by interactions between upper ocean mixing dynamics and climate.¹⁴ Vertical stratification of the ocean, which is accompanied by increases in sea surface temperature (SST), results in decreased net primary productivity (Fig. 5-4).¹⁴ The vertical stratification of marine systems is caused by various factors including SST.^{15, 23, 116} For example, the seasonal stratification in a small marine basin is primarily determined by temperature,¹¹⁶ whereas at the annual scale, stratification is determined by salinity rather than temperature, increasing with decreasing salinity. Hence, increasing freshwater discharge into coastal areas due to climate change may increase the extent of stratification in marine systems

Furthermore, ocean stratification has been reported to increase with climate-related increasing strength of El Niño-Southern Ocean Oscillation (ENSO) cycles.¹⁴ Extensive declines in marine phytoplankton concentrations have occurred during the past century and these declines have been attributed in part to increases in oceanic stratification.²³ Increased stratification and sea surface temperatures likely will move towards to poles in the temperate regions during the upcoming century with resulting decreases in marine productivity and oxygen concentrations^{14, 27, 84} and concurrent adverse effects on life in the ocean.²⁷ The projected decreases in productivity will be driven by (1) reduced transport of nutrients from deeper in the ocean to the surface zone where photosynthesis occurs; (2) increased ocean

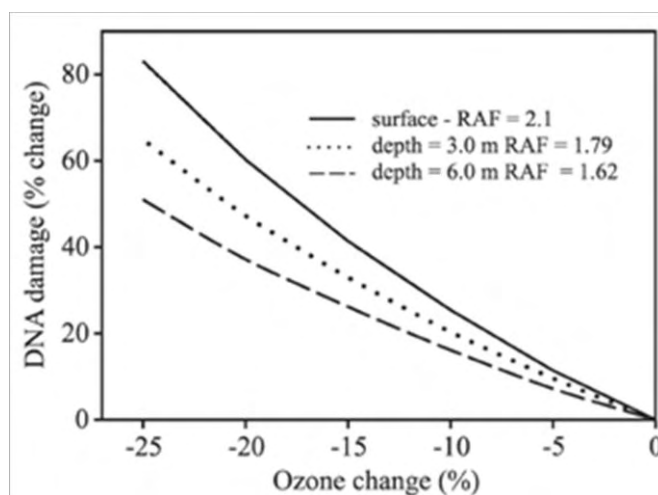


Fig. 5-2. Computed dependence of DNA damage and the associated radiation amplification factors on depletion of total ozone at different depths at Looe Key Reef in Florida, USA.²³³ The action spectrum of Setlow¹⁷⁶ was used in the computation of DNA damage. Dose and radiation amplification factor (RAF) are defined in McKenzie et al.¹³¹ When changes in total column ozone are small, the RAF corresponds to the relative fractional change in effective UV irradiance with fractional change in ozone. The estimated underwater changes in RAF are attributable to depth-dependent changes in absorption of short wavelength solar radiation by CDOM in the water column. [Fig. 10 from Zepp et al.²³³ Copyright (2008) by the American Society of Limnology and Oceanography, Inc., reproduced with permission].

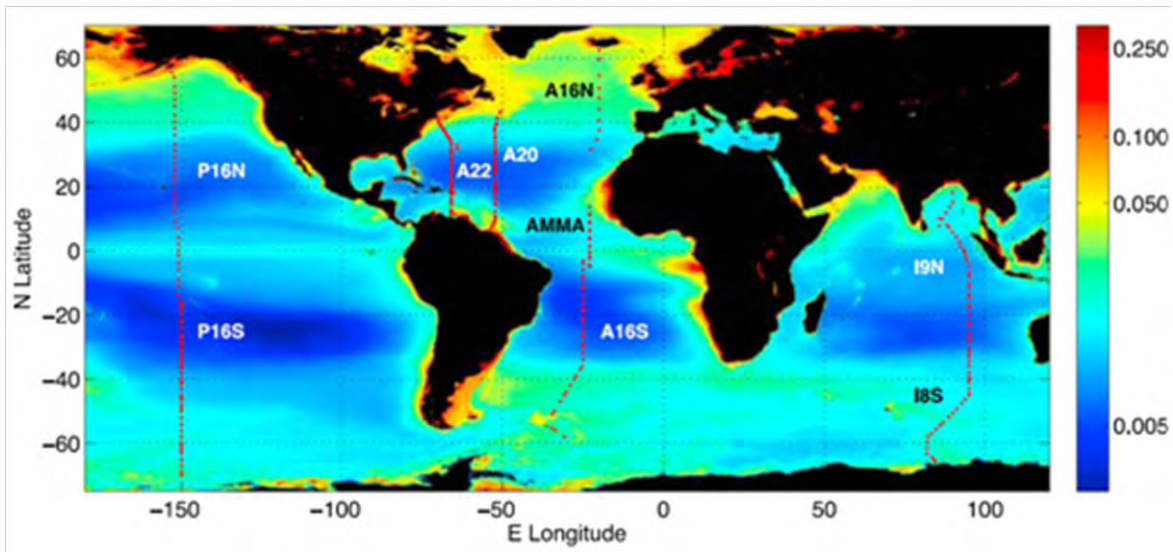


Fig. 5-3. Distribution of CDOM absorption coefficients at 443 nm from satellite ocean colour observations derived from Global System for Mobile Communications (GSM) satellite retrieval of merged SeaWiFS and MODIS Aquadata.^{148, 199} Field observations collected on meridional transects showed that UV absorption coefficients at 325 nm were approximately 10-fold greater than absorption coefficients at 443 nm. The increase in CDOM concentrations towards the poles reflects, in part, decreased photobleaching as surface UV irradiance decreases (Fig. 1 from Nelson et al.¹⁴⁸).

acidification caused by continued increases in CO₂; and (3) increased photodegradation of the UV-protective CDOM coupled with reduced inputs of CDOM from deeper in the ocean to the surface zone. Because CDOM is derived from biological degradation of the detritus from sinking dead phytoplankton, reduced productivity will drive further decreases in CDOM production, thus reinforcing penetration of UV radiation into the ocean. The negative effects of stratification on marine production should be offset somewhat by the reduction in UV-B radiation caused by increases in stratospheric ozone, which will be particularly pronounced in circumpolar regions of Earth. Increased stratification is expected to enhance the photobleaching of CDOM, so increasing the exposure of surface-dwelling organisms to UV-B radiation (see Chapter 4 and refs^{9, 221, 233}).

Increases in vertical stratification also are occurring in freshwater ecosystems. It has been known for some time that seasonal changes in vertical stratification of lakes leads to pronounced changes in CDOM distributions and UV penetration.²³¹

The detrimental effects of UV-B exposure on marine organisms might be partially offset by CO₂ fertilization effects¹⁷⁴ and ocean warming,¹⁴⁵ although increasing CO₂ concentration has been shown to enhance the sensitivity of some algal

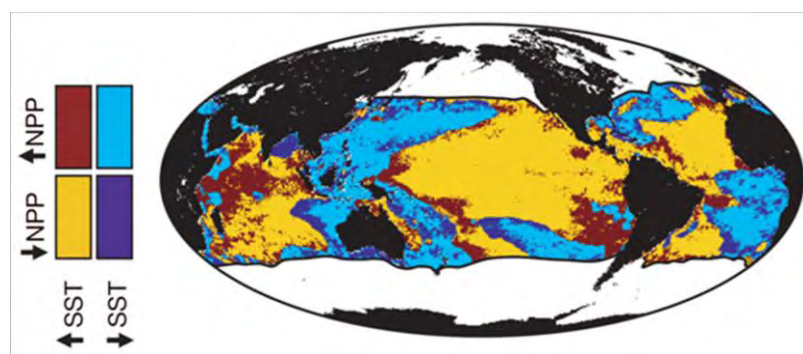


Fig. 5-4. Relationships between changes in sea surface temperatures (SST) and net primary productivity (NPP) in the ocean for the warming period from 1999 to 2004. Yellow, increase in SST, decrease in NPP. Light blue, decrease in SST, and increase in NPP. Dark blue, decreases in SST and NPP. Dark red, increases in SST and NPP (adapted from Figure 3(c) in Behrenfeld et al., 2006¹⁴; Copyright 2010 by Nature Publishing Group license no. 2531680927098, reproduced with permission).

species to UV-B radiation.^{12, 185} The effects of CO₂ may be a result of its effects on pH in aquatic systems, rather than on direct effects of CO₂ itself.

Ocean acidification (caused by the increasing absorption of human-derived CO₂ by seawater^{11, 70, 230} and to a smaller extent by atmospheric deposition of acidity¹¹ and increased vertical stratification²⁷) also attenuates oceanic CO₂ uptake by reducing the ability of calcifying marine organisms, including corals, to produce calcareous skeletal structures.^{27, 49, 61, 64, 76, 87, 94} Evidence exists that acidification may enhance the damaging effect of solar UV radiation on both photosynthesis and calcification.⁷⁶ Corals are also vulnerable to ocean warming,^{3, 33, 94, 170} and the adverse effects of solar UV radiation on corals are related to their increased susceptibility to UV damage with warming.⁶⁷ These changes combine to decrease the CO₂ buffer capacity of marine systems.^{55, 56, 61, 189, 202, 230} Furthermore, ocean acidification has been shown to decrease the availability of dissolved iron to phytoplankton as a result of decreasing efficiency of the enzymatic reduction of strongly bound Fe(III) species with decreasing pH.¹⁸¹ Since iron is an essential micronutrient, a decrease in iron bioavailability may decrease the uptake of CO₂ by oceanic phytoplankton. This negative effect of ocean acidification on iron bioavailability may be compensated in part by UV-induced reactions involving strongly bound iron species.¹⁹⁵

The combined effects of stratospheric ozone depletion and climate change affect the CO₂ sink strength of the oceans also via changing winds and ocean circulation changes.^{84, 113, 118, 205, 235} This effect is particularly pronounced in the Southern Ocean where increased greenhouse gas concentrations in conjunction with stratospheric ozone depletion results in an increased shift of the westerly winds toward the poles, i.e., an upward trend of the Southern Annular Mode (SAM).^{113, 118} As a consequence, enhanced wind-driven ventilation of carbon-rich deep water occurs in this region resulting in a reduced atmosphere-ocean gradient of CO₂.^{84, 113, 118} In addition to this effect, inhibition of photosynthesis caused by enhanced solar UV-B radiation associated with stratospheric ozone depletion (Chapter 1) also contributes to reduced CO₂ uptake in this region.⁷² A decrease in the CO₂ sink strength of the Southern Ocean is serious, since CO₂ uptake by the Southern Ocean accounts for >40% of the total annual oceanic CO₂ uptake.^{84, 113, 118}

The CO₂ source strength of aquatic systems may, on the other hand, increase, due to combined effects of solar UV radiation and climate change on carbon cycling. Climate-related changes in continental hydrological cycles, for example, amplification of precipitation extremes², as well as land-use changes,¹¹² are likely to increase the input of organic carbon into streams, rivers and lakes (Fig. 5-5).^{1, 6, 81, 93, 114, 211, 218} CDOM concentrations in high latitude lakes of the Northern Hemisphere may be enhanced by this increased runoff of CDOM into lakes and rivers from surrounding areas

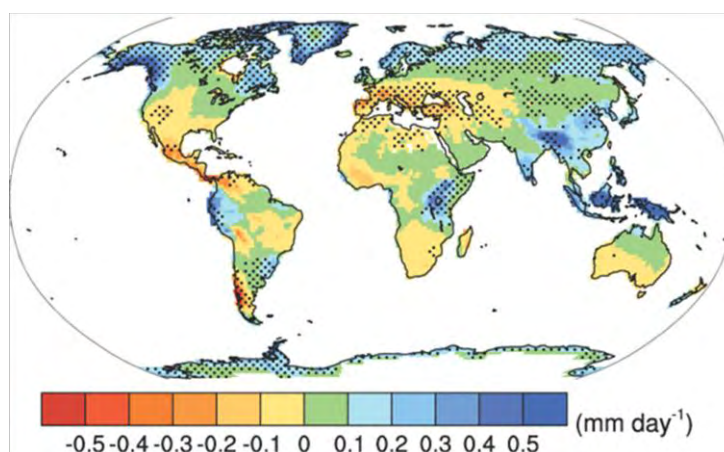


Fig. 5-5. Multi-model mean changes in runoff (mm day⁻¹) for the IPCC Special Report Emission Scenarios A1B (balanced) for the period 2080 to 2099 relative to 1980 to 1999 (see <http://www.ipcc.ch/pdf/special-reports/spm/sres-en.pdf>). Changes are annual means for this scenario. Runoff changes are shown at land points with valid data from at least 10 models (Figure 10.12(c) in Meehl et al.¹³⁴).

caused by warming, melting of ice and snow cover, and precipitation changes. Enhanced export of organic carbon from terrestrial to marine systems is a likely consequence of these changes.^{108, 187, 213, 218} Runoff is projected to be particularly pronounced in the circumpolar regions of the Northern Hemisphere where large stocks of organic carbon are stored (Fig. 5-5). The net result will be increased release of soil organic carbon, including CDOM, in circumpolar regions into streams and rivers and increased continental runoff of the CDOM will occur. Thus mobilized, the CDOM will be much more susceptible to UV-induced photodegradation to CO₂ and other trace gases.

The organic carbon that runs off into aquatic systems likely will be substantially decomposed by several processes, including those initiated by solar UV radiation. Terrestrially derived DOM exhibits a higher photoreactivity than DOM derived from aquatic microbial sources because of differences in chemical composition.^{18, 38, 80, 99, 139, 140, 154, 155, 171, 191, 194, 208} Photochemically reactive DOM is subject to UV-induced transformations^{81, 99, 161, 210, 212} that enhance DOM bioavailability to heterotrophic bacteria^{81, 99, 161, 210, 218} and, in turn, microbial respiration with production of CO₂ and consumption of O₂.^{210, 213} Mineralization of DOM also occurs as a purely abiotic, UV-induced process.^{16, 127, 139, 140, 171, 212, 227, 229} Photoreactions driven by solar UV radiation also release DOM from sediments.^{128, 169} The rate of UV-induced DOM transformations and mineralization is likely to increase as a consequence of enhanced stratification and acidification of aquatic systems.^{37, 44, 212, 232, 233}

Effects involving interactions between solar UV radiation and climate change on nutrient cycling

The combined effects of solar UV radiation and climate change can affect the concentration and biological availability of major nutrients and of essential metals, which determine, in part, the rate of photosynthesis by terrestrial plants and phytoplankton. We focus on nitrogen in its various chemical forms since nitrogen is one of the key nutrients in terrestrial and aquatic ecosystems.⁴⁷ With regard to essential metals, we concentrate on the effects of solar UV radiation and climate change on iron bioavailability, since iron is required for biological photosynthesis and N₂ fixation by phytoplankton.²²⁸

Nitrogen inputs

In the case of terrestrial ecosystems, the effects of UV-B radiation on biological nitrogen fixation are variable, both for fixation by free-living microbes and for those in symbiosis with higher plants, such as legumes.²³² There is evidence that UV-B radiation can affect nitrogen-fixation in legumes and by cyanobacteria (free living or in symbiotic relationships with plants such as algae and lichens),^{51, 52, 232} but we are unaware of any recent research into this effect. Anthropogenic nitrogen inputs are increasingly important in many terrestrial systems as fertilizers in managed ecosystems,⁷⁴ and more generally from nitrogenous air pollutants. However, interactions between these changing nitrogen inputs and changing solar UV radiation remain poorly understood (Chapter 3).

A substantial part of the ocean (67% - 75%) has been estimated to be limited by nitrogen⁵⁹, particularly by nitrate (NO₃⁻).⁴⁷ However, limitation of phytoplankton photosynthesis by nitrate is predicted to increase because of climate-related increase in low- and mid-latitude regions in bacterial denitrification and increases in thermal stratification of marine systems that reduce delivery of nutrients from deeper water layers into the surface layer where photosynthesis occurs.^{27, 48, 116} As a result, the ability of phytoplankton to take up N₂ may become increasingly important.^{53, 142} Nitrogen fixation in the ocean is inhibited by exposure to UV radiation through damage to N₂-fixing organisms.⁸⁶ Therefore, atmospheric

changes that affect solar UV radiation and changes in upper ocean CDOM (discussed earlier) that affect UV penetration into the ocean are likely to be linked to changes in oceanic N₂ fixation. Nitrogen derived from riverine inputs and atmospheric deposition is an important and increasing source of nitrogen for organisms in the ocean.^{59, 74}

Some oceanic areas, the so-called high-nutrient, low-chlorophyll regions, are co-limited by trace metals, particularly iron, which is required for N₂ fixation by phytoplankton.²²⁸ Precipitation^{13, 105, 219} and deposition of continental dust¹⁹⁵ are important natural sources of iron to the ocean that are sensitive to climate change. However, not all chemical forms of iron are available to phytoplankton. It is likely that weakly bound, dissolved Fe(III) is highly bioavailable.¹⁴⁶ For the formation of weakly bound Fe(III) under seawater conditions, Fe(II) is a key intermediate species. Important pathways of Fe(II) formation are UV-induced reactions of iron oxides^{21, 73} and of dissolved Fe(III) species.^{10, 62, 101, 219} In addition, strongly bound Fe(III) species can be reduced to Fe(II) by enzymatic reactions, the efficiency of which has been shown to decrease with decreasing pH.²³⁰ Hence, while solar UV radiation generally increases iron bioavailability, effects of climate change such as ocean acidification may have the opposite effect.

Nutrient release by decomposition

The effects of UV-B radiation on litter decomposition in terrestrial ecosystems are complex, involving direct effects of photochemical degradation and indirect biological effects on decomposer organisms (Chapter 4). Extending this to the release of nutrients from decomposing litter is difficult, as there are very few studies that have directly evaluated the effects of UV radiation on litter nutrient release. However, several recent studies on photodegradation in semi-arid ecosystems have shown that litter exposed to UV radiation demonstrated reduced N immobilization^{26, 184} or no N immobilization in semi-arid ecosystems independent of direct UV effects.^{24, 158} It is currently not clear whether these effects are biotically or abiotically driven, but the effects do suggest that the lack of immobilization of nitrogen may result in increased N losses over the longer term, affecting carbon-nitrogen interactions in these ecosystems. As climate change may lead to increases in arid zones which could increase the relative importance of photodegradation, it appears that there may be an impact on nitrogen dynamics as well as on the demonstrated effects on carbon litter quality.⁴

In contrast, dissolved organic nitrogen (DON) is one of the important constituents of N from continental runoff and atmospheric deposition, and UV-induced photoammonification of this DON can be an important and increasing source of biologically available N.^{209, 232} As discussed earlier, there is substantial evidence that productivity has been decreasing in the mid-latitudes and has been very low in the tropics for some time. Thus, although inputs of nitrogen, including DON, from land can stimulate productivity and release of important greenhouse gases such as nitrous oxide in coastal regions of the ocean (Fig. 5-7 and related discussion below), it is clear that reduction of nutrient upwelling in the open ocean has had and will continue to have a much larger effect on reducing productivity on a global basis.

Loss of nutrients

Biological processes convert the reactive nitrogen in terrestrial systems into gases such as ammonium, nitric oxide and nitrous oxide. Ecosystem-atmosphere exchange of these gases is discussed in more detail later in the assessment.

Abiotic processes that are affected by climate change also contribute to nutrient loss. In arid ecosystems, such as deserts, abiotic processes accelerate the flux of nitrogen from the land surface to the atmosphere.¹²⁹ The high soil-surface temperatures (greater than 50°C),

driven by solar radiation in open ecosystems, were a significant cause of abiotic nitrogen loss in Mojave Desert soils. Other studies that were assessed in our last quadrennial report^{5, 232} indicated that solar UV radiation was involved in the decomposition of plant litter in other arid ecosystems and thus UV radiation also may play a role in nitrogen loss under such conditions (see above). Photodegradation of the lignin content of litter may enhance its biological lability for decomposers (Chapter 3). Fires, leaching and runoff are other important pathways for nutrient loss from terrestrial ecosystems that are affected by climate change.⁷

Combined effects of solar UV radiation and climate change on the biogeochemistry of trace gases and aerosols

In addition to carbon dioxide, terrestrial and aquatic ecosystems are sources and sinks of aerosols and trace gases such as methane, nitrogen oxides, nitrous oxide, halogens, and sulphur compounds (Tables 5-1 and 5-2). Climate change affects the emissions of trace gases from terrestrial and aquatic ecosystems and the formation of aerosols, but also the removal of aerosols by rainfall. These effects of climate change will interact with those of solar UV radiation to alter the spatial distribution and net exchange of trace gases and aerosols, which in turn affect solar UV radiation and climate.

Methane

Of the long-lived greenhouse gases, methane (CH₄) produces the second highest radiative forcing after CO₂ (Table 5-2).⁷⁰ As with CO₂, the atmospheric concentration of methane in recent decades is the highest ever¹¹⁷ and these increases can be attributed to a number of human activities.⁷⁰ However, unlike the continuing, well-defined and well-understood increase in CO₂, the processes driving changes in methane concentrations remain relatively poorly understood. For example the known sources of methane appear to underestimate methane produced in the tropics.^{17, 54, 138} The influence of UV-B radiation on methane budgets has been the subject of considerable research since our last assessment, due to the discovery of a new source of methane production from terrestrial plants.¹⁰²

Terrestrial ecosystems have long been known to be a major natural source of methane, but production was thought to be confined to wetlands where plants were growing in poorly-aerated, water-saturated soils with very low oxygen concentrations. We reported previously that increased UV-B irradiance could reduce emissions of methane from peatland ecosystems and paddy fields, and this was partly explained by changes in plant morphology that affected the movement of methane from the soil to the atmosphere.¹⁴⁹ However, the observation of Keppler and colleagues¹⁰² that methane could be produced by plants growing in well-aerated soils (i.e. aerobic conditions), and that the rate of production was much greater in sunlight than in the dark, has led to considerable discussion of both the contribution of terrestrial vegetation to global methane production and the role of UV-B radiation.

The observation of methane production from plants grown in aerobic conditions has proved to be highly controversial,^{65, 66, 95, 96, 106, 173, 179} partly because not all studies have been able to detect aerobic methane production under laboratory conditions.^{13, 60} However, there is now good evidence that this is a photochemical process brought about by previously undefined chemical reactions occurring in plant cell walls.^{103, 137, 179} Despite the improved understanding of the underlying processes, the contribution of aerobic methane production from terrestrial vegetation to global methane remains unclear. Measurements of the exchange of methane between the atmosphere and terrestrial ecosystems other than wetlands are variable and some are sinks of methane rather than sources.^{22, 32, 135} Calculations to scale-up from la-

laboratory measurements of aerobic methane production to estimate its contribution to global methane budgets are also extremely variable, and while early estimates suggested a substantial role,¹⁰² the current balance of evidence suggests a rather minor contribution compared with other sources.^{20, 106, 150} For example, a recent study concluded that aerobic emissions of methane from UV irradiation of plants corresponded to <0.2% of total global methane sources (Fig. 5-6).²⁰ This conclusion was based on modelled estimates that used an action spectrum for photoproduction of methane from pectin,¹³² a common component of plant leaves. We agree with the recent review¹⁵⁰ that quantification of all sources of methane is important in setting global methane inventories, and this should include assessment of the roles of terrestrial plants.

Carbon monoxide

The carbon monoxide (CO) concentration in the troposphere has important effects on atmospheric composition through its effects on hydroxyl radical ($\bullet\text{OH}$) concentration (Chapter 6). CO makes a small direct contribution to radiative forcing (Table 5-2) but calculations taking into account its interactions with aerosols result in substantial increases in its estimated role in radiative forcing.¹⁸² Natural sources have been estimated to account for up to half of global CO emissions,⁷⁰ and of these, wildfires, especially their smouldering phase, are an important source that is increasing with climate change. Carbon monoxide is one of the main trace gases derived from UV-induced photochemical reactions of living and non-living organic matter in terrestrial and aquatic ecosystems. The projected global increases in open, arid ecosystems also will likely enhance this terrestrial source of CO. It is well-established that plant litter from a variety of species can photochemically produce CO.²³² A number of recent studies have confirmed that the photoproduction of carbon monoxide in the ocean and freshwaters is primarily linked to CDOM photoreactions, although particulate organic matter also can photoproduce CO.^{83, 227} Several recent studies have indicated that CO photoproduction in the ocean is approximately balanced by microbial consumption,^{144, 192, 193, 226, 229} although microbial uptake is somewhat less important in northern waters²²⁶ and can be photoinhibited during daytime.²⁰⁶ CO is a reactive gas that has important effects on chemical reactions in the marine boundary layer and photoproduction of CO from CDOM may be its dominant source in remote areas of the ocean.²³²

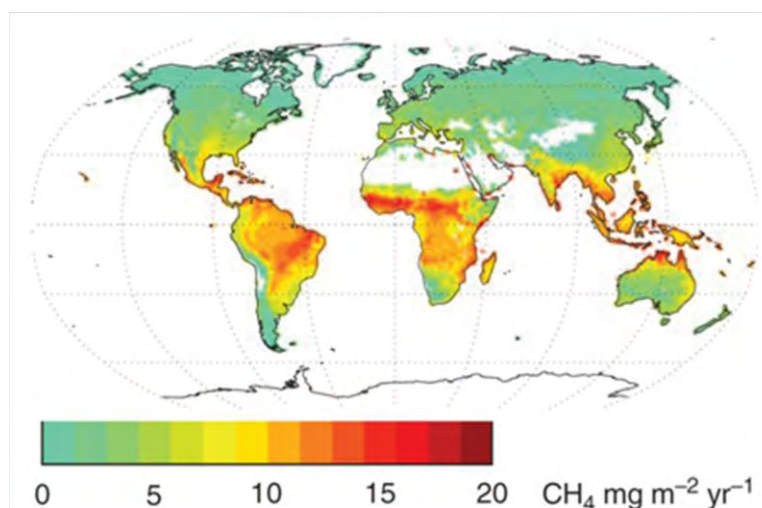


Fig. 5-6. Estimated total annual aerobic methane production induced by solar UV irradiation of plant foliage (adopted from Bloom et al.²⁰). The action spectrum for methane production used for this modelling simulation was obtained from McLeod et al.¹³² The global distribution for methane production from this source was estimated based on spectrally weighted global UV irradiance, Moderate Resolution Image Spectroradiometer (MODIS) leaf area index (LAI), and air temperature at 2 m (© 2010 by John Wiley and Sons, Inc.; license no. 2523120844682, reproduced with permission).

Nitrogen compounds

Ecosystem-atmosphere exchange of reactive nitrogen (ammonium and nitrogen oxide gases) is influenced by UV-B radiation and climate change.^{30, 88, 232} A number of human activities introduce reactive nitrogen into ecosystems⁷⁴ and direct uptake by terrestrial vegetation is one important sink for these compounds.¹⁸⁶ Nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$) are a class of reactive trace gases that strongly influence atmospheric chemistry including the formation of ozone and aerosols. An earlier study had shown that solar UV-B radiation could directly cause the release of NO_x from plant shoots by photodegrading nitrate or nitric acid on the leaf surface.¹⁶³ A recent report has provided additional evidence that there is an exchange of NO_x between the plants and the atmosphere that depends on UV irradiance and climatic factors such as periods of drought.¹⁶⁴

Nitrous oxide (N_2O) is an important greenhouse and ozone-depleting gas (Table 5-2) and its atmospheric concentration is rising. The bulk of emissions come from natural sources and the remainder from human activities, especially agricultural practices.²²⁵ Nitrous oxide and other greenhouse gases could be an unintended by-product of the agricultural production of biofuels.^{43, 135} The oceans are another important source of nitrous oxide to the atmosphere and increasing inputs of reactive N into the oceans likely will enhance marine nitrous oxide emissions.⁵⁹ Oxygen depletion in the ocean, coupled with increased inputs of reactive nitrogen from rivers and the atmosphere, will lead to changes in nitrogen cycling that will result in increased production and release of nitrous oxide that will further increase global warming as well as stratospheric ozone depletion (Fig. 5-7).³⁹ As CFC emissions drop in response to compliance to the Montreal Protocol, the importance of nitrous oxide as an ozone depleting substance (ODS) will escalate throughout the 21st century.¹⁶⁶ Thus, although changes in UV radiation at the Earth's surface may not directly affect processes that influence nitrous oxide emissions, nitrous oxide production likely will be affected by perturbations of other biogeochemical cycles that are linked to nitrogen cycling.

Halogen compounds

Naturally-produced halogen compounds (CHBr_3 , CH_2Br_2 , CH_3I , CH_3Cl , and CH_3Br) influence atmospheric ozone depletion. South American forests are the major global source of methyl chloride (CH_3Cl) but not methyl bromide (CH_3Br),⁷⁷ while temperate woodland ecosystems are a net source of CH_3Br .⁵⁷ The Arctic tundra is a regional sink for both CH_3Br and CH_3Cl .²⁰⁰

Coastal vegetation may be net sources of methyl halides,^{58, 121, 122, 167} or net sinks.^{214, 215} Even within individual ecosystems, methyl halide fluxes vary depending, for example, on weather, the extent of flooding, and the removal of vegetation.^{58, 121, 167, 214, 215} Soil fungi have been confirmed as potential sources of methyl halides.⁸ Climate change may affect halocarbon budgets from terrestrial systems through warming and decreasing soil

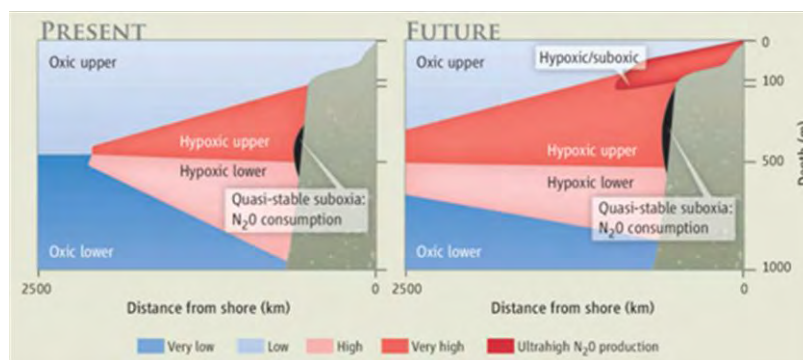


Fig. 5-7. Conceptualization of future changes in hypoxic regions of the ocean that may lead to enhanced nitrous oxide emissions to the atmosphere, especially from coastal regions. Climate changes are forecasted to increase hypoxia in the upper layers of the coastal ocean. The resulting oxygen-depleted waters have favourable conditions for high production of nitrous oxide (From L. A. Codispoti, Interesting times for marine N_2O , *Science*, 2010, 327, 1339-1340. Reprinted with permission from AAAS).

moisture.^{200, 223} Also agriculture and horticulture remain significant sources of methyl bromide, which has been used as a soil fumigant, but recent research has demonstrated the efficacy of a number of alternative technologies that may ultimately replace methyl bromide.^{71, 78, 97, 172}

Marine ecosystems, particularly tropical oceanic regions, are also important sources of halogen compounds, above all bromoform (CHBr_3), that are released from phytoplankton.^{29, 34, 100, 157} In polar marine regions, e.g. the Southern Ocean, emissions of halocarbons are in part due to halocarbon production by ice algae liberated from the sea ice,³⁴ a process that may be enhanced over the short term by accelerated sea-ice melting. Methyl chloride (CH_3Cl) has been increasing over the South Pole in response to climate change²²⁰ and possibly to UV-induced photoreactions involving chloride and CDOM.¹⁴³ Increased stratification may reduce outgassing of bromoform by limiting mixing between the surface and the subsurface layer where maximum concentrations are located.⁹² Climate change-related increased emissions of halocarbons from terrestrial and aquatic ecosystems and reactions of chlorine- and bromine- monoxide radicals, formed in UV-induced processes, with stratospheric ozone and trace gases such as DMS²⁹ could contribute to UV-mediated, positive feedbacks to climate change.

Aerosols

Atmospheric aerosols play a major role in local air quality and the global radiation budget.^{147, 182} An interesting link between climate change and UV radiation is the interactions of the physical climate system with aerosols, for example, due to rainfall and other precipitation that removes aerosols from the atmosphere. A newly identified feedback is the interactions between the physical climate system and biogeochemistry. An excellent example is that as CO_2 increases, there are changes in the hydrologic cycle (i.e. the regional distribution and timing of precipitation) that alters the distributions of aerosols and gases. The attenuation of sunlight by aerosols and clouds represents another mostly overlooked interaction between climate change, stratospheric ozone depletion and UV radiation, since light attenuation by these substances affects UV radiation as well as longer wavelengths. As a result, changes in clouds and aerosols are likely to result in changes in UV radiation reaching Earth's surface that for many parts of the globe are at least as great as those caused by ozone depletion (Chapter 1).

Changes in UV radiation may affect phytoplankton emissions of sulphur compounds and hydrocarbons that form aerosols that, in turn, affect clouds over the ocean. DMS is the major source of volatile sulphur to the marine atmosphere. UV-B radiation plays a major role in the cycling of DMS and related compounds both in polar⁵⁰ and temperate oceans.¹⁹⁶ DMS concentrations in the sub-polar and sub-tropical North Pacific have increased linearly between 1970 and 2000 with a concomitant increase of the DMS flux from sea to air.²¹⁶ Melting sea ice can release substantial quantities of DMS, leading to elevated concentration of DMS in seawater,²⁰⁷ and this input would be expected to increase due to climate change. The effects of changing UV radiation on DMS are likely to be complex. Both UV radiation and nitrogen limitation have enhanced the algal metabolism that produces DMS.^{183, 197} On the other hand, UV exposure can reduce nitrogen limitation in surface waters,^{188, 209} and this process may decrease algal DMS production. Furthermore, photolysis of DMS is an important sink of DMS in the upper ocean.^{104, 232}

Volatile organic compounds (VOCs) produced by terrestrial plants can contribute to aerosol production.^{110, 136} The effects of UV-B radiation on these emissions appear to vary between different types of plant VOC,^{19, 204, 222} but new evidence has shown that compounds produced by plants in response to UV exposure can form a major element of VOC emission and aerosol production from desert ecosystems.¹²³

Combined effects of solar UV radiation and climate change on contaminants in aquatic and terrestrial ecosystems

The effects of solar UV radiation on atmospheric pollutants have been recently assessed (Chapter 1). In addition, the future projected changes in solar UV radiation (Chapter 1) could affect the quality of surface freshwaters by reducing UV-induced degradation of organic and inorganic contaminants and permitting longer range transport of these contaminants through the atmosphere. These changes may increase or decrease the toxicity of pollutants, depending on the toxicity of photoproducts relative to the initial pollutant in the case of organic pollutants. With regard to inorganic pollutants, we focus on two metals (mercury and copper) that are global pollutants that affect the health of ecosystems as well as human health, and the toxicity of which is likely to increase upon UV-induced transformations.

Inorganic contaminants

Mercury. Mercury is known as a global pollutant that is widespread in the environment, e.g., in the North Pacific Ocean.¹⁹⁸ In the troposphere, mercury in its elemental form (Gaseous Elemental Mercury, GEM) is transported over long distances and eventually deposited, e.g., in Antarctic ice and snow.²²⁴ BrO and Br produced by UV-induced chemistry (see above under „Halogen compounds“) rapidly remove GEM from the atmosphere by oxidizing it.⁴⁶ Mercury isotopic composition in the Arctic is strongly influenced by sunlight-induced photoreactions of mercury in the snow.¹⁸⁰ In aquatic systems the oxidation of dissolved gaseous mercury (DGM) to divalent mercury (Hg(II)) is induced by solar UV radiation.^{63, 141, 152, 159, 217} Biological processes then convert Hg(II) to methyl mercury,^{193, 198, 202} which is the biologically available, and thus harmful form of mercury that accumulates in the aquatic food web.^{36, 119} Fish and other seafood are important sources of mercury in the human diet.¹⁵³ Overall, rates of bioaccumulation and transfer through the aquatic food web are susceptible to ecological, biogeochemical and climatic influences.¹⁵⁶ Although poorly understood, it is likely that climate change related shifts in atmospheric circulation and precipitation patterns, coupled with shifts in the global distribution of UV-B radiation, will strongly alter the distribution and biological impacts of mercury-containing compounds.

Copper. UV-B-mediated degradation of DOM may enhance the toxicity of copper. The complexation of copper (Cu) by DOM regulates Cu toxicity by decreasing the concentration of the bioavailable form of copper, which is Cu²⁺.²⁸ UV-mediated degradation of DOM compounds that form strong complexes with copper has been shown to increase the concentration of the bioavailable and hence toxic form of Cu.^{28, 111, 178} This phenomenon may be especially critical in freshwater aquatic ecosystems that receive sewage discharges with high concentrations of copper.

Organic contaminants

Many synthetic organic chemicals accumulate in organisms and hence in food chains, including the human food chain.¹⁷⁵ The environmental fate of these organic pollutants depends on many factors,¹⁷⁵ and will be subject to the effects of various elements of climate change.¹⁰⁹ UV radiation also affects the environmental chemistry of organic pollutants such as pesticides, accelerating the rate of degradation in water, ice and snow,^{126, 151, 165} both through direct and indirect photodegradation mediated by reactive oxygen species.⁸⁵ These processes may remove the original pollutant, but the degradation products may also be toxic to organisms and damaging to human health.

Concluding remarks

As this assessment makes clear, the interactions between changing solar UV radiation, climate change and other drivers of global change are diverse and complex, but while there is still great uncertainty in many aspects of these interactions, in our view it is now possible to make an initial assessment of the direction of change for a range of interactions and their relative magnitude. Table 5-3 summarizes the results of the more detailed considerations provided in this assessment.

There is no doubt that interactions between climate change and UV radiation will act concurrently on the environment throughout the 21st century. Looking ahead over that time-period, climate models are taking into account carbon cycle-climate feedbacks.^{41, 84, 113, 118, 124, 125, 168, 174, 235} These models rarely include the interactions between solar UV radiation and climate on biogeochemical cycling, but as indicated above, the understanding of the effects of solar UV radiation on biogeochemical cycling that has come from research driven by concerns over stratospheric ozone depletion, provides clear indications that such interactions may be wide-ranging and substantial. Should UV-related impacts on the carbon cycle alter the predictive ability of projecting atmospheric CO₂ concentrations in the future, this will increase the cascading levels of uncertainty in the upcoming Fifth Assessment Report of the IPCC (AR5) simulations of climate change (<http://www.ipcc.ch/activities/activities.htm>).⁶⁸

Table 5-3. Projected changes in biogeochemical cycles during 2010-2100 in response to changes in solar UV radiation and co-occurring global drivers. These estimates are based on considerations of the projected changes in UV radiation that are assessed in Chapter 1 coupled with our assessment of the effects of these changes on global biogeochemical cycles based on current scientific information that is included in this report. Note that we consider magnitude of change relative to global biogeochemical cycles, so that changes leading to large but localized changes may be assessed as having small effects globally. Also, our emphasis was on interactions that were related to changes in UV radiation, rather on all possible effects and interactions occurring as part of global environmental change. Even focusing on interactions related to changes in UV radiation, there are substantial uncertainties associated with some aspects of this assessment that are highlighted in the Table 5-and in more detail in the text of the Chapter.

TERRESTRIAL

Change	Expected direction(s) of change, 2010-2100	Effect of change on UV radiation reaching surface	Magnitude of effect on UV irradiance	Area affected	Relative magnitude of effect of interaction on global biogeochemical cycling
Stratospheric ozone	Increase ¹³⁰	Decrease	Medium-large	Regional	Decrease at high latitudes may result in increased sequestration, but probably small effect in isolation.
Cloud cover	Increase overall, but marked variation, including decreases in some places (including tropics) ¹³⁰	Decrease overall, but marked variation, including increases in some places (including tropics)	Large	Global, but marked regional variation	Net effect remains hard to determine due to geographical variation in sign of changes in cloud, and interactions with other factors.
Atmospheric aerosols	Decrease ¹³⁰	Increase	Small to medium	Regional	Small
Latitudinal change in location of ecosystems in response to climate change	Shift poleward ⁶⁸	Decrease	Small-medium	Regional: mid-high latitudes	Interactions with cloud and ozone change might result in moderate increases in sequestration.
Altitudinal change in location of ecosystems in response to climate change	Shift to higher altitudes	Increase	Small	Local	Small
Change in phenology in response to climate change	Shift to early spring and later autumn	Decrease in both spring and autumn	Small	Regional: mid-high latitudes	Small
Changes to vegetation	Increase or decrease ⁶⁸	Decrease or increase	Little effect of	Global, but marked	Net effect remains hard to

Effects of solar UV radiation and climate change on biogeochemical cycling

Change	Expected direction(s) of change, 2010-2100	Effect of change on UV radiation reaching surface	Magnitude of effect on UV irradiance	Area affected	Relative magnitude of effect of interaction on global biogeochemical cycling
cover due to climate change			increased cover, but decreases will increase penetration to the surface	regional variation.	determine due to geographical variation in changes.
Changes to ice and snow cover due to climate change	Decrease ¹⁹⁰	Decreased albedo leading to decreased UV exposure to above-ground organisms	Large	Local to poles	Large

OCEANS AND LAKES

Change	Expected direction(s) of change, 2010-2100	Effect of change on UV radiation reaching surface organisms	Relative magnitude of effect on UV irradiance	Area affected	Relative magnitude of effect of interaction on global biogeochemical cycling
Stratospheric ozone	Increase ¹³⁰	Decrease	Large at high latitudes with UV-B radiation, especially in the Southern Hemisphere	Regional	Increased primary productivity at the poles, especially in Southern Hemisphere
Cloud cover	Increase overall, but marked variation, including decreases in some places (inc tropics) ¹³⁰	Decrease overall, but marked variation, including increases in some places (inc tropics)	Large	Global, but with marked regional variation	Increased primary productivity at the poles, especially in Southern Hemisphere
Atmospheric aerosols	Increase/decrease ¹³⁰	Decrease/increase	Small	Regional-global	Small
Input of coloured dissolved organic matter	Increased ^{1, 6, 81, 93, 114, 211, 218}	Decreased	Largest effect in circumpolar N. Hemisphere	Local (coastal)	Increased conversion of terrestrial organic carbon to CO ₂
Stratification	Increases ^{14, 15, 23}	Increases	Large in tropics,	Affects both ocean	Significant decrease in

Change	Expected direction(s) of change, 2010-2100	Effect of change on UV radiation reaching surface organisms	Relative magnitude of effect on UV irradiance	Area affected	Relative magnitude of effect of interaction on global biogeochemical cycling
			growing in mid-latitudes	and freshwater lakes	productivity in the mid-latitudes
Changes to ice cover due to climate change	Decrease ¹⁹⁰	Increase	Large	Local to poles	Large
Water availability and quality	Increasing at high latitudes; decreasing at low latitudes; changed availability from alpine snow-melt	Variable effects caused by runoff of soils and CDOM	Large	Regional; more flooding at high latitudes & drought at low latitudes	Variable effects on water quality via pollutant photodegradation; increased long range transport of pollutants

References

- 1 Agren A, Jansson M, Ivarsson H, Bishop K and Seibert J, 2008, Seasonal and runoff-related changes in total organic carbon concentrations in the River Ore, Northern Sweden, *Aquat. Sci.*, **70**, 21-29.
- 2 Allan RP and Soden BJ, 2008, Atmospheric warming and the amplification of precipitation extremes, *Science.*, **321**, 1481-1484.
- 3 Anthony KRN and Kerswell AP, 2007, Coral mortality following extreme low tides and high solar radiation, *Mar. Biol.*, **151**, 1623-1631.
- 4 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.
- 5 Austin AT and Vivanco L, 2006, Plant litter decomposition in a semi-arid ecosystem controlled by photodegradation, *Nature*, **442**, 555-558.
- 6 Baker A, Bolton L, Newson M and Spencer RGM, 2008, Spectrophotometric properties of surface water dissolved organic matter in an afforested upland peat catchment, *Hydrol. Process.*, **22**, 2325-2336.
- 7 Baldocchi D, 2008, Breathing of the terrestrial biosphere: lessons learned from a global network of carbon dioxide flux measurement systems, *Aust. J. Bot.*, **56**, 1-26.
- 8 Ban-nai T, Muramatsu Y and Amachi S, 2006, Rate of iodine volatilization and accumulation by filamentous fungi through laboratory cultures, *Chemosphere*, **65**, 2216-2222.
- 9 Banaszak AT and Lesser MP, 2009, Effects of solar ultraviolet radiation on coral reef organisms, *Photochem. Photobiol. Sci.*, **8**, 1276-1294.
- 10 Barbeau K, 2006, Photochemistry of organic iron(III) complexing ligands in oceanic systems, *Photochem. Photobiol.*, **82**, 1505-1516.
- 11 Bates NR and Peters AJ, 2007, The contribution of atmospheric acid deposition to ocean acidification in the subtropical North Atlantic Ocean, *Mar. Chem.*, **107**, 547-558.
- 12 Beardall J, Sobrino C and Stojkovic S, 2009, Interactions between the impacts of ultraviolet radiation, elevated CO₂, and nutrient limitation on marine primary producers, *Photochem. Photobiol. Sci.*, **8**, 1257-1265.
- 13 Beerling DJ, Hewitt CN, Pyle JA and Raven JA, 2007, Critical issues in trace gas biogeochemistry and global change, *Philos. Trans. Roy. Soc. Lond. A Math. Phys. Engin.*, **365**, 1629-1642.
- 14 Behrenfeld MJ, O'Malley RT, Siegel DA, McClain CR, Sarmiento JL, Feldman GC, Milligan AJ, Falkowski PG, Letelier RM and Boss ES, 2006, Climate-driven trends in contemporary ocean productivity, *Nature*, **444**, 752-755.
- 15 Behrenfeld MJ, Westberry TK, Boss ES, O'Malley RT, Siegel DA, Wiggert JD, Franz BA, McClain CR, Feldman GC, Doney SC, Moore JK, Dall'Olmo G, Milligan AJ, Lima I and Mahowald N, 2009, Satellite-detected fluorescence reveals global physiology of ocean phytoplankton, *Biogeosci.*, **6**, 779-794.
- 16 Bélanger S, Xie HX, Krotkov N, Larouche P, Vincent WF and Babin M, 2006, Photomineralization of terrigenous dissolved organic matter in Arctic coastal waters from 1979 to 2003: Interannual variability and implications of climate change, *Glob. Biogeochem. Cycles*, **20**, GB4005.
- 17 Bergamaschi P, Frankenberg C, Meirink JF, Krol M, Dentener F, Wagner T, Platt U, Kaplan JO, Korner S, Heimann M, Dlugokencky EJ and Goede A, 2007, Satellite cartography of atmospheric methane from SCIAMACHY on board ENVISAT: 2. Evaluation based on inverse model simulations, *J. Geophys. Res. Atmos.*, **112**, D02304.

- 18 Biers EJ, Zepp RG and Moran MA, 2007, The role of nitrogen in chromophoric and fluorescent dissolved organic matter formation, *Mar. Chem.*, **103**, 46-60.
- 19 Blande JD, Turunen K and Holopainen JK, 2009, Pine weevil feeding on Norway spruce bark has a stronger impact on needle VOC emissions than enhanced ultraviolet-B radiation, *Environ. Pollut.*, **157**, 174-180.
- 20 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.
- 21 Borer P, Sulzberger B, Hug SJ, Kraemer SM and 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.
- 22 Bowling DR, Miller JB, Rhodes ME, Burns SP, Monson RK and Baer D, 2009, Soil, plant, and transport influences on methane in a subalpine forest under high ultraviolet irradiance, *Biogeosci.*, **6**, 1311-1324.
- 23 Boyce DG, Lewis MR and Worm B, 2010, Global phytoplankton decline over the past century, *Nature*, **466**, 591-596.
- 24 Brandt L, King J, Hobbie S, Milchunas D and Sinsabaugh R, 2010, The role of photodegradation in surface litter decomposition across a grassland ecosystem precipitation gradient, *Ecosystems*, **13**, 765-781.
- 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**, 13.
- 26 Brandt LA, King JY and Milchunas DG, 2007, Effects of ultraviolet radiation on litter decomposition depend on precipitation and litter chemistry in a shortgrass steppe ecosystem, *Glob. Change Biol.*, **13**, 2193-2205.
- 27 Brewer PG and Peltzer ET, 2009, Limits to marine life, *Science.*, **324**, 347-348.
- 28 Brooks ML, McKnight DM and Clements WH, 2007, Photochemical control of copper complexation by dissolved organic matter in Rocky Mountain streams, Colorado, *Limnol. Oceanogr.*, **52**, 766-779.
- 29 Butler JH, King DB, Lobert JM, Montzka SA, Yvon-Lewis SA, Hall BD, Warwick NJ, Mondeel DJ, Aydin M and Elkins JW, 2007, Oceanic distributions and emissions of short-lived halocarbons, *Glob. Biogeochem. Cycles*, **21**, GB1023.
- 30 Caldwell MM, Bornman JF, Ballare CL, Flint SD and Kulandaivelu, 2007, Terrestrial ecosystems, increased ultraviolet radiation, and interactions with other climate change factors, *Photochem. Photobiol. Sci.*, **6**, 252-266.
- 31 Canadell JG, Le Quere C, Raupach MR, Field CB, Buitenhuis ET, Ciais P, Conway TJ, Gillett NP, Houghton RA and Marland G, 2007, Contributions to accelerating atmospheric CO₂ growth from economic activity, carbon intensity, and efficiency of natural sinks, *Proc. Nat. Acad. Sci. USA.*, **104**, 18866-18870.
- 32 Cao GM, Xu XL, Long RJ, Wang QL, Wang CT, Du YG and Zhao XQ, 2008, Methane emissions by alpine plant communities in the Qinghai-Tibet Plateau, *Biol. Lett.*, **4**, 681-684.
- 33 Carpenter KE, Abrar M, Aeby G, Aronson RB, Banks S, Bruckner A, Chiriboga A, Cortes J, Delbeek JC, DeVantier L, Edgar GJ, Edwards AJ, Fenner D, Guzman HM, Hoeksema BW, Hodgson G, Johan O, Licuanan WY, Livingstone SR, Lovell ER, Moore JA, Obura DO, Ochavillo D, Polidoro BA, Prect WF, Quibilan MC, Reboton C, Richards ZT, Rogers AD, Sanciangco J, Sheppard A, Sheppard C, Smith J, Stuart S, Turak E, Veron JEN, Wallace C, Weil E and Wood E, 2008, One-third of reef-

- building corals face elevated extinction risk from climate change and local impacts, *Science.*, **321**, 560-563.
- 34 Carpenter LJ, Wevill DJ, Palmer CJ and Michels J, 2007, Depth profiles of volatile iodine and bromine-containing halocarbons in coastal Antarctic waters, *Mar. Chem.*, **103**, 227-236.
- 35 Chapin FS, Randerson JT, McGuire AD, Foley JA and Field CB, 2008, Changing feedbacks in the climate-biosphere system, *Front. Ecol. Environ.*, **6**, 313-320.
- 36 Chasar LC, Scudder BC, Stewart AR, Bell AH and Aiken GR, 2009, Mercury cycling in stream ecosystems. 3. Trophic dynamics and methylmercury bioaccumulation, *Environ. Sci. Technol.*, **43**, 2733-2739.
- 37 Chen Z, Hu C, Conmy RN, Muller-Karger F and Swarzenski P, 2007, Colored dissolved organic matter in Tampa Bay, Florida, *Mar. Chem.*, **104**, 98-109.
- 38 Clark CD, Litz LP and Grant SB, 2008, Salt marshes as a source of chromophoric dissolved organic matter (CDOM) to Southern California coastal waters, *Limnol. Oceanogr.*, **53**, 1923-1933.
- 39 Codispoti LA, 2010, Interesting times for marine N₂O, *Science.*, **327**, 1339-1340.
- 40 Cowling SA, Jones CD and Cox PM, 2009, Greening the terrestrial biosphere: simulated feedbacks on atmospheric heat and energy circulation, *Clim. Dyn.*, **32**, 287-299.
- 41 Cox P and Jones C, 2008, Climate change - Illuminating the modern dance of climate and CO₂, *Science.*, **321**, 1642-1644.
- 42 Cox PM, Harris PP, Huntingford C, Betts RA, Collins M, Jones CD, Jupp TE, Marengo JA and Nobre CA, 2008, Increasing risk of Amazonian drought due to decreasing aerosol pollution, *Nature*, **453**, 212-U217.
- 43 Crutzen PJ, Mosier AR, Smith KA and Winiwarter W, 2008, N₂O release from agro-biofuel production negates global warming reduction by replacing fossil fuels, *Atmos. Chem. Phys.*, **8**, 389-395.
- 44 D'Sa EJ and DiMarco SF, 2009, Seasonal variability and controls on chromophoric dissolved organic matter in a large river-dominated coastal margin, *Limnol. Oceanogr.*, **54**, 2233-2242.
- 45 Dalzell BJ, Minor EC and Mopper KM, 2009, Photodegradation of estuarine dissolved organic matter: a multi-method assessment of DOM transformation, *Org. Geochem.*, **40**, 243-257.
- 46 Dastoor AP, Davignon D, Theys N, Van Roozendaal M, Steffen A and Ariya PA, 2008, Modeling dynamic exchange of gaseous elemental mercury at polar sunrise, *Environ. Sci. Technol.*, **42**, 5183-5188.
- 47 Davey M, Tarran GA, Mills MM, Ridame C, Geider RJ and LaRoche J, 2008, Nutrient limitation of picophytoplankton photosynthesis and growth in the tropical North Atlantic, *Limnol. Oceanogr.*, **53**, 1722-1733.
- 48 Davies A, Kemp AES and Pike J, 2009, Late Cretaceous seasonal ocean variability from the Arctic, *Nature*, **460**, 254-U118.
- 49 De'ath G, Lough JM and Fabricius KE, 2009, Declining coral calcification on the Great Barrier Reef, *Science.*, **323**, 116-119.
- 50 del Valle DA, Kieber DJ, Toole DA, Bisgrove J and Kiene RP, 2009, Dissolved DMSO production via biological and photochemical oxidation of dissolved DMS in the Ross Sea, Antarctica, *Deep Sea Res. Part I: Oceanog. Res. Pap.*, **56**, 166-177.
- 51 DeLuca TH, Nilsson MC and Zackrisson O, 2002, Nitrogen mineralization and phenol accumulation along a fire chronosequence in northern Sweden, *Oecologia*, **133**, 206-214.

- 52 DeLuca TH, Zackrisson O, Gundale MJ and Nilsson MC, 2008, Ecosystem feedbacks and nitrogen fixation in boreal forests, *Science.*, **320**, 1181-1181.
- 53 Deutsch C, Sarmiento JL, Sigman DM, Gruber N and Dunne JP, 2007, Spatial coupling of nitrogen inputs and losses in the ocean, *Nature*, **445**, 163-167.
- 54 do Carmo JB, Keller M, Dias JD, de Camargo PB and Crill P, 2006, A source of methane from upland forests in the Brazilian Amazon, *Geophys. Res. Lett.*, **33**, L04809.
- 55 Doney SC, Balch WM, Fabry VJ and Feely RA, 2009, Ocean acidification: A critical emerging problem for the ocean sciences, *Oceanography*, **22**, 16-+.
- 56 Doney SC, Fabry VJ, Feely RA and Kleypas JA, 2009, Ocean acidification: The other CO₂ problem, *Ann. Rev. Mar. Sci.*, **1**, 169-192.
- 57 Drewer J, Heal KV, Smith KA and Heal MR, 2008, Methyl bromide emissions to the atmosphere from temperate woodland ecosystems, *Glob. Change Biol.*, **14**, 2539-2547.
- 58 Drewer J, Heal MR, Heal KV and Smith KA, 2006, Temporal and spatial variation in methyl bromide flux from a salt marsh, *Geophys. Res. Lett.*, **33**, L16808.
- 59 Duce RA, LaRoche J, Altieri K, Arrigo KR, Baker AR, Capone DG, Cornell S, Dentener F, Galloway J, Ganeshram RS, Geider RJ, Jickells T, Kuypers MM, Langlois R, Liss PS, Liu SM, Middelburg JJ, Moore CM, Nickovic S, Oschlies A, Pedersen T, Prospero J, Schlitzer R, Seitzinger S, Sorensen LL, Uematsu M, Ulloa O, Voss M, Ward B and Zamora L, 2008, Impacts of atmospheric anthropogenic nitrogen on the open ocean, *Science.*, **320**, 893-897.
- 60 Dueck TA, de Visser R, Poorter H, Persijn S, Gorissen A, de Visser W, Schapendonk A, Verhagen J, Snel J, Harren FJM, Ngai AKY, Verstappen F, Bouwmeester H, Voeselek L and van der Werf A, 2007, No evidence for substantial aerobic methane emission by terrestrial plants: a C¹³-labelling approach, *New. Phytol.*, **175**, 29-35.
- 61 Fabry VJ, Seibel BA, Feely RA and Orr JC, 2008, Impacts of ocean acidification on marine fauna and ecosystem processes, *ICES J. Mar. Sci.*, **65**, 414-432.
- 62 Fan SM, 2008, Photochemical and biochemical controls on reactive oxygen and iron speciation in the pelagic surface ocean, *Mar. Chem.*, **109**, 152-164.
- 63 Fantozzi L, Ferrara R, Frontini FP and Dini F, 2007, Factors influencing the daily behaviour of dissolved gaseous mercury concentration in the Mediterranean Sea, *Mar. Chem.*, **107**, 4-12.
- 64 Feely RA, Sabine CL, Hernandez-Ayon JM, Ianson D and Hales B, 2008, Evidence for upwelling of corrosive "acidified" water onto the continental shelf, *Science.*, **320**, 1490-1492.
- 65 Feil S, 2006, Plants surprise as methane producers, *Chemie in Unserer Zeit*, **40**, 158-158.
- 66 Ferretti DF, Miller JB, White JWC, Lassey KR, Lowe DC and Etheridge DM, 2007, Stable isotopes provide revised global limits of aerobic methane emissions from plants, *Atmos. Chem. Phys.*, **7**, 237-241.
- 67 Ferrier-Pages C, Richard C, Forcioli D, Allemand D, Pichon M and Shick JM, 2007, Effects of temperature and UV radiation increases on the photosynthetic efficiency in four scleractinian coral species, *Biol. Bull.*, **213**, 76-87.
- 68 Fischlin AGF, Midgley GF, Price JT, Leemans R, Gopal B, Turley C, Rounsevell MDA, Dube OP, Tarazona J and Velichko AA, 2007, Ecosystems, their properties, goods, and services in *Climate Change 2007: Impacts, Adaptation and Vulnerability. Contribution of Working Group II to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change* eds.: Parry ML, Canziani OF, Palutikof

- JP, Linden PJvd and Hanson CE, Cambridge University Press, Cambridge, UK, pp. 211-272.
- 69 Fletcher SEM, Gruber N, Jacobson AR, Gloor M, Doney SC, Dutkiewicz S, Gerber M, Follows M, Joos F, Lindsay K, Menemenlis D, Mouchet A, Muller SA and Sarmiento JL, 2007, Inverse estimates of the oceanic sources and sinks of natural CO₂ and the implied oceanic carbon transport, *Glob. Biogeochem. Cycles*, **21**, GB1010.
- 70 Forster P, Ramaswamy V, Artaxo P, Bernsten T, Betts R, Fahey DW, Haywood J, Lean J, Lowe DC, Myhre G, Nganga J, Prinn R, Raga G, Schulz M and Dorland RV, 2007, Changes in Atmospheric Constituents and in Radiative Forcing, in *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change* eds.: Solomon S, Qin D, Manning M, Chen Z, Marquis M, Averyt KB, M.Tignor and Miller HL, Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, pp. 129-234.
- 71 French-Monar RD, Jones JB, Ozores-Hampton M and Roberts PD, 2007, Survival of inoculum of *Phytophthora capsici* in soil through time under different soil treatments, *Plant Disease*, **91**, 593-598.
- 72 Fritz JJ, Neale PJ, Davis RF and Peloquin JA, 2008, Response of Antarctic phytoplankton to solar UVR exposure: inhibition and recovery of photosynthesis in coastal and pelagic assemblages, *Mar. Ecol. Prog. Ser.*, **365**, 1-16.
- 73 Fujii M, Rose AL, Waite TD and Omura T, 2006, Superoxide-mediated dissolution of amorphous ferric oxyhydroxide in seawater, *Environ. Sci. Technol.*, **40**, 880-887.
- 74 Galloway JN, Townsend AR, Erisman JW, Bekunda M, Cai ZC, Freney JR, Martinelli LA, Seitzinger SP and Sutton MA, 2008, Transformation of the nitrogen cycle: Recent trends, questions, and potential solutions, *Science*, **320**, 889-892.
- 75 Ganguly AR, Steinhäuser K, Erickson III DJ, Branstetter M, Parish ES, Singh N, Drake JB and Buja L, 2009, Higher trends but larger uncertainty and geographic variability in 21st century temperature and heat waves, *Proc. Nat. Acad. Sci. USA*, **106**, 15555-15559
- 76 Gao KS, Ruan ZX, Villafane VE, Gattuso JP and Helbling EW, 2009, Ocean acidification exacerbates the effect of UV radiation on the calcifying phytoplankter *Emiliania huxleyi*, *Limnol. Oceanogr.*, **54**, 1855-1862.
- 77 Gebhardt S, Colomb A, Hofmann R, Williams J and Lelieveld J, 2008, Halogenated organic species over the tropical South American rainforest, *Atmos. Chem. Phys.*, **8**, 3185-3197.
- 78 Gerik JS, 2007, Floriculture production with iodomethane, 1,3-dichloropropene and chloropicrin as an alternative to methyl bromide, *Phytopathology*, **97**, S40-S40.
- 79 Giese M, Gao YZ, Zhao Y, Pan QM, Lin S, Peth S and Brueck H, 2009, Effects of grazing and rainfall variability on root and shoot decomposition in a semi-arid grassland, *Appl. Soil Ecol.*, **41**, 8-18.
- 80 Gonsior M, Peake B, Cooper W, Jaffe R, Young H, Kahn A and Kowalczyk P, 2008, Spectral characterization of chromophoric dissolved organic matter (CDOM) in a fjord (Doubtful Sound, New Zealand), *Aquat. Sci.*, **70**, 397-409.
- 81 Gonsior M, Peake BM, Cooper WT, Podgorski D, D'Andrilli J and Cooper WJ, 2009, Photochemically induced changes in dissolved organic matter identified by ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry, *Environ. Sci. Technol.*, **43**, 698-703.
- 82 Grebel JE, Pignatello JJ, Song WH, Cooper WJ and Mitch WA, 2009, Impact of halides on the photobleaching of dissolved organic matter, *Mar. Chem.*, **115**, 134-144.

- 83 Gros V, Peeken I, Bluhm K, Zollner E, Sarda-Esteve R and Bonsang B, 2009, Carbon monoxide emissions by phytoplankton: evidence from laboratory experiments, *Environ. Chem.*, **6**, 369-379.
- 84 Gruber N, Gloor M, Fletcher SEM, Doney SC, Dutkiewicz S, Follows MJ, Gerber M, Jacobson AR, Joos F, Lindsay K, Menemenlis D, Mouchet A, Muller SA, Sarmiento JL and Takahashi T, 2009, Oceanic sources, sinks, and transport of atmospheric CO₂, *Glob. Biogeochem. Cycles*, **23**, 21.
- 85 Guerard JJ, Miller PL, Trouts TD and Chin YP, 2009, The role of fulvic acid composition in the photosensitized degradation of aquatic contaminants, *Aquat. Sci.*, **71**, 160-169.
- 86 Häder D-P, Kumar HD, Smith RC and Worrest RC, 2007, Effects of solar UV radiation on aquatic ecosystems and interactions with climate change, *Photochem. Photobiol. Sci.*, **6**, 267-285.
- 87 Hall-Spencer JM, Rodolfo-Metalpa R, Martin S, Ransome E, Fine M, Turner SM, Rowley SJ, Tedesco D and Buia MC, 2008, Volcanic carbon dioxide vents show ecosystem effects of ocean acidification, *Nature*, **454**, 96-99.
- 88 Hari P, Raivonen M, Vesala T, Munger JW, Pilegaard K and Kulmala M, 2003, Atmospheric science - Ultraviolet light and leaf emission of NO_x, *Nature*, **422**, 134-134.
- 89 Hefner KH, Fisher JM and Ferry JL, 2006, A multifactor exploration of the photobleaching of Suwannee River dissolved organic matter across the freshwater/saltwater interface, *Environ. Sci. Technol.*, **40**, 3717-3722.
- 90 Helms JR, Stubbins A, Ritchie JD, Minor EC, Kieber DJ and Mopper K, 2008, Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photobleaching of chromophoric dissolved organic matter, *Limnol. Oceanogr.*, **53**, 955-969.
- 91 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.
- 92 Hense I and Quack B, 2009, Modelling the vertical distribution of bromoform in the upper water column of the tropical Atlantic Ocean, *Biogeosci.*, **6**, 535-544.
- 93 Hernes PJ, Spencer RGM, Dyda RY, Pellerin BA, Bachand PAM and Bergamaschi BA, 2008, The role of hydrologic regimes on dissolved organic carbon composition in an agricultural watershed, *Geochim. Cosmochim. Acta.*, **72**, 5266-5277.
- 94 Hoegh-Guldberg O, Mumby PJ, Hooten AJ, Steneck RS, Greenfield P, Gomez E, Harvell CD, Sale PF, Edwards AJ, Caldeira K, Knowlton N, Eakin CM, Iglesias-Prieto R, Muthiga N, Bradbury RH, Dubi A and Hatziolos ME, 2007, Coral reefs under rapid climate change and ocean acidification, *Science*, **318**, 1737-1742.
- 95 Hopkin M, 2007, Missing gas saps plant theory, *Nature*, **447**, 11-11.
- 96 Houweling S, Rockmann T, Aben I, Keppler F, Krol M, Meirink JF, Dlugokencky EJ and Frankenberg C, 2006, Atmospheric constraints on global emissions of methane from plants, *Geophys. Res. Lett.*, **33**, L15821.
- 97 Iriarte F and Roskopf E, 2007, Spore viability bioassay, in vitro and greenhouse evaluation of six potential methyl bromide alternatives, *Phytopathology.*, **97**, S50-S50.
- 98 Ishikawa H, Osono T and Takeda H, 2007, Effects of clear-cutting on decomposition processes in leaf litter and the nitrogen and lignin dynamics in a temperate secondary forest, *J. Forest Res.*, **12**, 247-254.

- 99 Judd KE, Crump BC and Kling GW, 2007, Bacterial responses in activity and community composition to photo-oxidation of dissolved organic matter from soil and surface waters, *Aquat. Sci.*, **69**, 96-107.
- 100 Karlsson A, Auer N, Schulz-Bull D and Abrahamsson K, 2008, Cyanobacterial blooms in the Baltic - A source of halocarbons, *Mar. Chem.*, **110**, 129-139.
- 101 Kelton N, Molot LA and Dillon PJ, 2007, Effect of ultraviolet and visible radiation on iron lability in boreal and artificial waters, *Aquat. Sci.*, **69**, 86-95.
- 102 Keppler F, Hamilton JTG, Brass M and Rockmann T, 2006, Methane emissions from terrestrial plants under aerobic conditions, *Nature*, **439**, 187-191.
- 103 Keppler F, Hamilton JTG, McRoberts WC, Vigano I, Brass M and Rockmann T, 2008, Methoxyl groups of plant pectin as a precursor of atmospheric methane: evidence from deuterium labelling studies, *New. Phytol.*, **178**, 808-814.
- 104 Kieber DJ, Toole DA, Jankowski JJ, Kiene RP, Westby GR, del Valle DA and Slezak D, 2007, Chemical "light meters" for photochemical and photobiological studies, *Aquat. Sci.*, **69**, 360-376.
- 105 Kieber RJ, Parler NE, Skrabal SA and Willey JD, 2008, Speciation and photochemistry of mercury in rainwater, *J. Atmos. Chem.*, **60**, 153-168.
- 106 Kirschbaum MUF, Bruhn D, Etheridge DM, Evans JR, Farquhar GD, Gifford RM, Paul KI and Winters AJ, 2006, A comment on the quantitative significance of aerobic methane release by plants, *Funct. Plant Biol.*, **33**, 521-530.
- 107 Knorr W, 2009, Is the airborne fraction of anthropogenic CO₂ emissions increasing?, *Geophys. Res. Lett.*, **36**, 5.
- 108 Kowalczyk P, Durako MJ, Young H, Kahn AE, Cooper WJ and Gonsior M, 2009, Characterization of dissolved organic matter fluorescence in the South Atlantic Bight with use of PARAFAC model: Interannual variability, *Mar. Chem.*, **113**, 182-196.
- 109 Lamon L, Valle MD, Critto A and Marcomini A, 2009, Introducing an integrated climate change perspective in POPs modelling, monitoring and regulation, *Environ. Pollut.*, **157**, 1971-1980.
- 110 Laothawornkitkul J, Taylor JE, Paul ND and Hewitt CN, 2009, Biogenic volatile organic compounds in the Earth system (Vol 183, pg 27, 2009), *New. Phytol.*, **184**, 276-276.
- 111 Larson JH, Frost PC, Zheng ZY, Johnston CA, Bridgham SD, Lodge DM and Lamberti GA, 2007, Effects of upstream lakes on dissolved organic matter in streams, *Limnol. Oceanogr.*, **52**, 60-69.
- 112 Le Quere C, Raupach MR, Canadell JG, Marland G, Bopp L, Ciais P, Conway TJ, Doney SC, Feely RA, Foster P, Friedlingstein P, Gurney K, Houghton RA, House JI, Huntingford C, Levy PE, Lomas MR, Majkut J, Metzl N, Ometto JP, Peters GP, Prentice IC, Randerson JT, Running SW, Sarmiento JL, Schuster U, Sitch S, Takahashi T, Viovy N, van der Werf GR and Woodward FI, 2009, Trends in the sources and sinks of carbon dioxide, *Nat. Geosci.*, **2**, 831-836.
- 113 Lenton A, Codron F, Bopp L, Metzl N, Cadule P, Tagliabue A and Le Sommer J, 2009, Stratospheric ozone depletion reduces ocean carbon uptake and enhances ocean acidification, *Geophys. Res. Lett.*, **36**, 5.
- 114 Lepisto A, Kortelainen P and Mattsson T, 2008, Increased organic C and N leaching in a northern boreal river basin in Finland, *Glob. Biogeochem. Cycles*, **22**, GB3029.
- 115 Leu E, Falk-Petersen S and Hessen DO, 2007, Ultraviolet radiation negatively affects growth but not food quality of arctic diatoms, *Limnol. Oceanogr.*, **52**, 787-797.
- 116 Li WKW and Harrison WG, 2008, Propagation of an atmospheric climate signal to phytoplankton in a small marine basin, *Limnol. Oceanogr.*, **53**, 1734-1745.

- 117 Loulergue L, Schilt A, Spahni R, Masson-Delmotte V, Blunier T, Lemieux B, Barnola JM, Raynaud D, Stocker TF and Chappellaz J, 2008, Orbital and millennial-scale features of atmospheric CH₄ over the past 800,000 years, *Nature*, **453**, 383-386.
- 118 Lovenduski NS, Gruber N and Doney SC, 2008, Toward a mechanistic understanding of the decadal trends in the Southern Ocean carbon sink, *Glob. Biogeochem. Cycles*, **22**, 9.
- 119 Luengen AC and Flegal AR, 2009, Role of phytoplankton in mercury cycling in the San Francisco Bay estuary, *Limnol. Oceanogr.*, **54**, 23-40.
- 120 Luo YQ, Gerten D, Le Maire G, Parton WJ, Weng ES, Zhou XH, Keough C, Beier C, Ciais P, Cramer W, Dukes JS, Emmett B, Hanson PJ, Knapp A, Linder S, Nepstad D and Rustad L, 2008, Modeled interactive effects of precipitation, temperature, and [CO₂] on ecosystem carbon and water dynamics in different climatic zones, *Glob. Change Biol.*, **14**, 1986-1999.
- 121 Manley SL, Wang NY, Walser ML and Cicerone RJ, 2006, Coastal salt marshes as global methyl halide sources from determinations of intrinsic production by marsh plants, *Glob. Biogeochem. Cycles*, **20**, GB3015.
- 122 Manley SL, Wang NY, Walser ML and Cicerone RJ, 2007, Methyl halide emissions from greenhouse-grown mangroves, *Geophys. Res. Lett.*, **34**, L01806.
- 123 Matsunaga SN, Guenther AB, Potosnak MJ and Apel EC, 2008, Emission of sunscreen salicylic esters from desert vegetation and their contribution to aerosol formation, *Atmos. Chem. Phys.*, **8**, 7367-7371.
- 124 Matthews HD, Eby M, Ewen T, Friedlingstein P and Hawkins BJ, 2007, What determines the magnitude of carbon cycle-climate feedbacks?, *Glob. Biogeochem. Cycles*, **21**, GB2012.
- 125 Matthews HD, Gillett NP, Stott PA and Zickfeld K, 2009, The proportionality of global warming to cumulative carbon emissions, *Nature*, **459**, 829-U823.
- 126 Matykiewiczova N, Klanova J and Klan P, 2007, Photochemical degradation of PCBs in snow, *Environ. Sci. Technol.*, **41**, 8308-8314.
- 127 Mayer LM, Schick LL, Bianchi TS and Wysocki LA, 2009, Photochemical changes in chemical markers of sedimentary organic matter source and age, *Mar. Chem.*, **113**, 123-128.
- 128 Mayer LM, Schick LL, Hardy KR and Estapa ML, 2009, Photodissolution and other photochemical changes upon irradiation of algal detritus, *Limnol. Oceanogr.*, **54**, 1688-1698.
- 129 McCalley CK and Sparks JP, 2009, Abiotic Gas Formation Drives Nitrogen Loss from a Desert Ecosystem, *Science*, **326**, 837-840.
- 130 McKenzie RL, Aucamp PJ, Bais AF, Bjorn LO and Ilyas M, 2007, Changes in biologically-active ultraviolet radiation reaching the Earth's surface, *Photochem. Photobiol. Sci.*, **6**, 218-231.
- 131 McKenzie RL, Aucamp PJ, Bais AF, Björn LO, Ilyase M and Madronich S, 2011, Ozone depletion and climate change: impacts on UV radiation, *Photochem. Photobiol. Sci.*, **10**, In Press.
- 132 McLeod AR, Fry SC, Loake GJ, Messenger DJ, Reay DS, Smith KA and Yun BW, 2008, Ultraviolet radiation drives methane emissions from terrestrial plant pectins, *New. Phytol.*, **180**, 124-132.
- 133 Meador JA, Baldwin AJ, Catala P, Jeffrey WH, Joux F, Moss JA, Pakulski JD, Stevens R and Mitchell DL, 2009, Sunlight-induced DNA Damage in Marine Micro-organisms Collected Along a Latitudinal Gradient from 70 degrees N to 68 degrees S, *Photochem. Photobiol.*, **85**, 412-421.

- 134 Meehl GA, Stocker TF, Collins WD, Friedlingstein P, Gaye AT, Gregory JM, Kitoh A, Knutti R, Murphy JM, Noda A, Raper SCB, Watterson IG, A.J. Weaver AJ and Zhao Z-C, 2007, Global Climate Projections, in *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change* eds.: Solomon S, Qin D, Manning M, Chen Z, Marquis M, Averyt KB, Tignor M and Miller HL, Cambridge University Press, Cambridge, U. K.; New York, NY, USA, pp. 747-845.
- 135 Melillo JM, Reilly JM, Kicklighter DW, Gurgel AC, Cronin TW, Paltsev S, Felzer BS, Wang XD, Sokolov AP and Schlosser CA, 2009, Indirect Emissions from Biofuels: How Important?, *Science*, **326**, 1397-1399.
- 136 Mentel TF, Wildt J, Kiendler-Scharr A, Kleist E, Tillmann R, Dal Maso M, Fisseha R, Hohaus T, Spahn H, Uerlings R, Wegener R, Griffiths PT, Dinar E, Rudich Y and Wahner A, 2009, Photochemical production of aerosols from real plant emissions, *Atmos. Chem. Phys.*, **9**, 4387-4406.
- 137 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.
- 138 Miller JB, Gatti LV, d'Amelio MTS, Crotwell AM, Dlugokencky EJ, Bakwin P, Artaxo P and Tans PP, 2007, Airborne measurements indicate large methane emissions from the eastern Amazon basin, *Geophys. Res. Lett.*, **34**, L10809.
- 139 Minor EC, Dalzell BJ, Stubbins A and Mopper K, 2007, Evaluating the photoalteration of estuarine dissolved organic matter using direct temperature-resolved mass spectrometry and UV-visible spectroscopy, *Aquat. Sci.*, **69**, 440-455.
- 140 Minor EC, Pothén J, Dalzell BJ, Abdulla H and Mopper K, 2006, Effects of salinity changes on the photodegradation and ultraviolet-visible absorbance of terrestrial dissolved organic matter, *Limnol. Oceanogr.*, **51**, 2181-2186.
- 141 Monperrus M, Tessier E, Amouroux D, Leynaert A, Huonnic P and Donard OFX, 2007, Mercury methylation, demethylation and reduction rates in coastal and marine surface waters of the Mediterranean Sea, *Mar. Chem.*, **107**, 49-63.
- 142 Moore JK and Doney SC, 2007, Iron availability limits the ocean nitrogen inventory stabilizing feedbacks between marine denitrification and nitrogen fixation, *Glob. Biogeochem. Cycles*, **21**, GB2001.
- 143 Moore RM, 2008, A photochemical source of methyl chloride in saline waters, *Environ. Sci. Technol.*, **42**, 1933-1937.
- 144 Moran MA and Miller WL, 2007, Resourceful heterotrophs make the most of light in the coastal ocean, *Nature Rev. Microbiol.*, **5**, 792-800.
- 145 Moran XAG, Sebastian M, Pedros-Alio C and Estrada M, 2006, Response of Southern Ocean phytoplankton and bacterioplankton production to short-term experimental warming, *Limnol. Oceanogr.*, **51**, 1791-1800.
- 146 Morel FMM, Kustka AB and Shaked Y, 2008, The role of unchelated Fe in the iron nutrition of phytoplankton, *Limnol. Oceanogr.*, **53**, 400-404.
- 147 Myhre G, 2009, Consistency between satellite-derived and modeled estimates of the direct aerosol effect, *Science*, **325**, 187-190.
- 148 Nelson NB, Siegel DA, Carlson CA and Swan CM, 2010, Tracing global biogeochemical cycles and meridional overturning circulation using chromophoric dissolved organic matter, *Geophys. Res. Lett.*, **37**, L03610.
- 149 Niemi R, Martikainen PJ, Silvola J, Wulff A, Turtola S and Holopainen T, 2002, Elevated UV-B radiation alters fluxes of methane and carbon dioxide in peatland microcosms, *Glob. Change Biol.*, **8**, 361-371.

- 150 Nisbet RER, Fisher R, Nimmo RH, Bendall DS, Crill PM, Gallego-Sala AV, Hornibrook ERC, Lopez-Juez E, Lowry D, Nisbet PBR, Shuckburgh EF, Sriskantharajah S, Howe CJ and Nisbet EG, 2009, Emission of methane from plants, *Proc. R. Soc. Lond. B. Biol. Sci.*, **276**, 1347-1354.
- 151 Niu JF, Yu G and Liu XT, 2005, Advances in photolysis of persistent organic pollutants in water, *Prog. Chem.*, **17**, 938-948.
- 152 O'Driscoll NJ, Poissant L, Canario J, Ridal J and Lean DRS, 2007, Continuous analysis of dissolved gaseous mercury and mercury volatilization in the upper St. Lawrence River: Exploring temporal relationships and UV attenuation, *Environ. Sci. Technol.*, **41**, 5342-5348.
- 153 Ortega-Garcia JA, Rodriguez K, Martin M, Velez DD, V, Sanchez-Alarcon MC, Cantero AMT, Galindo-Cascales CG-V, J.M., Sanchez-Sauco MF, Sanchez-Solis M, Alfonso-Marsilla B and Romero-Braquehais F, 2009, Estimated intake levels of methylmercury in children, childbearing age and pregnant women in a Mediterranean region, Murcia, Spain, *Eur. J. Pediatr.*, **168**, 1075-1080.
- 154 Osburn CL, O'Sullivan DW and Boyd TJ, 2009, Increases in the longwave photobleaching of chromophoric dissolved organic matter in coastal waters, *Limnol. Oceanogr.*, **54**, 145-159.
- 155 Osburn CL, Retamal L and Vincent WF, 2009, Photoreactivity of chromophoric dissolved organic matter transported by the Mackenzie River to the Beaufort Sea, *Mar. Chem.*, **115**, 10-20.
- 156 Outridge PM, Macdonald RW, Wang F, Stern GA and Dastoor AP, 2008, A mass balance inventory of mercury in the Arctic Ocean, *Environ. Chem.*, **5**, 89-111.
- 157 Palmer CJ and Reason CJ, 2009, Relationships of surface bromoform concentrations with mixed layer depth and salinity in the tropical oceans, *Glob. Biogeochem. Cycles*, **23**, 10.
- 158 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, *Sci. Technol.*, **315**, 361-364.
- 159 Peters SC, Wollenberg JL, Morris DP and Porter JA, 2007, Mercury emission to the atmosphere from experimental manipulation of DOC and UVR in mesoscale field chambers in a freshwater lake, *Environ. Sci. Technol.*, **41**, 7356-7362.
- 160 Piao SL, Ciais P, Friedlingstein P, Peylin P, Reichstein M, Luysaert S, Margolis H, Fang JY, Barr A, Chen AP, Grelle A, Hollinger DY, Laurila T, Lindroth A, Richardson AD and Vesala T, 2008, Net carbon dioxide losses of northern ecosystems in response to autumn warming, *Nature*, **451**, 49-U43.
- 161 Piccini C, Conde D, Pernthaler J and Sommaruga R, 2009, Alteration of chromophoric dissolved organic matter by solar UV radiation causes rapid changes in bacterial community composition, *Photochem. Photobiol. Sci.*, **8**, 1321-1328.
- 162 Quay P, Sonnerup R, Stutsman J, Maurer J, Kortzinger A, Padin XA and Robinson C, 2007, Anthropogenic CO₂ accumulation rates in the North Atlantic Ocean from changes in the C¹³/C¹² of dissolved inorganic carbon, *Glob. Biogeochem. Cycles*, **21**, GB1009.
- 163 Raivonen M, Bonn B, Sanz MJ, Vesala T, Kulmala M and Hari P, 2006, UV-induced NO_y emissions from Scots pine: Could they originate from photolysis of deposited HNO₃?, *Atmos. Environ.*, **40**, 6201-6213.
- 164 Raivonen M, Vesala T, Pirjola L, Altimir N, Keronen P, Kulmala M and Hari P, 2009, Compensation point of NO_x exchange: Net result of NO_x consumption and production, *Agric. Forest Meteorol.*, **149**, 1073-1081.

- 165 Ram K and Anastasio C, 2009, Photochemistry of phenanthrene, pyrene, and fluoranthene in ice and snow, *Atmos. Environ.*, **43**, 2252-2259.
- 166 Ravishankara AR, Daniel JS and Portmann RW, 2009, Nitrous Oxide (N₂O): The Dominant Ozone-Depleting Substance Emitted in the 21st Century, *Science.*, **326**, 123-125.
- 167 Rhew RC, Teh YA and Abel T, 2007, Methyl halide and methane fluxes in the northern Alaskan coastal tundra, *J. Geophys. Res. Biogeosci.*, **112**, G02009.
- 168 Ricciuto DM, Davis KJ and Keller K, 2008, A Bayesian calibration of a simple carbon cycle model: The role of observations in estimating and reducing uncertainty, *Glob. Biogeochem. Cycles*, **22**, GB2030.
- 169 Riggsbee JA, Orr CH, Leech DM, Doyle MW and Wetzel RG, 2008, Suspended sediments in river ecosystems: Photochemical sources of dissolved organic carbon, dissolved organic nitrogen, and adsorptive removal of dissolved iron, *J. Geophys. Res. Biogeosci.*, **113**, 12.
- 170 Rodriguez-Roman A, Hernandez-Pech X, Thome PE, Enriquez S and Iglesias-Prieto R, 2006, Photosynthesis and light utilization in the Caribbean coral *Montastraea faveolata* recovering from a bleaching event, *Limnol. Oceanogr.*, **51**, 2702-2710.
- 171 Rodriguez-Zuniga UF, Milori D, Da Silva WTL, Martin-Neto L, Oliveira LC and Rocha JC, 2008, Changes in optical properties caused by UV-irradiation of aquatic humic substances from the amazon river basin: Seasonal variability evaluation, *Environ. Sci. Technol.*, **42**, 1948-1953.
- 172 Rosskopf EN, Gerik JS, Kokalis-Burelle N, Church GT and McSorley B, 2007, Status of methyl bromide alternatives for ornamental crop production in Florida and California, *Phytopathology.*, **97**, S101-S101.
- 173 Sanhueza E, 2007, Methane soil-vegetation-atmosphere fluxes in tropical ecosystems, *Interciencia*, **32**, 30-34.
- 174 Schmittner A, Oschlies A, Matthews HD and Galbraith ED, 2008, Future changes in climate, ocean circulation, ecosystems, and biogeochemical cycling simulated for a business-as-usual CO₂ emission scenario until year 4000 AD, *Glob. Biogeochem. Cycles*, **22**, GB1013.
- 175 Schwarzenbach RP, Escher BI, Fenner K, Hofstetter TB, Johnson CA, von Gunten U and Wehrli B, 2006, The challenge of micropollutants in aquatic systems, *Science.*, **313**, 1072-1077.
- 176 Setlow RB, 1974, The wavelengths in sunlight effective in producing skin cancer: A theoretical analysis, *Proc. Nat. Acad. Sci. USA*, **71**, 3363-3366.
- 177 Shank GC, Nelson K and Montagna PA, 2009, Importance of CDOM distribution and photoreactivity in a shallow Texas estuary, *Estuaries Coasts*, **32**, 661-677.
- 178 Shank GC, Whitehead RF, Smith ML, Skrabal SA and Kieber RJ, 2006, Photodegradation of strong copper-complexing ligands in organic-rich estuarine waters, *Limnol. Oceanogr.*, **51**, 884-892.
- 179 Sharpatyi VA, 2007, On the mechanism of methane emission by terrestrial plants, *Oxidat. Comm.*, **30**, 48-50.
- 180 Sherman LS, Blum JD, Johnson KP, Keeler GJ, Barres JA and Douglas TA, 2010, Mass-independent fractionation of mercury isotopes in Arctic snow driven by sunlight, *Nat. Geosci.*, **3**, 173-177.
- 181 Shi DL, Xu Y, Hopkinson BM and Morel FMM, 2010, Effect of ocean acidification on iron availability to marine phytoplankton, *Science.*, **327**, 676-679.
- 182 Shindell DT, Faluvegi G, Koch DM, Schmidt GA, Unger N and Bauer SE, 2009, Improved attribution of climate forcing to emissions, *Science.*, **326**, 716-718.

- 183 Slezak D, P. KR, Toole DA, R. S and Kieber DJ, 2007, Effects of solar radiation on the fate of dissolved DMSP and conversion to DMS in seawater, *Aquat. Sci.*, **69**, 377-393.
- 184 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.
- 185 Sobrino C, Ward ML and Neale PJ, 2008, Acclimation to elevated carbon dioxide and ultraviolet radiation in the diatom *Thalassiosira pseudonana*: Effects on growth, photosynthesis, and spectral sensitivity of photoinhibition, *Limnol. Oceanogr.*, **53**, 494-505.
- 186 Sparks JP, 2009, Ecological ramifications of the direct foliar uptake of nitrogen, *Oecologia*, **159**, 1-13.
- 187 Spencer RGM, Aiken GR, Butler KD, Dornblaser MM, Striegl RG and Hernes PJ, 2009, Utilizing chromophoric dissolved organic matter measurements to derive export and reactivity of dissolved organic carbon exported to the Arctic Ocean: A case study of the Yukon River, Alaska, *Geophys. Res. Lett.*, **36**, L06401.
- 188 Stedmon CA, Markager S, Tranvik L, Kronberg L, Slatis T and Martinsen W, 2007, Photochemical production of ammonium and transformation of dissolved organic matter in the Baltic Sea, *Mar. Chem.*, **104**, 227-240.
- 189 Steinacher M, Joos F, Frolicher TL, Plattner GK and Doney SC, 2009, Imminent ocean acidification in the Arctic projected with the NCAR global coupled carbon cycle-climate model, *Biogeosci.*, **6**, 515-533.
- 190 Stroeve J, Holland MM, Maier W, Scambos T and Serreze M, 2007, Arctic ice decline: Faster than forecast, *Geophys. Res. Lett.*, **34**, L09501.
- 191 Stubbins A, Hubbard V, Uher G, Law CS, Upstill-Goddard RC, Aiken GR and Mopper K, 2008, Relating carbon monoxide photoproduction to dissolved organic matter functionality, *Environ. Sci. Technol.*, **42**, 3271-3276.
- 192 Stubbins A, Uher G, Law CS, Mopper K, Robinson C and Upstill-Goddard RC, 2006, Open-ocean carbon monoxide photoproduction, *Deep Sea Res. Part II: Top. Stud. Oceanogr.*, **53**, 1695-1705.
- 193 Stubbins A, Uhera G, Kitidis V, Law CS, Upstill-Goddard RC and Woodward EMS, 2006, The open-ocean source of atmospheric carbon monoxide, *Deep Sea Res. Part II: Top. Stud. Oceanogr.*, **53**, 1685-1694.
- 194 Sulzberger B and 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.
- 195 Sunda WG, 2010, Iron and the carbon pump, *Science.*, **327**, 654-655.
- 196 Sunda WG and Hardison DR, 2008, Contrasting seasonal patterns in dimethylsulfide, dimethylsulfoniopropionate, and chlorophyll a in a shallow North Carolina estuary and the Sargasso Sea, *Aquat. Microb. Ecol.*, **53**, 281-294.
- 197 Sunda WG, Hardison R, Kiene RP, Bucciarelli E and Harada H, 2007, The effect of nitrogen limitation on cellular DMSP and DMS release in marine phytoplankton: Climate feedback implications, *Aquat. Sci.*, **69**, 341-351.
- 198 Sunderland EM, Krabbenhoft DP, Moreau JW, Strode SA and Landing WM, 2009, Mercury sources, distribution, and bioavailability in the North Pacific Ocean: Insights from data and models, *Glob. Biogeochem. Cycles*, **23**, GB2010.
- 199 Swan CM, Siegel DA, Nelson NB, Carlson CA and Nasir E, 2009, Biogeochemical and hydrographic controls on chromophoric dissolved organic matter distribution in the Pacific Ocean, *Deep Sea Res. Part I: Oceanog. Res. Pap.*, **56**, 2175-2192.

- 200 Teh YA, Mazeas O, Atwood AR, Abel T and Rhew RC, 2009, Hydrologic regulation of gross methyl chloride and methyl bromide uptake from Alaskan Arctic tundra, *Glob. Change Biol.*, **15**, 330-345.
- 201 Thomas H, Prowse AEF, Lima ID, Doney SC, Wanninkhof R, Greatbatch RJ, Schuster U and Corbiere A, 2008, Changes in the North Atlantic Oscillation influence CO₂ uptake in the North Atlantic over the past 2 decades, *Glob. Biogeochem. Cycles*, **22**, 13.
- 202 Thomas H, Prowse AEF, van Heuven S, Bozec Y, de Baar HJW, Schiettecatte LS, Suykens K, Kone M, Borges AV, Lima ID and Doney SC, 2007, Rapid decline of the CO₂ buffering capacity in the North Sea and implications for the North Atlantic Ocean, *Glob. Biogeochem. Cycles*, **21**, 13.
- 203 Throop HL and Archer SR, 2007, Interrelationships among shrub encroachment, land management, and litter decomposition in a semidesert grassland, *Ecol. Appl.*, **17**, 1809-1823.
- 204 Tiiva P, Rinnan R, Faubert P, Rasanen 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.
- 205 Toggweiler JR, 2009, Shifting westerlies, *Science*, **323**, 1434-1435.
- 206 Tolli JD and Taylor CD, 2005, Biological CO oxidation in the Sargasso Sea and in Vineyard Sound, Massachusetts, *Limnol. Oceanogr.*, **50**, 1205-1212.
- 207 Trevena AJ and Jones GB, 2006, Dimethylsulphide and dimethylsulphoniopropionate in Antarctic sea ice and their release during sea ice melting, *Mar. Chem.*, **98**, 210-222.
- 208 Tzortziou M, Neale PJ, Osburn CL, Megonigal JP, Maie N and Jaffe R, 2008, Tidal marshes as a source of optically and chemically distinctive colored dissolved organic matter in the Chesapeake Bay, *Limnol. Oceanogr.*, **53**, 148-159.
- 209 Vähätalo AV and Jarvinen M, 2007, Photochemically produced bioavailable nitrogen from biologically recalcitrant dissolved organic matter stimulates production of a nitrogen-limited microbial food web in the Baltic Sea, *Limnol. Oceanogr.*, **52**, 132-143.
- 210 Vähätalo AV and Wetzel RG, 2008, Long-term photochemical and microbial decomposition of wetland-derived dissolved organic matter with alteration of C¹³:C¹² mass ratio, *Limnol. Oceanogr.*, **53**, 1387-1392.
- 211 van Dongen BE, Zencak Z and Gustafsson Ö, 2008, Differential transport and degradation of bulk organic carbon and specific terrestrial biomarkers in the surface waters of a sub-arctic brackish bay mixing zone, *Mar. Chem.*, **112**, 203-314.
- 212 Vione D, Lauri V, Minero C, Maurino V, Malandrino M, Carlotti ME, Olariu RI and Arsene C, 2009, Photostability and photolability of dissolved organic matter upon irradiation of natural water samples under simulated sunlight, *Aquat. Sci.*, **71**, 34-45.
- 213 Vonk JE, van Dongen BE and Gustafsson Ö, 2008, Lipid biomarker investigation of the origin and diagenetic state of sub-arctic terrestrial organic matter presently exported into the northern Bothnian Bay, *Mar. Chem.*, **112**, 1-10.
- 214 Wang JX, Li RJ, Guo YY, Qin P and Sun SC, 2006, The flux of methyl chloride along an elevational gradient of a coastal salt marsh, Eastern China, *Atmos. Environ.*, **40**, 6592-6605.
- 215 Wang JX, Li RJ, Guo YY, Qin P and Sun SC, 2006, Removal of methyl chloroform in a coastal salt marsh of eastern China, *Chemosphere*, **65**, 1371-1380.
- 216 Watanabe YW, Yoshinari H, Sakamoto A, Nakano Y, Kasamatsu N, Midorikawa T and Ono T, 2007, Reconstruction of sea surface dimethylsulfide in the North Pacific during 1970s to 2000s, *Mar. Chem.*, **103**, 347-358.

- 217 Whalin L, Kim E-H and Mason R, 2007, Factors influencing the oxidation, reduction, methylation and demethylation of mercury species in coastal waters, *Mar. Chem.*, **107**, 278-294.
- 218 Wiegner TN, Tubal RL and MacKenzie RA, 2009, Bioavailability and export of dissolved organic matter from a tropical river during base- and -stormflow conditions, *Limnol. Oceanogr.*, **54**, 1233-1242.
- 219 Willey JD, Kieber RJ, Seaton PJ and Miller C, 2008, Rainwater as a source of Fe(II)-stabilizing ligands to seawater, *Limnol. Oceanogr.*, **53**, 1678-1684.
- 220 Williams MB, Aydin M, Tatum C and Saltzman ES, 2007, A 2000 year atmospheric history of methyl chloride from a South Pole ice core: Evidence for climate controlled variability, *Geophys. Res. Lett.*, **34**, L07811.
- 221 Williamson CE, De Lange HJ and Leech DM, 2007, Do zooplankton contribute to an ultraviolet clear-water phase in lakes?, *Limnol. Oceanogr.*, **52**, 662-667.
- 222 Winter TR and Rostas M, 2008, Ambient ultraviolet radiation induces protective responses in soybean but does not attenuate indirect defense, *Environ. Pollut.*, **155**, 290-297.
- 223 Wishkerman A, Gebhardt S, McRoberts CW, Hamilton JTG, Williams J and Keppler F, 2008, Abiotic methyl bromide formation from vegetation, and its strong dependence on temperature, *Environ. Sci. Technol.*, **42**, 6837-6842.
- 224 Witherow RA and Lyons WB, 2008, Mercury deposition in a polar desert ecosystem, *Environ. Sci. Technol.*, **42**, 4710-4716.
- 225 Wuebbles DJ, 2009, Nitrous oxide: No laughing matter, *Science*, **326**, 56-57.
- 226 Xie HX, Belanger S, Demers S, Vincent WF and Papakyriakou TN, 2009, Photobiogeochemical cycling of carbon monoxide in the southeastern Beaufort Sea in spring and autumn, *Limnol. Oceanogr.*, **54**, 234-249.
- 227 Xie HX and Zafiriou OC, 2009, Evidence for significant photochemical production of carbon monoxide by particles in coastal and oligotrophic marine waters, *Geophys. Res. Lett.*, **36**, 5.
- 228 Yool A, Martin AP, Fernandez C and Clark DR, 2007, The significance of nitrification for oceanic new production, *Nature*, **447**, 999-1002.
- 229 Zafiriou OC, Xie HX, Nelson NB, Najjar RG and Wang W, 2008, Diel carbon monoxide cycling in the upper Sargasso Sea near Bermuda at the onset of spring and in midsummer, *Limnol. Oceanogr.*, **53**, 835-850.
- 230 Zeebe RE, Zachos JC, Caldeira K and Tyrrell T, 2008, Oceans - Carbon emissions and acidification, *Science*, **321**, 51-52.
- 231 Zepp RG, Callaghan TV and Erickson DJ, 2003, Interactive effects of ozone depletion and climate change on biogeochemical cycles, *Photochem. Photobiol. Sci.*, **2**, 51-61.
- 232 Zepp RG, Erickson DJ, III, Paul ND and Sulzberger B, 2007, Interactive effects of solar UV radiation and climate change on biogeochemical cycling, *Photochem. Photobiol. Sci.*, **6**, 286-700.
- 233 Zepp RG, Shank GC, Stabenau E, Patterson KW, Cyterski M, Fisher W, Bartels E and 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.
- 234 Zhang YL, Liu ML, Qin BQ and Feng S, 2009, Photochemical degradation of chromophoric-dissolved organic matter exposed to simulated UV-B and natural solar radiation, *Hydrobiologia*, **627**, 159-168.
- 235 Zickfeld K, Eby M and Weaver AJ, 2008, Carbon-cycle feedbacks of changes in the Atlantic meridional overturning circulation under future atmospheric CO₂, *Glob. Biogeochem. Cycles*, **22**, GB3024.

Chapter 6. Changes in air quality and tropospheric composition due to depletion of stratospheric ozone and interactions with climate

X. Tang^a, S. R. Wilson^b, K. R. Solomon^c, M. Shao^a, and S. Madronich^d

^a *Peking University, College of Environmental Science and Engineering, Beijing 100871, China*

^b *School of Chemistry, University of Wollongong, NSW, 2522, Australia*

^c *Centre for Toxicology and School of Environmental Sciences, University of Guelph, ON, N1G 2W1, Canada*

^d *Atmospheric Chemistry Division, National Center for Atmospheric Research, Boulder, Colorado, 80307, USA*

Summary

Air pollution will be directly influenced by future changes in emissions of pollutants, climate, and stratospheric ozone, and will have significant consequences for human health and the environment. UV radiation is one of the controlling factors for the formation of photochemical smog, which includes tropospheric ozone (O₃) and aerosols; it also initiates the production of hydroxyl radicals (·OH), which control the amount of many climate- and ozone-relevant gases (e.g., methane and HCFCs) in the atmosphere. Numerical models predict that future changes in UV radiation and climate will modify the trends and geographic distribution of ·OH, thus affecting the formation of photochemical smog in many urban and regional areas. Concentrations of ·OH are predicted to decrease globally by an average of 20% by 2100, with local concentrations varying by as much as a factor of two above and below current values. However, significant differences between modelled and measured values in a limited number of case studies show that chemistry of hydroxyl radicals in the atmosphere is not fully understood. Photochemically produced tropospheric ozone is projected to increase. If emissions of anthropogenic air pollutants from combustion of fossil fuels, burning of biomass, and agricultural activities continue to increase, concentrations of tropospheric O₃ will tend to increase over the next 20-40 years in certain regions of low and middle latitudes because of interactions of emissions, chemical processes, and climate change. Climate-driven increases in temperature and humidity will also increase production of tropospheric O₃ in polluted regions, but reduce it in more pristine regions. Higher temperatures tend to increase emissions of nitrogen oxides (NO_x) from some soils and release of biogenic volatile organic compounds (VOCs) from vegetation, leading to greater background concentrations of ozone in the troposphere. The net effects of future changes in UV radiation, meteorological conditions, and anthropogenic emissions may be large, thus posing challenges for prediction and management of air quality. Aerosols composed of organic substances have a major role in both climate and air quality, and contribute a large uncertainty to the energy budget of the atmosphere. These aerosols are mostly formed via the UV-initiated oxidation of VOCs from anthropogenic and biogenic sources, although the details of the chemistry are still poorly understood and current models under-predict their abundance. A better understanding of their formation, chemical composition, and optical properties is required to assess their significance for air quality and to better quantify their direct and indirect radiative forcing of climate. Emissions of compounds containing fluorine will continue to have effects on the chemistry of the atmosphere and on climate change. The HCFCs and HFCs used as substitutes for ozone-depleting CFCs can break down into trifluoroacetic acid (TFA), which will accumulate in the oceans, salt lakes, and playas. Based on historical use and projections of future uses, includ-

ing new products entering the market, such as the fluoro-olefins, increased loadings of TFA in these environmental sinks will be small. Even when added to existing amounts from natural sources, risks to humans or the environment from the historical use of CFCs or continued use of their replacements is judged to be negligible.

Introduction

Poor air quality (from the presence of pollutants in the atmosphere) plays a significant role in both human and environmental health. Globally, outdoor air pollution is estimated to lead to 850,000 premature deaths each year, mostly from respiratory and cardiovascular diseases.^{75, 108} The cost of crop damage in the U.S. was estimated between 3.5 and 6.1 billion dollars annually.⁷⁰ These problems are expected to continue well into the future: Predictions based on numerical models indicate that annual deaths due to ground-level oxidants alone could reach 2 million in 2050,⁸⁸ while the annual cost of crop damage is predicted to be of the order of US\$20 billion by 2030.⁹⁸ Variations in stratospheric ozone and climate change are important drivers of changes in the production and fate of air pollutants.

Solar UV-B radiation (280 – 315 nm) and UV-A (315 – 400 nm) provide the energy for many of the chemical transformations that occur in the atmosphere. These wavelengths photo-dissociate (break down via photolysis) a number of important atmospheric gases, e.g. nitrogen dioxide (NO₂), formaldehyde (HCHO), and ozone (O₃). These processes will be altered by anything that changes the amount of UV radiation, including the elevation of the sun and attenuation by clouds and some air pollutants. Decreases in stratospheric ozone lead to enhanced UV-B radiation in the lower atmosphere (troposphere), and increase the rate of the photolytic processes.¹⁰⁶ Increasing temperature from climate change also increases the rates of many reactions, leading to higher concentrations of surface O₃ in polluted regions, and causing increments in mortality that could exceed those resulting from climate-related increase in storminess.⁴³ As a result, there is a direct link between stratospheric ozone depletion, climate change, and air quality.

The replacements for the original ozone-depleting chemicals (chlorofluorocarbons (CFCs)), such as the hydrochlorofluorocarbons (HCFCs) and the hydrofluorocarbons (HFCs), decompose primarily in the lower atmosphere. This decomposition can produce breakdown products, such as trifluoroacetic acid, that need to be considered for their impacts on humans and the environment.¹⁰⁶

Here we present an assessment of recent work on our understanding of the impacts of ozone depletion, ozone depleting chemicals and their replacements on atmospheric composition and how these may interact with climate change to adversely affect the environment and human health. This is an update of the information in the previous report.¹⁰⁶

Photochemistry in the troposphere

Solar UV radiation is a major driver of tropospheric chemistry, causing photo-dissociation of various relatively stable molecules into more reactive fragments. These fragments initiate a series of chemical reactions that fundamentally change the composition of the atmosphere at all scales, from urban to regional to global, and affect many environmental issues including air quality, visibility, formation of particles and clouds, acidification of precipitation, and lifetimes of removal from the atmosphere of gases including sulfur and nitrogen oxides, methane, and other volatile organic compounds (VOCs), as well as HFCs and HCFCs that affect the ozone layer and climate.

A simplified schematic of tropospheric chemistry is given in Fig. 6-1. The key initiating reaction is the interaction of tropospheric O_3 with UV photons (shown as $h\nu$ in Fig. 6-1) leading to the photo-dissociation, or photolysis, of O_3 to produce electronically excited oxygen atoms, $O(^1D)$, and molecular oxygen O_2 (Fig. 6-1, reaction 1). A fraction of $O(^1D)$ atoms can react with atmospheric water vapour, H_2O , to form hydroxyl radicals, $\cdot OH$ (Fig. 6-1, reaction 2).

As shown in Table 1-1 in Chapter 1, for each percent decrease in the ozone column amount, the rate coefficient for reaction 1 (Fig. 6-1) increases by ca 1.5%. This non-linear response means that tropospheric chemistry is very sensitive to the amounts of stratospheric ozone. This has been a clear stress point for change in stratospheric ozone as changes in concentration of $\cdot OH$, globally averaged, could have significant impacts on the chemical composition of the atmosphere.

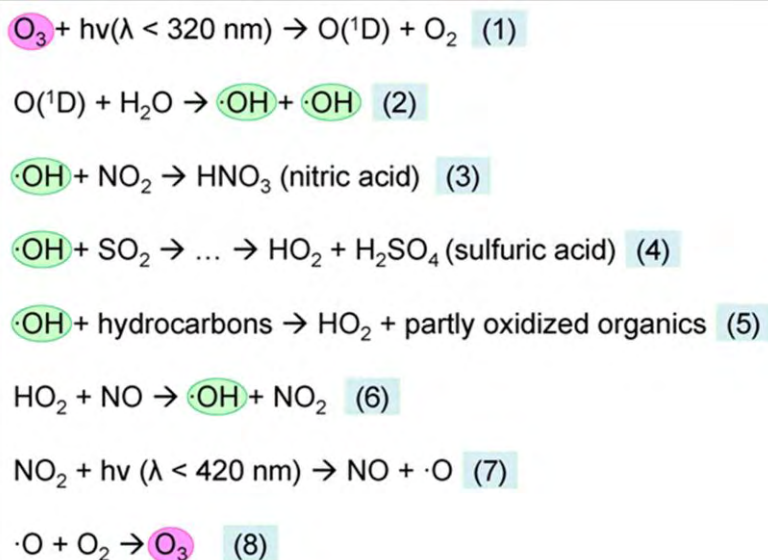


Fig. 6-1. Key reactions in the chemistry of air pollutants in the troposphere.

The hydroxyl radical is widely regarded as the cleaning agent of the atmosphere because it converts many atmospheric chemicals, including major air pollutants, into forms that are more water-soluble and therefore more easily removed from the atmosphere in precipitation. For example, $\cdot OH$ reacts with nitrogen and sulphur dioxides to make the corresponding nitric and sulfuric acids, and with hydrocarbons and other VOCs to make a variety of partly oxidized organics (aldehydes, alcohols, ketones, etc.) (Fig. 6-1, reactions 3-5). Many of the reactions involve multiple steps including catalytic cycles.⁶⁷

Some of these gaseous products tend to have low vapour pressures and thus can condense to form air-borne particles (solid and liquid aerosols), with associated reductions in transparency of the atmosphere and damage to human health, especially in highly polluted urban areas. The hydroperoxy radical (HO_2) and its organic analogues, produced in the above reactions, are also the major source of tropospheric ozone, via the sequence shown in Fig. 6-1, reactions 6-8.

UV-B radiation is important for the initial production of $\cdot OH$ radicals (reaction 1 followed by reaction 2, Fig. 6-1), while UV-A radiation is important for the formation of ambient ozone (reaction 7 followed by reaction 8, Fig. 6-1). Although not shown in the simplified scheme of Fig. 6-1, the UV photolysis of several other molecules also can be important in specific environments, e.g., formaldehyde and nitrous acid in urban areas, peroxides in more pristine areas, and ketones in the upper troposphere.

In addition to UV radiation, other factors also influence the amounts of $\cdot OH$, O_3 , and aerosols in the atmosphere. These include emission of nitrogen oxides ($NO_x = NO + NO_2$) and VOCs, temperature, water vapour, and meteorological transport and mixing processes, some of which are also influenced by changes in climate.

Hydroxyl radicals in the atmosphere – a product of photolysis by UV

The UV-generated hydroxyl radical, $\cdot\text{OH}$, is central to the chemistry of the troposphere, as discussed above; yet accurate measurements of its amounts in the atmosphere are extremely challenging both to perform and to interpret. The measurement difficulty arises because $\cdot\text{OH}$ is highly reactive and therefore present in very small amounts, typically less than one part per trillion (ppt, equal to one $\cdot\text{OH}$ molecule for every trillion air molecules). Several techniques for $\cdot\text{OH}$ measurement have been developed and refined in recent years, and comparisons among them show that they are highly correlated, but calibration of such measurements remains an issue⁸⁵ causing considerable uncertainty in absolute measurements of concentrations of $\cdot\text{OH}$.

The very short lifetime (< 1 s) also means that the concentration of $\cdot\text{OH}$ is very variable, both in space and in time. This makes the interpretation of measurements difficult because amounts of $\cdot\text{OH}$ measured at any location or time are unlikely to be representative of large geographic scales (e.g. regional, continental, hemispheric, or global), of vertical distributions (near-surface vs. middle and upper troposphere), or of temporal variations (daytime vs. night-time, seasonal cycles, etc.). Thus, even if the uncertainty of direct $\cdot\text{OH}$ measurements were reduced, such measurements would not be useful for assessing global changes in $\cdot\text{OH}$ concentrations (and the associated long-term changes in the global atmospheric self-cleaning ability), as a result of trends in UV radiation due to depletion of O_3 , climate change, or increased global pollution.

Alternative less direct methods for inferring globally averaged concentrations of $\cdot\text{OH}$ rely on observations of long-term changes in the concentrations of compounds whose lifetimes are determined by $\cdot\text{OH}$ radicals. A compound frequently used for this purpose is methyl chloroform, an industrial solvent present in the atmosphere. Methyl chloroform is anthropogenically produced and is removed from the atmosphere mainly by reaction with $\cdot\text{OH}$. In principle, the measurement of the amount of methyl chloroform in the atmosphere, coupled with self-reported estimates of the amount emitted by industry into the atmosphere should allow the global average concentration of $\cdot\text{OH}$ and any changes to be estimated. However, such estimates have differed, depending on details of the analysis (e.g.,^{5, 79}). A recent assessment of the global concentration of $\cdot\text{OH}$ ¹⁰³ determined from methyl chloroform warns that the uncertainties in quantifying the transport of compounds through the atmosphere could limit the ability of this method to detect changes in $\cdot\text{OH}$. New developments in modelling a range of chemicals simultaneously in the atmosphere⁷⁸ and the addition of long-term records of volatile organic compounds³² offer opportunities to reduce some of these modelling limitations in the future.

Possible changes in $\cdot\text{OH}$ since pre-industrial times have been summarized recently.³⁸
³⁹ No reliable observational proxies are known for such long-term changes, requiring reliance on atmospheric chemistry-transport models and assumptions about historical emissions of the compounds that affect $\cdot\text{OH}$, especially nitrogen oxides (which tend to increase $\cdot\text{OH}$) and VOCs (which tend to decrease $\cdot\text{OH}$). The production of $\cdot\text{OH}$ in the atmosphere is estimated to have increased by 60 to 70% in the last century, approximately compensating for increases in the rate of removal.^{53, 105} Depending on the model and assumptions used, concentrations of $\cdot\text{OH}$ may have decreased by less than 10% or as much as 33% since pre-industrial times.

More recent changes in $\cdot\text{OH}$ in the last few decades have been influenced by varying emissions of precursors, changes in tropospheric UV radiation associated with stratospheric O_3 depletion, as well as interannual variability. The global concentration of $\cdot\text{OH}$ due to changes in atmospheric composition has been calculated to have decreased⁵¹ (0.8% per dec-

ade over 1890 – 1990) and to have increased¹⁵ (0.8% per decade over 1990 – 2001), with a high degree of uncertainty.⁴⁰ From a UV perspective, $\cdot\text{OH}$ has been calculated to have increased by 3.5% due solely to depletion of stratospheric ozone⁹⁰, although this trend is expected to reverse in future decades as stratospheric O_3 returns to pre-1980 levels (see Chapter 1).

The future of $\cdot\text{OH}$ in the atmosphere depends on a wide range of factors. As an example of possible changes, Wild and Palmer¹⁰⁵ have taken a scenario (SRES A2p)⁷¹ where, in 2100, the emission of VOCs, NO_x , CO, and methane has approximately doubled over 2000 levels. However, the meteorology and stratospheric ozone is held constant so that the results can isolate the impact of emissions. Under these conditions, the photochemically generated ozone increases also by a factor closer to two. The $\cdot\text{OH}$ concentration, as shown in Fig. 6-2, varies also by a factor of two, but with both significant increases and decreases. The net change in $\cdot\text{OH}$ is a 20% reduction of its global concentration. However, this change is likely to be reduced by climate change (increases in temperature and humidity). Isaksen et al.⁴⁰ similarly conclude that the competing nature of the effects makes the overall trend of $\cdot\text{OH}$ in the future unclear. Future changes in UV-B radiation will modify both the trends and distribution of $\cdot\text{OH}$ in the troposphere. Global-scale reductions in $\cdot\text{OH}$ would have considerable implications for the concentrations of many climate- and ozone-relevant gases in the atmosphere, e.g., if $\cdot\text{OH}$ is reduced by 20%, methane and HCFCs concentrations would increase by about 20% even if their emissions were held constant.

Direct measurements of $\cdot\text{OH}$ can be useful for testing current understanding of photochemistry on short time scales, especially when ancillary observations (e.g., of UV radiation, temperature, humidity, O_3 , NO_x , carbon monoxide, and VOCs) are available. Over the past several decades, a general understanding has been developed of the processes that control formation of $\cdot\text{OH}$ and its destruction (e.g.,^{7, 22, 42, 87}). However, and due in part to the more advanced techniques for measuring $\cdot\text{OH}$ and related species (especially the closely coupled radicals HO_2 and RO_2), several recent studies have shown that, while some aspects of $\cdot\text{OH}$ chemistry are well understood, other aspects remain unexplained. Measurements in both polluted regions³⁶ and in unpolluted rainforest⁵² show concentrations of $\cdot\text{OH}$ that are several times higher than those expected using accepted chemical pathways – see red and green (upper and middle) arrows in Fig. 6-3. The higher concentration of $\cdot\text{OH}$ is suspected to stem from enhanced regeneration of $\cdot\text{OH}$ by currently unidentified atmospheric compounds indicated by the yellow (lower) arrows in Fig. 6-3. Direct measurements of the total reactivity of $\cdot\text{OH}$ radicals also suggest a faster loss of $\cdot\text{OH}$ than would be computed from the sum of all individually measured compounds known to react with $\cdot\text{OH}$.^{11, 61} Similar problems exist with the hydroperoxyl radical HO_2 , which, in urban

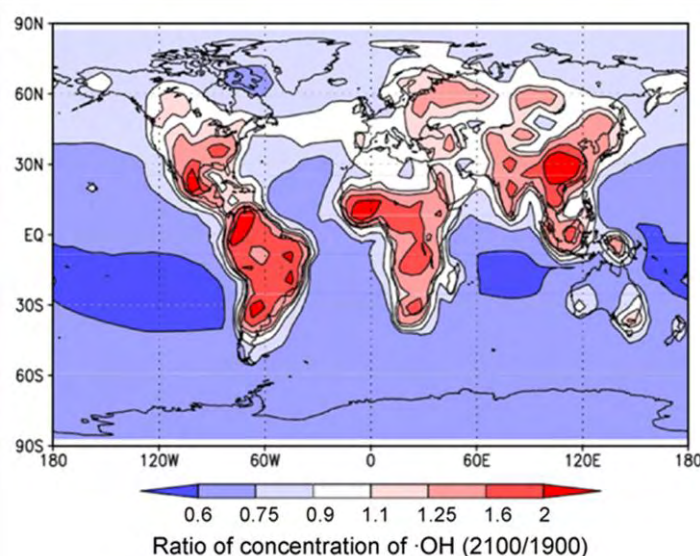


Fig. 6-2. Ratio of the concentration of $\cdot\text{OH}$ in 2100 to that calculated in 1900 at the surface (from¹⁰⁵).

environments with high concentrations of NO_x, is observed at much higher concentrations than predicted by models (e.g.,¹⁹).

These recently discovered discrepancies remain largely unexplained and are not yet considered in global chemistry-transport models (e.g., those reviewed by IPCC 2007³⁹) used to estimate past, current, and future trends of $\cdot\text{OH}$. It is unclear to what extent the new chemical pathways, when finally unravelled and quantified, will change these estimates, and further studies will clearly be needed to re-evaluate how tropospheric $\cdot\text{OH}$ is responding to changes in stratospheric O₃, climate, and emissions of air pollutants.

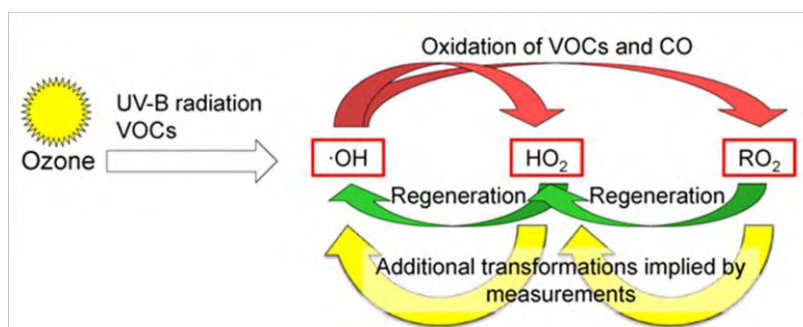


Fig. 6-3. Proposed changes in the chemistry of $\cdot\text{OH}$ in the atmosphere. The red (upper) and green (middle) arrows summarize the accepted reactions in a polluted atmosphere³⁶ and the yellow (lower) arrows show the additional transformations, implied by measurements, for regenerating $\cdot\text{OH}$. VOC = volatile organic compounds, CO = carbon monoxide, $\cdot\text{OH}$ = hydroxyl radical, HO_2 = hydroperoxy radical, RO_2 = organic peroxy radicals.

Tropospheric ozone

Tropospheric O₃ is one of the most important regional-scale air pollutants, causing adverse effects on respiratory health of humans,^{31, 75, 108} and decreases in crop production.^{25, 27} About 5-10% of the total atmospheric ozone column resides in the troposphere. Stratospheric ozone can affect the quality of air at ground level directly by transport from the stratosphere and indirectly via changes in photochemical processes.⁴¹ The transport of stratospheric ozone and photochemistry within the troposphere can be significantly modified by increased temperatures and humidity resulting from climate change, through changes in atmospheric circulation (including changes in stratosphere-troposphere exchange), changes in the hydrological cycle, and changes in emissions of precursors of air pollutants.

The environmental impact of increases in ozone at ground level is widely acknowledged.⁹⁶ The World Health Organization (WHO) recommended air quality guideline for protection of human health was reduced in 2005 to an 8-h time-weighted mean concentration of 50 parts per billion by volume (ppbv). WHO notes that O₃ from “natural causes” could occasionally exceed the guideline.¹⁰⁸ As a result, relatively small changes in ozone at ground level may have significant effects on measures of air quality through more frequent exceedences of the guideline.

Pre-industrial values of tropospheric O₃ were probably much lower than current values, especially in populated regions of the Northern Hemisphere.¹⁰⁰ Since the mid-1980s, concentrations of tropospheric O₃ in a number of locations have increased at rates of 0.3 to 0.5 ppbv per year, mostly as a result of anthropogenic activity.^{13, 27, 37} Such estimates are logically limited to sites where ground measurements exist. It would be better if more global estimates based on measurements from satellites were possible. These have been attempted using a number of satellites (e.g.,^{23, 56}), although this process is difficult as it involves measuring the relatively small amount of O₃ that lies below stratospheric O₃. New satellite-borne instrumentation and analyses are making significant advances in this area.^{49, 107} While the

satellite observations are most sensitive to O₃ in the mid troposphere (5 – 10 km above the surface), this method has the potential to provide significant information about ground level ozone levels.²⁴ Such information will be important in assessing the role of international impacts on regional air quality, an area of significant on-going research.⁸³

An analysis of air masses in the mid-troposphere (3–8 km above sea level) over western North America for the period 1995–2008, found significant increases in concentrations of O₃ (0.63 ± 0.34 ppbv per year) during the spring months.¹³ During spring, intercontinental transport of O₃ is most efficient, particularly in the prevailing westerlies between Asia and North America. Even greater increases in concentrations of O₃ (0.80 ± 0.34 ppb per year) were observed in air masses of Asian origin. This suggests that the rise in anthropogenic emissions of precursors to O₃ over Asia may be partly responsible for increases in tropospheric O₃ over western North America. This has significant implications for human and environmental health as well as for the impacts of climate change, either where the O₃ forms, or in regions to which O₃ might be transported.

UV radiation exerts a strong influence on the formation and destruction of tropospheric ozone, through the system of photochemical reactions shown in Fig. 6-1. Increases in UV radiation are expected to decrease concentrations of tropospheric O₃ in clean environments, but increase concentrations of O₃ in polluted, NO_x-rich environments.⁵⁵ Recent work has examined changes in UV radiation due to particulate pollutants (aerosols). Reduction of UV radiation in urban areas due to the presence of aerosols has been observed, and this has been found to reduce the rate of formation of ozone.^{10, 65}

Predicting future changes presents significant technical challenges, as there is a need to understand both global and small scale effects at the interface between the stratosphere and troposphere and at ground level. Models have been improved to limit the tendencies to simulate too rapid transport of ozone from the stratosphere to ground level.^{50, 73} Similarly, the impact of biases in temperature and humidity on modelled estimates of concentration of ozone has been estimated.⁷⁴ This work should improve confidence in performance of the models, although the importance of quantifying stratosphere-troposphere exchange reliably remains a challenge. In a number of regions in the northern hemisphere, an increase in temperature was found to be correlated with higher concentrations of ozone.¹⁷ While very useful as an indicator of likely atmospheric behaviour in a warming climate, such observations do not allow the assessment of the relative importance of other contributing factors.

Detailed numerical models based on projections to 2050 (Fig. 6-4) and beyond, predict concentrations of tropospheric O₃ to further increase up to 4 ppbv in the mid-latitudes because of climate change and interactions of climate change with atmospheric chemistry.²⁵ The drivers for this are a doubling of CO₂, an assumed 50% increase in emissions of isoprene from plant-cover, and a doubling of emissions of soil-derived NO_x in conjunction with releases from human activity,¹¹⁵ plants (see Chapter 3) and from the ocean.⁷² However, other models predict different geographical and temporal distributions of the changes in tropospheric O₃. For example, another study⁴⁴ shows maximum increases in O₃ occurring by 2030 in the Middle East and Europe, in contrast to the more widespread changes shown in Fig. 6-4C.

Predictions of changes in tropospheric O₃ at a regional scale depend on the interplay of several factors. Rising global emissions of anthropogenic air pollutants will tend to increase O₃. However, climatic factors resulting in greater humidity will lead to greater rates of destruction of O₃ in the tropics but not in the mid-latitudes, which are predicted to be drier.²⁷ Changes in precipitation and local circulation can also be significant.¹⁷ Increased temperatures of some soils can increase NO_x emissions, leading to increases in O₃.¹⁰⁹ Climate-

induced changes in atmospheric circulation may increase the stratosphere-to-troposphere O_3 flux, leading to long-term changes in both stratospheric and tropospheric O_3 . In addition, biogenic emissions are sensitive to other climate variables including temperature, CO_2 and solar radiation^{48, 112} and may affect future budgets of O_3 . As there is uncertainty in these predictions as well as in the interactions between O_3 and factors related to climate change, the final effects on O_3 in the troposphere and stratosphere are unclear and additional information will be needed to address this issue.

Changes in cloudiness could have a profound effect on both O_3 and $\cdot OH$, and atmospheric photochemistry in general. Numerical models indicate that clouds currently have only a modest impact on global O_3 averaged over the troposphere, due to the offset between shading below cloud and radiation enhancement above cloud (Fig. 6-5).^{101, 112} Regionally, however, the impact can be large, and climate variations could lead to both an increase or decrease in cloudiness. Changes in the vertical distributions of O_3 and $\cdot OH$ can also be large.⁵⁴

The impact on ground-level ozone of increased downward transport of stratospheric ozone due to the control of ozone-depleting substances under the Montreal Protocol and climate change has been estimated, assuming that there is no change in emissions into the atmosphere other than an assumed increase in greenhouse gases.¹¹⁴ For simplicity, photolysis has also been assumed to be unaffected by stratospheric ozone change. While there is a large increase in transport of ozone into the troposphere (43%), the climate model predicts little change in O_3 in the northern hemisphere at ground level. However, in the southern hemisphere winter, an increase of 8 ppbv of O_3 , which represents an increase of ca 50%, and little change in summer are predicted. This highlights the importance of including return of stratospheric ozone in estimates of future air quality. However, the magnitude of the overall changes will depend on the interplay of all the factors discussed here.

In contrast to the adverse direct effects of tropospheric O_3 on human health, in plants the physiological responses to future climate change (increased dryness and CO_2) will decrease uptake of O_3 , mitigating the impact

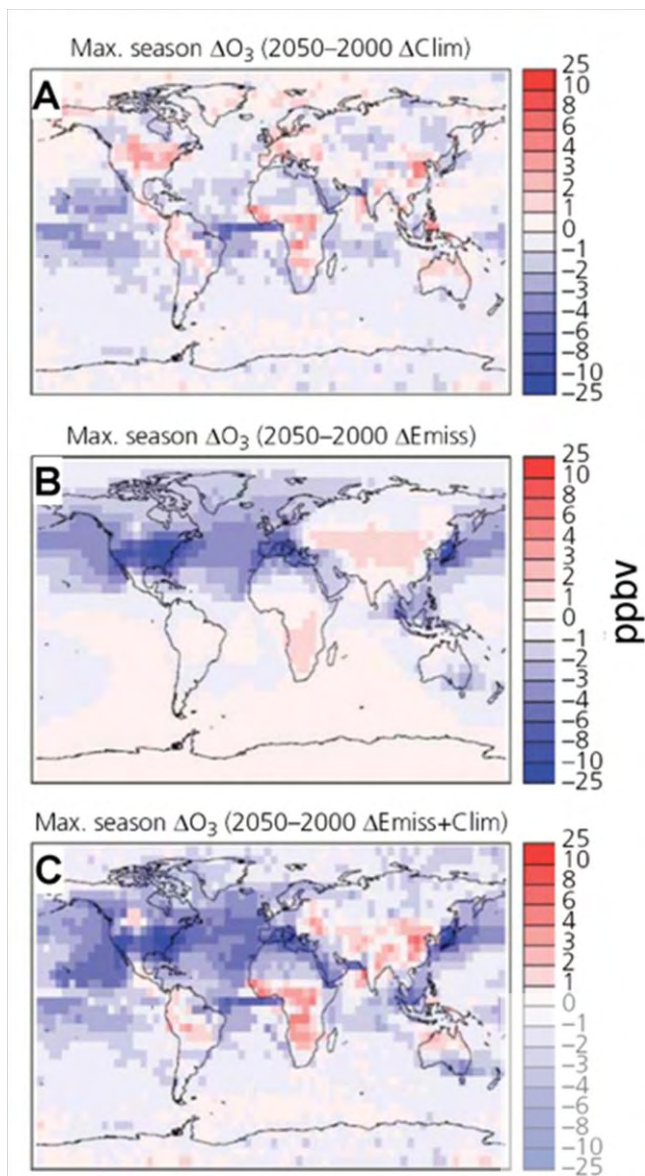


Fig. 6-4. Predicted changes in surface ozone between 2000 and 2050.²⁵ Panel A shows changes predicted for additional emissions of precursors. Panel B shows the change in ozone predicted to result from changes in climate. Panel C shows the result for the combined impact of increased emissions of precursors of O_3 and increases resulting from climate change (reproduced with permission from the Royal Society).

of increases in O_3 on crop production in these regions. In areas with greater warming and less drying, such as in northern latitudes, risks of ozone damage to crops have been projected to increase because of increasing hemispheric transport of pollution leading to greater concentrations of ozone in the growing season when plants are more sensitive.²⁷ Drying as a result of climate change could also have an impact on the frequency and extent of fires, and thus affect the regional atmospheric burdens of aerosols and other pollutants. These different regional vulnerabilities will need to be considered in future control strategies for sources of air pollution.

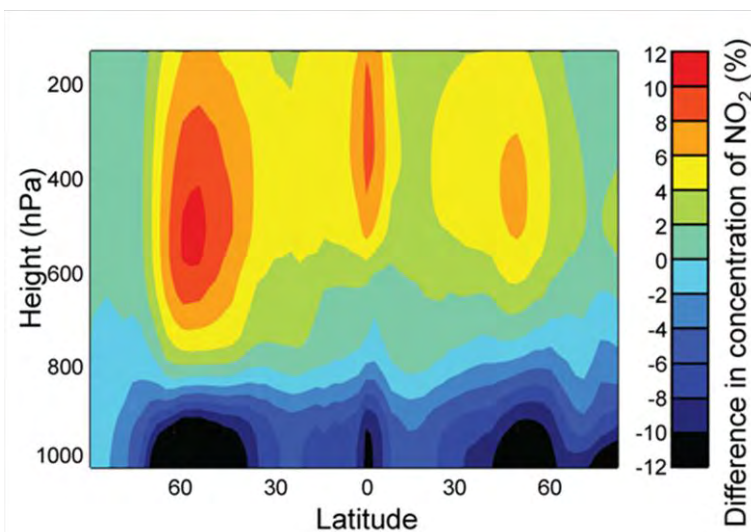


Fig. 6-5. Prediction of the change in the rate of photolysis of NO_2 from calculations that include and exclude clouds.¹⁰¹ At low altitudes, photolysis is decreased by the presence of clouds. At higher altitudes, the photolysis rates are increased due to the reflection from the cloud tops.

Aerosols in the troposphere

Aerosols (small air-borne particles) have a significant impact on human health through effects on respiratory and cardiovascular systems,¹⁰⁸ and can have a large impact on the physics and chemistry of the atmosphere. As noted previously,¹⁰⁶ aerosols scatter and absorb incoming solar radiation, changing the atmospheric energy balance and the rate of photochemical reactions. They also affect the formation of clouds, modifying their optical properties, their precipitation efficiency, and lifetimes. The IPCC³⁹ has recognized the effects of aerosols as the highest uncertainty in the radiative forcing budget of the atmosphere.

Aerosols can be generated from a wide range of sources and can be primary (directly emitted) or secondary (generated in the atmosphere). While sea-salt and dust are major sources by mass, both biogenic sources (such as emissions from plants) and anthropogenic activities represent significant sources of organic material. Soot and primary organic aerosols (POAs) are emitted during burning of fossil fuels and biomass. For example, a recent study found that, in Beijing, concentrations of POAs were due mostly to biomass burning, cooking, vehicular exhaust, and coal burning.¹⁰⁴ Secondary aerosols include sulfate, produced from the oxidation of SO_2 in the gas phase by $\cdot OH$ radicals and in the aqueous phase by peroxides, nitrates, and secondary organic aerosols (SOAs) from the photo-oxidation of hydrocarbons (reactions 3-4, Fig. 6-1).⁶⁷

The formation of SOAs has received much attention in the past few years, following the realizations that (i) traditional models fall short of explaining the observed concentrations of SOA, with discrepancies ranging from a factor of three to two orders of magnitude,⁹⁹ and (ii) the atmospheric concentrations of SOAs are frequently as large as, or larger than, those of other aerosols including sulfate.¹¹⁶ While many of these studies took place in urban areas, SOAs from forested regions were also identified as important,²⁸ and even the ubiquitous biogenic hydrocarbon isoprene was shown to produce significant yields of SOAs.¹² In urban areas, a likely source for the previously unexplained SOAs may be the evaporation of primary organic aerosols (POAs) followed by the gas phase reaction with $\cdot OH$ radicals and conden-

sation of the reaction products as SOAs.^{45, 84} Other studies have shown that the anthropogenic and natural sources of aerosols may be linked intrinsically through the gas phase photochemistry, e.g., with anthropogenic NO_x accelerating the production of SOAs from biogenic (non-anthropogenic) hydrocarbons.³⁴ Analysis of the ratios of carbon isotopes (¹⁴C/¹²C) shows that, even in polluted urban areas, a significant fraction of the particulate carbon is not from fossil fuels but is rather from biogenic emissions and burning of biomass, e.g., 30% in Los Angeles,³³ 30-50% in Beijing,¹¹¹ 30-40% in Tokyo,¹¹⁰ and 30-60% in Mexico City.^{35, 63}

Neither anthropogenic nor biogenic organic aerosols are well simulated by current numerical models, although it is clear that UV radiation initiates the cascade of chemical reactions resulting in the formation, via photo-generation of ·OH radicals and their reactions with VOCs to yield condensable organic compounds. Wet and dry deposition is believed to be the major removal process, although there is increasing evidence that UV radiation may have a role in the destruction of SOA, by the photolysis of surface-bound carbonyl compounds and the subsequent release of gases such as carbon monoxide, formaldehyde, and formic acid^{60, 102} (see action spectra in Fig. 1-6 in Chapter 1).

Some models for studying the evolution of organic aerosols in specific, relatively simple environments are in early stages of development. For example, a numerical model has been developed that reproduces observed aerosol production over a conifer forest, using observed changes in the environment including temperature and UV-B radiation.⁴ This model has then been applied to predicting particle formation in future climate scenarios. Changes in O₃, temperature and water vapour were considered. Temperature is the independent variable, with changes in O₃ assumed to be driven by increased release of volatile organic compounds from trees. Unfortunately, due to the uncertainties, the impact of changes in UV-B radiation has not been estimated. Another model of changes in aerosol production over the U.S. includes changes in cloudiness but does not explicitly include UV-B radiation.¹¹⁷

Even for inorganic aerosols, future changes are difficult to calculate because they depend not only on stratospheric ozone, but also on tropospheric chemical processes and on climate change. For example, numerical models show that future concentrations of sulfate and nitrate aerosols will depend sensitively on ·OH radical concentrations, which in turn depend on emissions of NO_x, methane, and other VOCs.⁸⁹ Wind is also a major factor determining dust and sea spray emissions, size distributions, and transport,^{9, 59} and higher wind speeds over oceans and land will increase their concentrations. Mulcahy et al.⁶⁹ found a strong increase of the optical depths of sea spray with wind speed, leading to reductions in direct solar radiation equivalent to or greater than that seen in significant pollution events.

Some advances have been made in the past few years in determining the optical properties of aerosols at UV wavelengths. One previously unexpected result was that the absorption of these short wavelengths by aerosols is quite large, and cannot be explained by their known chemical composition.^{2, 3, 14, 62} A possible explanation is that this absorption is due to organic compounds contained within the SOA particles, but which are not yet fully understood as discussed above.^{2, 14} These UV properties of the aerosols can provide a significant feedback on to the photochemistry: absorbing aerosols tend to reduce the available UV radiation and thus slow the production of tropospheric O₃,¹⁰ while scattering aerosols can increase the effective path-length of UV photons and lead to more rapid production of O₃.¹⁸

Halogens in the troposphere

As both measurement techniques and the understanding of possible chemical processes are improving, new information shows that the roles that halogens play in the lower atmosphere are more diverse than previously thought. Knowledge of the impacts of these halogens on

tropospheric ozone and how they interact with changes in UV-B radiation will be important for a more accurate prediction of risks from tropospheric ozone in the future.

Bromine and brominated substances. Bromine-containing compounds, such as bromoform (CHBr_3), are a well-known source of reactive halogen with relevance to both tropospheric and stratospheric ozone. Recent studies have further highlighted the likely significance and variety of oceanic sources.^{76, 113} Ocean surveys of bromine oxide (BrO), produced by the oxidation of compounds such as bromoform, have shown that coastal regions⁶⁴ and passively venting volcanoes¹ can be significant sources likely to affect concentrations of ozone in these regions.⁸²

Studies of the atmosphere around the Dead Sea have reported events of unexpectedly large depletions of surface concentrations of O_3 (up to 93% loss). The co-occurrence of significant amounts ($176 \text{ pmol mol}^{-1}$) of BrO in the surface boundary layer did not fully explain the loss of ozone.⁹¹ A partial explanation may be provided by newly identified reaction mechanisms of halogen-containing compounds and aerosols.⁸⁰ While these studies have focused on polluted atmospheres, the particle-based reactions may also explain observations of reactive halogen species in the upper troposphere.⁹⁵ In the future, increasing surface temperatures of tropical seas are expected to increase the movement of these reactive species from the troposphere to the stratosphere¹⁶ and contribute to depletion of stratospheric ozone, through changes in atmospheric circulation.

Iodine and iodinated substances. The species of iodine equivalent to those of bromine (discussed above) have been detected in marine coastal atmospheres at similar concentrations to the bromine compounds,⁵⁸ although the concentrations of precursors appear to be less than those of the bromine species⁴⁶ and it is not clear how widespread the sources of these compounds are. The significance of iodinated substances in terms of air quality is unclear at this time.

Chlorine and chlorinated substances. In contrast to other halogens, chlorine-containing species have been considered relatively unimportant for ozone in the troposphere even though there are a few pathways that were known to produce Cl atoms.²¹ Any Cl atoms will react rapidly to form HCl , which is then washed out of the atmosphere. However, studies on the surface chemistry of hydrochloric acid (HCl) and oxides of nitrogen (NO_x) have shown that when HCl and NO_x are adsorbed on surfaces (formerly thought of as a removal mechanism), they react to generate gaseous nitrosyl chloride (ClNO) and nitryl chloride (ClNO_2).⁸⁰ When these absorb UV- and visible-radiation, they break down to form highly reactive chlorine atoms that react with VOCs and result in increases in the concentrations of O_3 in the troposphere. In modelling this process in the South Coast Air Basin of California, the addition of the interaction between HCl from sea salt, NO_x , and solar radiation increased concentrations of O_3 by 40 ppbv (20%) at peak periods. Evidence from atmospheric observations is needed to assess the environmental importance of this mechanism.⁸¹

Anthropogenic emissions of halocarbons, e.g., methyl chloroform ($\text{C}_2\text{H}_3\text{Cl}_3$)⁶⁶ continue and also will contribute to depletion of stratospheric ozone. A study of emissions of HCFC-22 inferred from atmospheric observations indicated that the storage time was significant, delaying emissions and therefore delaying the impact of the production and release of these substances and the final recovery of stratospheric O_3 .⁹²

Fluorinated substances in the troposphere

Historically, the fluorinated substances, such as the chlorofluorocarbons (CFCs) had a major impact on stratospheric O_3 . For this reason, there is still strong interest in this class of compounds, new products, their replacements, and their degradation products. Sulfuryl fluoride

(SO₂F₂) is an industrial chemical released into the atmosphere in significant quantities (kilotonne (kt) per year). Sulfuryl fluoride has been suggested as a substitute for methyl bromide, a depletor of stratospheric ozone, in fumigation of crops and soils.⁹³ Global production in 2006 and 2007 was 3.5 and 2.3 kt, respectively but has increased steadily since 1960 when it was only 57 t and will likely increase into the future, especially if used more widely. The potential impact of sulfuryl fluoride in the atmosphere is now becoming clearer. Estimates of atmospheric lifetimes are >300, >5000, and >10⁷ years for removal processes driven by ·OH, ·Cl and O₃, respectively.⁹³ Although SO₂F₂ is relatively soluble in water,⁸ at this time the significance of other potential removal processes such as partitioning to cloud water (followed by deposition) is not known. The rate of hydrolysis in water with pH similar to cloud water (5.9) is small ($2.6 \times 10^{-6} \text{ s}^{-1}$),⁸ which is consistent with lack of observed hydrolysis in the atmosphere.⁷⁷ The rate under alkaline conditions (pH 8.3) is 100 times faster, suggesting that it will not accumulate in surface waters unless these have pH <6. The ultimate hydrolysis products (inorganic sulfate and fluoride) are judged to present negligible risks to the environment. Recently published measurements of SO₂F₂ in current and archived atmospheric samples show that the global tropospheric background concentration is smaller in the southern than in the northern hemisphere but has increased by $5 \pm 1\%$ per year from 1978 to 2007.⁶⁸ Models have predicted global atmospheric lifetimes of 36 to 40 years with a major sink in the oceans. Modelled emissions underestimated production by 33%, suggesting that, during use as a fumigant, about one third is destroyed and does not enter the atmosphere.⁶⁸ Based on uncertain data, the GWP for SO₂F₂ (i.e., its global warming potential relative to CO₂) is estimated to range from 120-7600 for a 100-year time horizon.⁹³ This, and likely increases in use of SO₂F₂ in the future, suggest that monitoring concentrations in the atmosphere needs to be continued.

As has been discussed previously,¹⁰⁶ several of the hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) used as substitutes for ozone-depleting CFCs, can break down into trifluoroacetic acid (TFA). Two new fluorinated olefins (HFOs) that are entering the market may also break down into TFA.^{47, 57} HFO-1234yf (2,3,3,3-tetrafluoro-1-propene, Fig. 6-6) is a refrigerant, particularly for air-conditioning in vehicles.^{47, 57} HFO-1234ze (1,3,3,3-tetrafluoroprop-1-ene, Fig. 6-6) is a new agent used for blowing of insulating and structural foams. An analysis of emissions and subsequent production of TFA from HFO-1234yf, based on penetration in the US domestic market up to 2050, was combined with three-dimensional air quality modelling to estimate the concentrations of TFA in rainwater and to predict the potential increase in ground level O₃.⁵⁷ This analysis concluded that the projected maximum concentration of TFA in rainwater should not result in a significant risk of adverse effects in the environment and that production of O₃, resulting from emissions of HFO-1234yf, is unlikely to be a major concern for local air quality in most locations. A similar analysis of HFO-1234ze concluded that little or no TFA would be produced, because of structural differences between the two molecules that would prevent the formation of TFA from HFO-1234ze (Fig 6-6). However, there are no experimental data in the literature to test this theory.⁹⁷

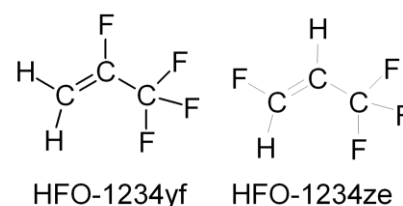


Fig. 6-6. Structures of the refrigerant HFO-1234yf and blowing agent HFO-1234ze.

The final environmental sink for TFA is in the oceans, playas, and landlocked lakes. Concentrations of TFA in rainwater range from <0.5 to 350 ng L⁻¹, depending on location and proximity to human activity⁸⁶ and this source is predominantly anthropogenic. As TFA is very stable and very water soluble, it accumulates in the oceans where concentrations, largely

from natural sources, are ca 200 ng L⁻¹.²⁶ Based on historical production of HFCs and HCFCs as potential sources of TFA, as well as projections of future uses, a worst-case estimate of release of TFA from complete conversion of HFCs and HCFCs yielded a global increase of 22,000 kt of TFA by the time of planned phase-out of the HFCs and HCFCs (2030-2045). Assuming release of 50 – 100 kt HFO-1234yf per year for 100 years from 2015, complete conversion to TFA (50 – 100 kt/year, as they have the same molecular weight) would increase concentrations in the oceans by 3.7 – 7.4 ng L⁻¹, a small increase above the background concentration of 200 ng L⁻¹ as estimated by Frank et al.²⁶

Because of high water solubility, low octanol-water (K_{OW}), and octanol-air (K_{OA}) partition coefficients, TFA does not accumulate in aquatic or terrestrial organisms and does not bioaccumulate in food chains. As TFA is a strong acid (dissociation constant, pK_a , = 0.3), it is completely ionised at normal environmental pH and is present as a salt form in the soils, surface water, and oceans. No adverse effects of salts of TFA in mammals or humans were identified in earlier reviews⁹⁴ or in the peer reviewed literature up to August 2010. Concentrations of salts of TFA causing measurable effects in organisms in the environment are large (222,000 to 10,000,000 ng L⁻¹)^{29, 30} and provide an estimated 10,000-fold margin of safety for worst-case scenarios. Projected future increased loadings to playas, land-locked lakes, and the oceans (via precipitation and inflow of fresh water) due to climate change and continued use of HCFCs, HFCs, and replacement products,^{57, 106} are still judged to present negligible risks for aquatic organisms and humans.

Some questions have been raised about the formation of monofluoroacetic acid (MFA). MFA is a naturally occurring compound that is a toxic constituent of the poisonous South African plant *Dichapetalus cymosum*, also known as *gifblaar*, and several other poisonous plant species.⁶ MFA is highly toxic to animals because it inhibits the energy-producing Krebs (citric acid) cycle by blocking the action of a key enzyme, aconitase. MFA is not formed from TFA except in very unusual situations where dehalogenation could occur, such as in anaerobic sediments.⁶ Small amounts of MFA are produced from the heating of Teflon (600°C)²⁰ but there is no evidence to suggest that it is formed from CFCs or their replacement HFCs. If it were formed, MFA would be degraded rapidly by microorganisms and, in soil, has a short half-life, and no potential for accumulation in the environment.⁶

Conclusions

The impacts of air pollution on human health and the environment will be influenced directly by future changes in emissions of pollutants, climate, and stratospheric ozone. UV radiation is one of the controlling factors for the formation of photochemical smog, which includes tropospheric O₃ and aerosols; it also initiates the production of ·OH, which controls the amount of many climate- and ozone-relevant gases, such as methane and HCFCs in the atmosphere. Uncertainties still exist in quantifying the chemical processes and wind-driven transport of pollutants. The net effects of future changes in UV radiation, meteorological conditions, and anthropogenic emissions may be large but will depend on local conditions, thus posing challenges for prediction and management of air quality. Numerical models predict that future changes in UV radiation and climate will modify the trends and geographic distribution of ·OH, thus affecting the formation of photochemical smog in urban areas and regions with greater concentrations of precursors. This will also affect concentrations of greenhouse gasses in the atmosphere. Concentrations of ·OH are predicted to decrease globally by an average of 20% by 2100, with local concentrations varying by as much as a factor of two above and below current values. However, significant differences between modelled and measured values in a limited number of case studies show that chemistry of ·OH radicals

in the atmosphere is not fully understood. Therefore, consequences for human health and the environment are uncertain.

Photochemically produced tropospheric O₃ is projected to increase. If emissions of anthropogenic air pollutants from combustion of fossil fuels, burning of biomass, and agricultural activities continue to increase, concentrations of tropospheric O₃ will increase over the next 20-40 years in certain regions of low and mid-latitudes because of interactions of emissions, chemical processes, and climate change. Climate-driven increases in temperature and humidity will also increase production of tropospheric O₃ in polluted regions, but reduce it in more pristine regions. Higher temperatures will tend to increase emissions of NO_x from some soils and release of biogenic VOCs from plants, leading to greater background concentrations of O₃ in the troposphere. For the future protection of human health and the environment, more effective controls will need to be considered for emissions of NO_x and VOCs related to human activities. In addition, the development of ozone-tolerant crops will ameliorate the effects of O₃ on the production of food and fibre.

Aerosols composed of organic substances have a major role in both climate and air quality, and contribute a large uncertainty to the energy budget of the atmosphere. Aerosols are mostly formed via the UV-initiated oxidation of VOCs from anthropogenic and biogenic sources, although the details of the chemistry are still poorly known and current models under-predict their abundance. A better understanding of their formation, chemical composition, and optical properties is required to assess their significance for air quality and to better quantify their direct and indirect radiative forcing of climate.

Emissions of compounds containing fluorine will continue to have effects on the chemistry of the atmosphere and on climate change. Models predict global atmospheric lifetimes of 36 to 40 years for sulfuryl fluoride (SO₂F₂), a substitute for the fumigant, methyl bromide. Based on the estimated GWP for SO₂F₂ and likely increased use in the future, there is a potential for adverse effects that should be considered in the future. The hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) used as substitutes for ozone-depleting CFCs, can break down into trifluoroacetic acid (TFA), which is very stable and will accumulate in the oceans, salt lakes, and playas. Based on historical use and projections of future uses, including new products entering the market such as the fluoro-olefins, increased loadings of TFA in these environmental sinks will be small. Even when added to existing amounts from natural sources, risks from TFA to humans and organisms in the aquatic environment are judged to be negligible. There is no indication that the highly toxic chemical, monofluoroacetic acid would be produced in toxicologically significant amounts by degradation of trifluoroacetic acid or directly from hydrochlorofluorocarbons and hydrofluorocarbons used as substitutes for ozone-depleting chlorofluorocarbons (CFCs). The resulting risk to humans or the environment from the historical use of CFCs or continued use of their replacements is judged to be negligible.

References

- 1 Bani P, Oppenheimer C, Tsanev VI, Carn SA, Cronin SJ, Crimp R, Calkins JA, Charley D, Lardy M and Roberts TR, 2009, Surge in sulphur and halogen degassing from Ambrym volcano, Vanuatu, *Bull. Volcanol.*, **71**, 1159-1168.
- 2 Barnard JC, Volkamer R and 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.

- 3 Bergstrom RW, Pilewskie P, Russell PB, Redemann J, Bond TC, Quinn PK and Sierau B, 2007, Spectral absorption properties of atmospheric aerosols, *Atmos. Chem. Phys.*, **7**, 5937–5943.
- 4 Bonn B, Boy M, Kulmala M, Groth A, Trawny K, Borchert S and Jacobi S, 2009, A new parametrization for ambient particle formation over coniferous forests and its potential implications for the future, *Atmos. Chem. Phys.*, **9**, 8079–8090.
- 5 Bousquet P, Hauglustaine DA, Peylin P, Carouge C and Ciais P, 2005, Two decades of OH variability as inferred by an inversion of atmospheric transport and chemistry of methyl chloroform, *Atmos. Chem. Phys.*, **5**, 2635–2656.
- 6 Boutonnet JC, Bingham P, Calamari D, de Rooij C, Franklin J, Kawano T, Libre M-J, McCulloch A, Malinverno G, Odom JM, Rusch GM, Smythe K, Sobolev I, Thompson R and Tiedje M, 1999, Environmental risk assessment of trifluoroacetic acid, *Human Ecol. Risk Assess.*, **5**, 59–124.
- 7 Brasseur GP, Orlando JJ and Tyndall GS, 1999, *Atmospheric Chemistry and Global Change*, Oxford University Press, Oxford.
- 8 Cady GH and Misra S, 1974, Hydrolysis of sulfuryl fluoride, *Inorg. Chem.*, **13**, 837–841.
- 9 Carslaw KS, Boucher O, Spracklen DV, Mann GW, Rae JGL, Woodward S and Kulmala M, 2010, A review of natural aerosol interactions and feedbacks within the Earth system, *Atmos. Chem. Phys.*, **10**, 1701–1737.
- 10 Castro T, Madronich S, Rivale S, Muhlia A and Mar B, 2001, The influence of aerosols on photochemical smog in Mexico City, *Atmos. Environ.*, **35**, 1765–1772.
- 11 Chatani S, Shimo N, Matsunaga S, Kajii Y, Kato S, Nakashima Y, Miyazaki K, Ishii K and Ueno H, 2009, Sensitivity analyses of OH missing sinks over Tokyo metropolitan area in the summer of 2007, *Atmos. Chem. Phys.*, **9**, 8975–8986.
- 12 Claeys M, Graham B, Vas G, Wang W, Vermeylen R, Pashynska V, Cafmeyer J, Guyon P, Andreae MO, Artaxo P and Maenhaut W, 2004, Formation of secondary organic aerosols through photooxidation of isoprene, *Science*, **303**, 1173–1176.
- 13 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 and Avery MA, 2010, Increasing springtime ozone mixing ratios in the free troposphere over western North America, *Nature*, **463**, 344–348.
- 14 Corr CA, Krotkov N, Madronich S, Slusser JR, Holben B, Gao W, Flynn J, Lefer B and Kreidenweis SM, 2009, Retrieval of aerosol single scattering albedo at ultraviolet wavelengths at the T1 site during MILAGRO, *Atmos. Chem. Phys.*, **9**, 5813–5827.
- 15 Dalsøren SB and Isaksen ISA, 2006, CTM study of changes in tropospheric hydroxyl distribution and its impact on methane, *Geophys. Res. Lett.*, **33**, L23811.
- 16 Deckert R and Dameris M, 2008, From ocean to stratosphere, *Science*, **322**, 53–55.
- 17 Denman KL, Brasseur G, Chidthaisong A, Ciais P, Cox PM, Dickinson RE, Hauglustaine D, Heinze C, Holland E, Jacob D, Lohmann U, Ramachandran S, Dias PLdS, Wofsy SC and Zhang X, 2007, Couplings Between Changes in the Climate System and Biogeochemistry, in *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change* ed.: Solomon S, D. Qin, M. Manning, Z. Chen, M. Marquis, K.B. Averyt, M. Tignor and H.L. Miller, Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.

- 18 Dickerson RR, Kondragunta S, Stenchikov G, Civerolo KL, Doddridge BG and Holben BN, 1997, The impact of aerosols on solar ultraviolet radiation and photochemical smog, *Science.*, **278**, 827-830.
- 19 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 and Holder H, 2009, Measurements of OH and HO₂ concentrations during the MCMA-2006 field campaign - Part 2: Model comparison and radical budget, *Atmos. Chem. Phys.*, **9**, 6655-6675.
- 20 Ellis DA, Mabury SA, Martin JW and Muir DCG, 2001, Thermolysis of fluoropolymers as a potential source of halogenated organic acids in the environment, *Nature*, **412**, 321-324.
- 21 Finlayson-Pitts BJ, Ezell MJ and Pitts JN, 1989, Formation of chemically active chlorine compounds by reactions of atmospheric NaCl particles with gaseous N₂O₅ and ClONO₂, *Nature*, **337**, 241-244.
- 22 Finlayson-Pitts BJ and Pitts J, 2000, *Chemistry of the Upper and Lower Atmosphere*, Academic Press, San Diego.
- 23 Fishman J, Wozniak AE and Creilson JK, 2003, Global distribution of tropospheric ozone from satellite measurements using the empirically corrected tropospheric ozone residual technique: Identification of the regional aspects of air pollution, *Atmos. Chem. Phys.*, **3**, 893-907.
- 24 Foret G, Hamaoui L, Schmechtig C, Eremenko M, Keim C, Dufour G, Boynard A, Coman A, Ung A and Beekmann M, 2009, Evaluating the potential of IASI ozone observations to constrain simulated surface ozone concentrations, *Atmos. Chem. Phys.*, **9**, 8479-8491.
- 25 Fowler D, Amann M, Anderson R, Ashmore M, Cox P, Depledge M, Derwent D, Grennfelt P, Hewitt N, Hov O, Jenkin M, Kelly F, Liss P, Pilling M, Pyle J, Slingo J and Stevenson D, 2008, *Ground-level ozone in the 21st century: Future trends, impacts and policy implications. Policy report 15/08*, Royal Society, London, UK.
- 26 Frank H, Christoph EH, Holm- Hansen O and Bullister JL, 2002, Trifluoroacetate in ocean waters, *Environ. Sci. Technol.*, **36**, 12-15.
- 27 Fuhrer J, 2009, Ozone risk for crops and pastures in present and future climates, *Naturwissenschaften.*, **96**, 173-194.
- 28 Goldstein AH and Galbally IE, 2007, Known and unexplored organic constituents in the earth's atmosphere, *Environ. Sci. Technol.*, **41**, 1515-1521.
- 29 Hanson ML and Solomon KR, 2004, Haloacetic acids in the aquatic environment I: Macrophyte toxicity, *Arch. Environ. Contam. Toxicol.*, **130**, 371-383.
- 30 Hanson ML and Solomon KR, 2004, Haloacetic acids in the aquatic environment II: Ecological risk assessment for aquatic macrophytes, *Arch. Environ. Contam. Toxicol.*, **130**, 385-401.
- 31 Hazucha MJ, Bates DV and Bromber PA, 2007, Mechanism of action of ozone on the human lung, *J. Appl. Physiol.*, **67**, 1535-1541.
- 32 Helmig D, Bottenheim J, Galbally IE, Lewis A, Milton MJT, Penkett S, Plassdülmer C, Reimann S, Tans P and Thiel S, 2009, Volatile Organic Compounds in the Global Atmosphere, *Eos Transactions*, **90**, 513-514.
- 33 Hildeman LM, Klinedinst DB, Klouda GA, Currie LA and Cass GR, 1994, Sources of urban contemporary carbon aerosol, *Environ. Sci. Technol.*, **28**, 1565-1576.

- 34 Hodzic A, Jimenez JL, Madronich S, Aiken AC, Bessagnet B, Curci G, Fast J, Lamarque JF, Onasch TB, Roux G, Schauer JJ, Stone EA and Ulbrich IM, 2009, Modeling organic aerosols during MILAGRO: importance of biogenic secondary organic aerosols, *Atmos. Chem. Phys.*, **9**, 6949-6981.
- 35 Hodzic A, Jimenez JL, Prevot ASH, Szidat S, Fast JD and Madronich S, 2010, Can 3-D models explain the observed fractions of fossil and non-fossil carbon in and near Mexico City?, *Atmos. Chem. Phys.*, **10**, 10997-11016.
- 36 Hofzumahaus A, Rohrer F, Lu KD, Bohn B, Brauers T, Chang CC, Fuchs H, Holland F, Kita K, Kondo Y, Li X, Lou SR, Shao M, Zeng LM, Wahner A and Zhang YH, 2009, Amplified trace gas removal in the troposphere, *Science*, **324**, 1702-1704.
- 37 Hudman RC, Murray LT, Jacob DJ, Millet DB, Turquety S, Wu S, Blake DR, Goldstein AH, Holloway J and Sachse GW, 2008, Biogenic versus anthropogenic sources of CO in the United States, *Geophys. Res. Lett.*, **35**, L04801.
- 38 IPCC, 2005, *Special Report on Safeguarding the Ozone Layer and the Global Climate System: Issues related to Hydrofluorocarbons and Perfluorocarbons*, Cambridge University Press, Cambridge, UK.
- 39 IPCC, 2007, *Climate Change 2007: The Physical Science Basis*, (Eds.: Solomon S, Qin D, Manning M, Marquis M, Avery K, Tignor MMB, Miller HL, Jr. and Chen Z), Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, p. 987.
- 40 Isaksen ISA, Rognerud B, Dalsøren S and Søvde A, 2009, Stratospheric Ozone Depletion and Tropospheric Chemistry, in *Twenty Years of Ozone Decline. Proceedings of the Symposium for the 20th Anniversary of the Montreal Protocol* eds.: Zerefos C, Contopoulos G and Skalkas G, Springer, Netherlands, pp. 279-290.
- 41 Isaksen ISA, Zerefos C, Kourtidis K, Meleti C, Dalsøren SB, Sundet JK, Grini A, Zanis P and Balis D, 2005, Tropospheric ozone changes at unpolluted and semipolluted regions induced by stratospheric ozone changes, *J. Geophys. Res.*, **110**, D02302.
- 42 Jacob DJ, 1999, *Introduction to Atmospheric Chemistry*, Princeton University Press, Princeton.
- 43 Jacobson MZ, 2008, On the causal link between carbon dioxide and air pollution mortality, *Geophys. Res. Lett.*, **35**, L03809.
- 44 Jacobson MZ and Streets DG, 2009, Influence of future anthropogenic emissions on climate, natural emissions, and air quality, *J. Geophys. Res.*, **114**, D08118.
- 45 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, Dunlea EJ, 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 and Worsnop DR, 2009, Evolution of organic aerosols in the atmosphere, *Science*, **326**, 1525-1529.

- 46 Jones CE, Hornsby KE, Dunk RM, Leigh RJ and Carpenter LJ, 2009, Coastal measurements of short-lived reactive iodocarbons and bromocarbons at Roscoff, Brittany during the RHaMBLe campaign, *Atmos. Chem. Phys.*, **9**, 8757-8769.
- 47 Kajihara H, Inoue K, Yoshida K and Nagaosa R, 2010, Estimation of environmental concentrations and deposition fluxes of R- 1234-YF and its decomposition products emitted from air conditioning equipment to atmosphere, in *2010 International Symposium on Next-generation Air Conditioning and Refrigeration Technology*, Tokyo, Japan.
- 48 Keenan T, Niinemets Ü, Sabate S, Gracia C and Peñuelas J, 2009, Process based inventory of isoprenoid emissions from European forests: model comparisons, current knowledge and uncertainties, *Atmos. Chem. Phys.*, **9**, 4053-4076.
- 49 Keim C, Eremenko M, Orphal J, Dufour G, Flaud JM, Hopfner M, Boynard A, Clerbaux C, Payan S, Coheur PF, Hurtmans D, Claude H, Dier H, Johnson B, Kelder H, Kivi R, Koide T, Bartolome ML, Lambkin K, Moore D, Schmidlin FJ and Stubi R, 2009, Tropospheric ozone from IASI: comparison of different inversion algorithms and validation with ozone sondes in the northern middle latitudes, *Atmos. Chem. Phys.*, **9**, 9329-9347.
- 50 Lam YF and Fu JS, 2009, A novel downscaling technique for the linkage of global and regional air quality modeling, *Atmos. Chem. Phys.*, **9**, 9169-9185.
- 51 Lamarque JF, Hess P, Emmons L, Buja L, Washington W and Granier C, 2005, Tropospheric ozone evolution between 1890 and 1990, *J. Geophys. Res.*, **110**, D08304.
- 52 Lelieveld J, Butler TM, Crowley JN, Dillon TJ, Fischer H, Ganzeveld L, Harder H, Lawrence MG, Martinez M, Taraborrelli D and Williams J, 2008, Atmospheric oxidation capacity sustained by a tropical forest, *Nature*, **452**, 737-740.
- 53 Lelieveld J, Peters W, Dentener FJ and Krol MC, 2002, Stability of tropospheric hydroxyl chemistry, *J. Geophys. Res.*, **107**, 4715.
- 54 Liu HY, Crawford JH, Pierce RB, Norris P, Platnick SE, Chen G, Logan JA, Yantosca RM, Evans MJ, Kittaka C, Feng Y and Tie XX, 2006, Radiative effect of clouds on tropospheric chemistry in a global three-dimensional chemical transport model, *J. Geophys. Res.*, **111**, D20303.
- 55 Liu SC and Trainer M, 1988, Responses of tropospheric ozone and odd hydrogen radicals to column ozone change, *J. Atmos. Chem.*, **6**, 221-233.
- 56 Liu X, Chance K, Sioris CE, Spurr RJD, Kurosu TP, Martin RV and Newchurch MJ, 2005, Ozone profile and tropospheric ozone retrievals from the Global Ozone Monitoring Experiment: Algorithm description and validation, *J. Geophys. Res.*, **110**, D20307.
- 57 Luecken DJ, Waterland RL, Papasavva S, Taddonio KN, Hutzell WT, Rugh JP and Andersen SO, 2010, Ozone and TFA impacts in North America from degradation of 2,3,3,3-Tetrafluoropropene (HFO-1234yf), a potential greenhouse gas replacement, *Environ. Sci. Technol.*, **44**, 343-348.
- 58 Mahajan AS, Oetjen H, Lee JD, Saiz-Lopez A, McFiggans GB and Plane JMC, 2009, High bromine oxide concentrations in the semi-polluted boundary layer, *Atmos. Environ.*, **43**, 3811-3818.
- 59 Mahowald NM, Muhs DR, Levis S, Rasch PJ, Yoshioka M, Zender CS and Luo C, 2006, Change in atmospheric mineral aerosols in response to climate: Last glacial

- period, preindustrial, modern, and double carbon dioxide climates, *J. Geophys. Res.*, **111**, D10202.
- 60 Mang SA, Henricksen DK, Bateman AP, Andersen MPS, Blake DR and Nizkorodov SA, 2008, Contribution of Carbonyl Photochemistry to Aging of Atmospheric Secondary Organic Aerosol, *J. Phys. Chem. A.*, **112**, 8337-8344.
 - 61 Mao J, Ren X, Brune WH, Olson JR, Crawford JH, Fried A, Huey LG, Cohen RC, Heikes B, Singh HB, Blake DR, Sachse GW, Diskin GS, Hall SR and Shetter RE, 2009, Airborne measurement of OH reactivity during INTEx-B, *Atmos. Chem. Phys.*, **9**, 163–173.
 - 62 Marley NA, Gaffney JS, Castro T, Salcido A and Frederick J, 2009, Measurements of aerosol absorption and scattering in the Mexico City Metropolitan Area during the MILAGRO field campaign: A comparison of results from the T0 and T1 sites, *Atmos. Chem. Phys.*, **9**, 189–206.
 - 63 Marley NA, Gaffney JS, Tackett M, Sturchio NC, Heraty L, Martinez N, Hardy KD, Marchany-Rivera A, Guilderson T, MacMillan A and Steelman K, 2009, The impact of biogenic carbon sources on aerosol absorption in Mexico City, *Atmos. Chem. Phys.*, **9**, 1537–1549.
 - 64 Martin M, Pöhler D, Seitz K, Sinreich R and Platt U, 2009, BrO measurements over the Eastern North-Atlantic, *Atmos. Chem. Phys.*, **9**, 9545-9554.
 - 65 Mena-Carrasco M, Carmichael GR, Campbell JE, Zimmerman D, Tang Y, Adhikary B, D'allura A, Molina LT, Zavala M, Garcia A, Flocke F, Campos T, Weinheimer AJ, Shetter R, Apel E, Montzka DD, Knapp DJ and Zheng W, 2009, Assessing the regional impacts of Mexico City emissions on air quality and chemistry, *Atmos. Chem. Phys.*, **9**, 3731–3743.
 - 66 Millet DB, Atlas EL, Blake DR, Blake NJ, Diskin GS, Holloway JS, Hudman RC, Meinardi S, Ryerson TB and Sachse GW, 2009, Halocarbon emissions from the United States and Mexico and their global warming potential, *Environ. Sci. Technol.*, **43**, 1055-1060.
 - 67 Monks PS, Granier C, Fuzzi S, Stohl A, Williams ML, Akimoto H, Amann M, Baklanov A, Baltensperger U, Bey I, Blake N, Blake RS, Carslaw K, Cooper OR, Dentener F, Fowler D, Fragkou E, Frost GJ, Generoso S, Ginoux P, Grewe V, Guenther A, Hansson HC, Henne S, Hjorth J, Hofzumahaus A, Huntrieser H, Isaksen ISA, Jenkin ME, Kaiser J, Kanakidou M, Klimont Z, Kulmala M, Laj P, Lawrence MG, Lee JD, Liousse C, Maione M, McFiggans G, Metzger A, Mieville A, Moussiopoulos N, Orlando JJ, O'Dowd CD, Palmer PI, Parrish DD, Petzold A, Platt U, Pöschl U, Prevot ASH, Reeves CE, Reimann S, Rudich Y, Sellegri K, Steinbrecher R, Simpson D, ten Brink H, Theloke J, van der Werf GR, Vautard R, Vestreng V, Vlachokostas C and von Glasow R, 2009, Atmospheric composition change - global and regional air quality, *Atmos. Environ.*, **43**, 5268-5350.
 - 68 Mühle J, Huang J, Weiss RF, Prinn G, Miller BR, Salameh PK, Harth M, Fraser PJ, Porter LW, Gwinn BR, O'Doherty S and Simmonds PG, 2009, Sulfuryl fluoride in the global atmosphere, *J. Geophys. Res.*, **114**, D05306.
 - 69 Mulcahy JP, O'Dowd CD, Jennings SG and Ceburnis D, 2008, Significant enhancement of aerosol optical depth in marine air under high wind conditions, *Geophys. Res. Lett.*, **35**, L16810.
 - 70 Murphy JJ, Delucchi MA, McCubbin DR and Kim HJ, 1999, The cost of crop damage caused by ozone air pollution from motor, *J. Environ. Manage.*, **55**, 273-289.

- 71 Nakicenovic N, Alcamo J, Davis G, Vries Bd, Fenhann J, Gaffin S, Gregory K, Grubler A, Jung TY, Kram T, Rovere ELL, L.Michaelis, Mori S, Morita T, Pepper W, Pitcher H, Price L, Raihi K, Roehrl A, Rogner H-H, Sankovski A, Schlesinger M, Shukla P, Smith S, Swart R, Rooijen Sv, Victor N and Dadi Z, 2000, *IPCC Special Report on Emissions Scenarios*, Cambridge University Press, Cambridge.
- 72 Nicholls JC, Davies CA and Trimmer M, 2007, High-resolution profiles and nitrogen isotope tracing reveal a dominant source of nitrous oxide and multiple pathways of nitrogen gas formation in the central Arabian Sea, *Limnol. Oceanogr.*, **52**, 156–168.
- 73 Nolte CG, Gilliland AB, Hogrefe C and Mickley LJ, 2008, Linking global to regional models to assess future climate impacts on surface ozone levels in the United States, *J. Geophys. Res.*, **113**, D14307.
- 74 O'Connor FM, Johnson CE, Morgenstern O and Collins WJ, 2009, Interactions between tropospheric chemistry and climate model temperature and humidity biases, *Geophys. Res. Lett.*, **36**, L16801.
- 75 Ostro B, 2004, Outdoor Air Pollutions: Assessing the Environmental Burden of Disease at National and Local Levels, World Health Organization Report No., Geneva, p. 62. www.who.int/quantifying_ehimpacts/publications/ebd5.pdf
- 76 Palmer CJ and Reason CJ, 2009, Relationships of surface bromoform concentrations with mixed layer depth and salinity in the tropical oceans, *Glob. Biogeochem. Cycles*, **23**, GB2014.
- 77 Papadimitriou VC, Portmann RW, Fahey DW, Mühle J, Weiss RF and Burkholder JB, 2008, Experimental and theoretical study of the atmospheric chemistry and global warming potential of SO₂F₂, *J. Phys. Chem. A.*, **112**, 12657-12666.
- 78 Pison I, Bousquet P, Chevallier F, Szopa S and Hauglustaine D, 2009, Multi-species inversion of CH₄, CO and H₂ emissions from surface measurements, *Atmos. Chem. Phys.*, **9**, 5281-5297.
- 79 Prinn RG, Huang J, Weiss RF, Cunnold DM, Fraser PJ, Simmonds PG, McCulloch A, Harth C, Reimann S, Salameh P, O'Doherty S, Wang RHJ, Porter LW, Miller BR and Krummel PB, 2005, Evidence for variability of atmospheric hydroxyl radicals over the past quarter century, *Geophys. Res. Lett.*, **32**, L07809.
- 80 Raff JD, Njagic B, Chnagg WL, Gordon MS, Daddub D, Gerber RB and Findlayson-Pitts BJ, 2009, Chlorine activation indoors and outdoors via surface-mediated reactions of nitrogen oxides with hydrogen chloride, *Proc. Nat. Acad. Sci. USA.*, **106**, 13647–13654.
- 81 Ravishankara AR, Daniel JS and Portmann RW, 2009, Nitrous oxide (N₂O): The dominant ozone-depleting substance emitted in the 21st century, *Science.*, **326**, 123-125.
- 82 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 and Plane JMC, 2008, Extensive halogen-mediated ozone destruction over the tropical Atlantic Ocean, *Nature*, **453**, 1232-1235.
- 83 Reidmiller DR, Fiore AM, Jaffe DA, Bergmann D, Cuvelier C, Dentener FJ, Duncan BN, Folberth G, Gauss M, Gong S, Hess P, Jonson JE, Keating T, Lupu A, Marmer E, Park R, Schultz MG, Shindell DT, Szopa S, Vivanco MG, Wild O and Zuber A, 2009, The influence of foreign vs. North American emissions on surface ozone, *Atmos. Chem. Phys.*, **9**, 5027-5042.

- 84 Robinson AL, Donahue NM, Shrivastava MK, Weitkamp EA, Sage AM, Grieshop AP, Lane TE, Pierce JR and Pandis SN, 2007, Rethinking organic aerosols: Semivolatile emissions and photochemical aging, *Science*, **315**, 1259-1262.
- 85 Schlosser E, Brauers T, Dorn HP, Fuchs H, Haseler 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-Dulmer C, Stange G and Schurath U, 2009, Technical Note: Formal blind intercomparison of OH measurements, *Atmos. Chem. Phys.*, **9**, 7923-7948.
- 86 Scott BF, Macdonald RW, Kannan K, Fisk A, Witter A, Yamashita N, Durham L, Spencer C and Muir DC, 2005, Trifluoroacetate profiles in the Arctic, Atlantic, and Pacific Oceans, *Environ. Sci. Technol.*, **39**, 6555-6560.
- 87 Seinfeld JH and Pandis SN, 1998, *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, John Wiley & Sons, New York.
- 88 Selin NE, Wu S, Nam KM, Reilly JM, Paltsev S, Prinn RG and Webster MD, 2009, Global health and economic impacts of future ozone pollution, *Environ. Res. Lett.*, **4**, 044014.
- 89 Shindell DT, Faluvegi G, Koch DM, Schmidt GA, Unger N and Bauer SE, 2009, Improved attribution of climate forcing to emissions, *Science*, **326**, 716-718.
- 90 Shindell DT, Faluvegi G, Stevenson DS, Krol MC, Emmons LK, Lamarque J-F, Pétron G, Dentener FJ, Ellingsen K, Schultz MG, Wild O, Amann M, Atherton CS, Bergmann DJ, Bey I, Butler T, Cofala J, Collins WJ, Derwent RG, Doherty RM, Drevet J, Eskes HJ, Fiore AM, Gauss M, Hauglustaine DA, Horowitz LW, Isaksen ISA, Lawrence MG, Montanaro V, Müller J-F, Pitari G, Prather MJ, Pyle JA, Rast S, Rodriguez JM, Sanderson MG, Savage NH, Strahan SE, Sudo K, Szopa S, Unger N, van Noije TPC and Zeng G, 2006, Multimodel simulations of carbon monoxide: Comparison with observations and projected near-future changes, *J. Geophys. Res.*, **111**, D19306
- 91 Smoydzin L and von Glasow R, 2009, Modelling chemistry over the Dead Sea: bromine and ozone chemistry, *Atmos. Chem. Phys.*, **9**, 5057-5072.
- 92 Stohl A, Seibert P, Arduini J, Eckhardt S, Fraser P, Grealley BR, Lunder C, Maione M, Mühle J, O'Doherty S, Prinn RG, Reimann S, Saito T, Schmidbauer N, Simmonds PG, Vollmer MK, Weiss RF and Yokouchi Y, 2009, An analytical inversion method for determining regional and global emissions of greenhouse gases: Sensitivity studies and application to halocarbons, *Atmos. Chem. Phys.*, **9**, 1597-1620.
- 93 Sulbaek Andersen MP, Blake DR, Rowland FS, Hurley MD and Wallington TJ, 2009, Atmospheric chemistry of sulfonyl fluoride: reaction with OH radicals, Cl atoms and O₃, atmospheric lifetime, IR spectrum, and global warming potential, *Environ. Sci. Technol.*, **43**, 1067-1070.
- 94 Tang X, Madronich S, Wallington T and Calamari D, 1998, Changes in tropospheric composition and air quality, *J. Photochem. Photobiol. B.*, **46**, 83-95.
- 95 Thornton BF, Toohey DW, Tuck AF, Elkins JW, Kelly KK, Hovde SJ, Richard EC, Rosenlof KH, Thompson TL, Mahoney MJ and Wilson JC, 2007, Chlorine activation near the midlatitude tropopause, *J. Geophys. Res.*, **112**, D18.
- 96 USEPA, 2006, Air Quality Criteria for Ozone and Related Photochemical Oxidants, United States Environmental Protection Agency Report No., Washington, DC, USA, February 2006, p. 2118.
<http://www.ntis.gov/search/product.aspx?ABBR=PB2006110277>

- 97 USEPA, 2009, Assessment of the Potential Impacts of HFO-1234yf and the Associated Production of Trifluoroacetic Acid (TFA) on Aquatic Communities and Local Air Quality, United States Environmental Protection Agency Report No., Washington, DC, USA, September 28, 2009, p. 9.
<http://www.regulations.gov/search/Regs/home.html#docketDetail?R=EPA-HQ-OAR-2008-0664>
- 98 Van Dingenen R, Dentener FJ, Raes F, Krol MC, Emberson L and Cofala J, 2009, The global impact of ozone on agricultural crop yields under current and future air quality legislation, *Atmos. Environ.*, **43**, 604-618.
- 99 Volkamer R, Jimenez JL, San Martini F, Dzepina K, Zhang Q, Salcedo D, Molina LT, Worsnop DR and Molina MJ, 2006, Secondary organic aerosol formation from anthropogenic air pollution: Rapid and higher than expected, *Geophys. Res. Lett.*, **33**, L17811.
- 100 Volz A and Kley D, 1988, Evaluation of the Montsouris series of ozone measurements made in the nineteenth century, *Nature*, **332**, 240-242.
- 101 Voulgarakis A, Wild O, Savage NH, Carver GD and Pyle JA, 2009, Clouds, photolysis and regional tropospheric ozone budgets, *Atmos. Chem. Phys.*, **9**, 8235-8246.
- 102 Walser ML, Park J, Gomez L, Russell AR and Nizkorodov SA, 2007, Photochemical aging of secondary organic aerosol particles generated from the oxidation of d-limonene, *Journal of Physical Chemistry A*, **111**, 1907-1913.
- 103 Wang JS, McElroy MB, Logan JA, Palmer PI, Chameides WL, Wang YX and Megretskaja IA, 2008, A quantitative assessment of uncertainties affecting estimates of global mean OH derived from methyl chloroform observations, *J. Geophys. Res.*, **113**, D12302.
- 104 Wang Q, Shao M, Zhang Y, Wei Y, Hu M and Guo S, 2009, Source apportionment of fine organic aerosols in Beijing, *Atmos. Chem. Phys.*, **9**, 8573-8585.
- 105 Wild O and Palmer PI, 2008, How sensitive is tropospheric oxidation to anthropogenic emissions?, *Geophys. Res. Lett.*, **35**, L22802.
- 106 Wilson SR, Solomon KR and Tang X, 2007, Changes in tropospheric composition and air quality due to stratospheric ozone depletion and climate change, *Photochem. Photobiol. Sci.*, **6**, 301-310.
- 107 Worden HM, Logan JA, Worden JR, Beer R, Bowman K, Clough SA, Eldering A, Fisher BM, Gunson MR, Herman RL, Kulawik SS, Lampel MC, Luo M, Megretskaja IA, Osterman GB and Shephard MW, 2007, Comparisons of Tropospheric Emission Spectrometer (TES) ozone profiles to ozonesondes: Methods and initial results, *J. Geophys. Res.*, **112**.
- 108 World Health Organization, 2006, WHO Air quality guidelines for particulate matter, ozone, nitrogen dioxide and sulfur dioxide - Global update 2005, World Health Organization Report No. WHO/SDE/PHE/OEH/06.02, Geneva, Switzerland.
www.who.int/phe/health_topics/outdoorair_aqg/en/
- 109 Wu S, Mickley LJ, Jacob DJ, Rind D and Streets DG, 2008, Effects of 2000-2050 changes in climate and emissions on global tropospheric ozone and the policy-relevant background surface ozone in the United States, *J. Geophys. Res.*, **113**, D18312.
- 110 Yamamoto N, Muramoto A, Yoshinaga J, Shibata K, Endo M, Endo O, Hirabayashi M, Tanabe K, Goto S, Yonheda M and Shibata Y, 2007, Comparison of carbonaceous

- aerosols in Tokyo before and after implementation of diesel exhaust restrictions, *Environ. Sci. Technol.*, **41**, 6357-6362.
- 111 Yang F, He K, Ye B, Chen, Cha L, Cadle SH, Chan T and Mulawa PA, 2005, One year record of organic and elemental carbon in fine particles in downtown Beijing and Shanghai, *Atmos. Chem. Phys.*, **5**, 1449-2005.
 - 112 Young PJ, Arneth A, Schurgers G, Zeng G and Pyle JA, 2009, The CO₂ inhibition of terrestrial isoprene emission significantly affects future ozone projections, *Atmos. Chem. Phys.*, **9**, 2793-2803.
 - 113 Yvon-Lewis SA, Saltzman ES and Montzka SA, 2009, Recent trends in atmospheric methyl bromide: analysis of post-Montreal Protocol variability, *Atmos. Chem. Phys.*, **9**, 5963-5974.
 - 114 Zeng G, Morgenstern O, Braesicke P and Pyle JA, 2010, Impact of stratospheric ozone recovery on tropospheric ozone and its budget, *Geophys. Res. Lett.*, **37**, L09805.
 - 115 Zeng G, Pyle JA and Young PJ, 2008, Impact of climate change on tropospheric ozone and its global budgets, *Atmos. Chem. Phys.*, **8**, 369–387.
 - 116 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, Shimon 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 and Worsnop DR, 2007, Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically-influenced Northern Hemisphere midlatitudes, *Geophys. Res. Lett.*, **34**, L13801.
 - 117 Zhang Y, Hu XM, Leung LR and Gustafson WI, 2008, Impacts of regional climate change on biogenic emissions and air quality, *J. Geophys. Res.*, **113**, D18310.

Chapter 7. Effects of solar UV and climate change on materials

A.L. Andrady,^a H. Hamid,^b and A. Torikai^c

^a Department of Chemical and Biomolecular Engineering, North Carolina State University, Raleigh, NC USA

^b Department of Chemical Engineering, King Fahd University of Petroleum & Minerals, Dhahran, Saudi Arabia

^c Materials Life Society of Japan, Chuo-ku, Tokyo, Japan.

Summary

Increased solar ultraviolet radiation (UV) reaches the surface of the Earth as a consequence of a depleted stratospheric ozone layer and changes in factors such as cloud cover, land-use patterns and aerosols. Climate change is expected to result in a 1.1-6.4°C increase in average temperature by the end of this century, depending on location. Increased levels of UV radiation, especially at high ambient temperatures, are well-known to accelerate the degradation of plastics, rubber and wood materials thereby reducing their useful lifetimes in outdoor applications. Plastics used routinely outdoors are generally light-stabilized using chemical additives to ensure their useful lifetimes. Wood products are coated for resistance to UV radiation, since photodamage results in enhanced water-susceptibility and their consequent biodegradation under outdoor exposure. The increased damage to materials due to an increased UV-B (280-315 nm) component in solar radiation reaching the Earth likely can be countered using light-stabilization technologies, surface coatings or, in most instances, by substituting the materials in question with greater UV radiation-resistant materials. However, even if these options could be used with all common materials affected, they will invariably result in higher costs. Reliable estimates of the incremental costs involved depend on the anticipated damage and the effectiveness of mitigation strategies employed. We summarize and assess recent findings on light-induced damage to plastic materials, including wood-plastics composites and nanocomposites. The combined effect of increased UV-B radiation and ambient temperature is of special interest, since these two factors represent particularly harsh environmental conditions for most materials. Advances in approaches to light stabilization of materials are also assessed.

Introduction

As wood and plastics in building and other products routinely used outdoors are ultraviolet (UV)-susceptible, their useful lifetimes outdoors will tend to decrease under exposure to sunlight with a high content of UV radiation. Experimentally, the effectiveness of different types of light-induced damage increases exponentially as the wavelength of radiation it is exposed to decreases. Therefore a small increment in solar UV radiation, particularly the UV-B component (280 nm- 315 nm), can significantly reduce the useful lifetimes of wood and plastic materials used in outdoor applications. Climate change is expected to result in an increase in the average temperature of 1.1-6.4°C by the end of the century, further exacerbating the situation, as materials degrade even faster at the higher temperatures. Oxidative reactions that cause the degradation in both wood and plastics can be initiated by UV radiation as well as thermal oxidation.

Building construction, furniture industry, agriculture and a variety of other applications rely on extensive use of materials made from wood, plastic and natural fibre. The annu-

al demand for industrial round-wood in the world is 1700 million cubic meters (2005 data),²¹ while that of plastics is 245 million tonnes.³ Plastics in particular are used in building materials, outdoor furniture, protective coatings, marine vessel hulls, aeronautics and agricultural greenhouse applications. They are a class of especially versatile and relatively inexpensive materials that is increasingly replacing conventional materials of construction in a variety of applications. Being light and strong, they are the materials of choice for numerous outdoor uses including even the fabrication of automobiles and modern aircraft. Recently, plastic-wood composites, especially those based on recycled plastic materials, have also received wider acceptance as a building material.²⁰ In the US, about a quarter of residential decks are now being made of wood-plastic composites. A fraction of all plastics and wood products manufactured are routinely exposed to solar radiation during use and undergo slow light-induced oxidative degradation. Common polymers are photolabile and tend to be easily affected by UV-B radiation in sunlight, high ambient temperatures²⁵ and high humidity levels.⁵⁶ It is the resulting loss in aesthetic, physical and mechanical properties that limit the useful outdoor lifetimes of plastics products. Of the 21 million metric tons of rubber used globally; about half is used in tires. While tires are protected against UV and thermal degradation, surface cracking due to ambient (tropospheric) ozone is well-known.⁸⁷

Additives that slow down degradation (i.e., UV-stabilizers) are generally used in plastics formulations. As with polymers, moisture and the UV-B component of sunlight are also the main agents responsible for weathering of wood.⁷² With either class of material, it is the higher-energy, shorter wavelength ultraviolet (UV-B) radiation (280 nm to 315 nm) in sunlight that is relatively most effective in causing degradation. Some degradation is attributed to the solar UV-A radiation component that will also be affected by climate change-induced variations in UV radiation.

However, unlike for biota where the only mitigation strategy is slow adaptation, the effects of increased UV-B radiation on materials can be countered actively either by increasing the concentration of UV stabilizers used in their formulations or by selecting more UV-resistant types of plastics for outdoor applications. With wood, protective surface coatings, such as clear polyurethane coatings, that block the UV-B radiation reaching the bulk of the material¹² can provide some measure of protection from effects of solar UV radiation. While these different mitigating strategies are reasonable and appear to be feasible, they will also result in increased cost of materials used under conditions where the protective role of the stratospheric ozone layer is partially compromised.

This Chapter assesses the recent research findings that allow a better quantification of light-induced damage to wood and plastics materials and which contribute to unravelling the chemical mechanisms of UV-induced damage. In assessing such damage it is important to consider the total life cycle of a plastic or wood product and investigate the impact of UV and climate change on the entire life of the product. Promising novel mitigation strategies for UV-induced degradation of plastics and wood materials are also addressed.

Susceptibility of plastics and wood to solar UV-B radiation

Of the estimated 245 million metric tons of plastic resin estimated to be produced worldwide in 2010, 42% will be used in the Asia Pacific and 21-23% in each of North America and Europe. While about a third of this volume is typically used in construction and building applications, the fraction that is in outdoor use has not been reliably estimated. The classes of plastic resins commonly used in the fabrication of products employed outdoors are summarized in Table 7-1 below. Poly(vinyl chloride) (PVC), polyethylene (PE), polypropylene

(PP), polycarbonate (PC) and unsaturated polyester materials are most frequently encountered in products used outdoors.²⁹ These are generally compounded with light-stabilizer additives to retard their rate of deterioration on exposure to solar UV-B radiation. However, in most instances, the useful lifetimes of relevant products are invariably limited by the loss of either their aesthetic or mechanical properties due to photoinitiated degradation in sunlight. Light stabilizers themselves, as well as other additives such as flame retardants compounded into polymers, can be photodegraded on exposure to solar UV radiation, further reducing the lifetime of the product.⁶⁷

Table 7-1. Major outdoor applications of common varieties of plastics

Application area	Examples of products	Types of plastics used
Building Construction	Window and door frames. Siding, fascia, pipe, conduits and rainwater goods.	Rigid and plasticized formulations of poly(vinyl chloride), wood-plastic composites.
Agriculture	Membrane roofing and geomembranes. Irrigation pipes, greenhouse film, water storage tanks, produce crates, agricultural netting and mulch films	Synthetic rubber (EPDM). Polyethylene, poly(vinyl chloride) and unsaturated polyester
Transportation	Automobile, aircraft, marine vessel and rail-car construction. Pallets. Glazing, coatings and mouldings used in vehicles and in traffic signals.	Unsaturated polyester, polyurethane, composites. Polycarbonates
Other	Outdoor furniture, playground equipment and artificial turf Rigid and flexible solar photovoltaic and panels. Solar water heaters.	Polyethylene, polypropylene and rigid poly(vinyl chloride) Poly(ethylene vinyl acetate) as encapsulant. Acrylic plastic glazing. Polyimide and polyester.

The developed nations use about 70 % of the world round-wood that is produced²⁶ with half of this volume being used as lumber in the building and furniture industry. In wood, as with filled, opaque, plastics, the zone of degradation due to exposure to solar UV-B radiation is limited to the depth of penetration of the radiation into the material. In opaque plastics, the degradative changes (usually discoloration and micro-cracking) are localized at the surface where the shorter wavelength UV-B radiation is absorbed.⁵⁹ Similar results are also reported for wood. In fir wood, the UV-induced degradation can occur to a depth of 70-140 μm .²⁹ The relative efficiency of different wavelengths of light in causing a specific type of degradation in material is quantified in an action spectrum of the material. These are plots of damage per incident photon (or moles of photons) *versus* the wavelength of radiation, and in the case of polymers, generally show an exponential increase in efficiency of degradation with decreasing wavelength. These differ from a plot of wavelength-dependent quantum efficiency in that it is the incident rather than the absorbed radiation that is used in generating action spectra. The extent of degradation in materials depends on the dose of solar radiation absorbed and therefore on that incident on the material.

Table 7-2 shows the wavelength ranges over which photo-damage by monochromatic radiation has been reported in common polymers. The related action spectra (of Log_e [damage] versus wavelength (nm)) typically display negative gradients that vary between 0.01 and 0.06 either for the virgin polymer or for specific formulations of the polymer.²⁴ The magnitude of these gradients are smaller compared to those for biological processes (see Chapter 1); but significant changes in useful lifetimes of plastics can be associated with relatively small increases in UV- radiation damage. Exposure to UV wavelengths clearly causes significant damage (and reduced lifetimes) to plastics. The action spectra are different for different modes of damage and the presence of additives such as UV-stabilizers can dramatically

change them. The published action spectra strictly reflect the wavelength sensitivity of specific formulations of the polymers for a given type of damage. They serve only as a guideline for the behaviour of the class of polymers in question exposed to solar radiation.

Table 7-2. Wavelength sensitivity spectra of materials reported in the literature

Polymer/material	Type of damage	Wavelength range*	Reference
Poly(vinyl chloride) [PVC]	Yellowing	280-340 nm	6
PVC (5%TiO ₂ filled)	Yellowing	280-340 nm	
Polycarbonate	Yellowing	260-300 nm	4
	Decrease in molecular weight	260-300 nm	79
Polystyrene [PS]	Change in absorbance	260-320 nm	78
PS (with flame retardant additive)	Decrease in molecular weight	260-320 nm	78
Linear Low Density Polyethylene [LLDPE]	Change in absorbance and decrease in molecular weight	260-280 nm	77
LLDPE (with flame retardant)	Change in absorbance and decrease in molecular weight	260-320 nm	77
High density polyethylene [HDPE]	Change in absorbance and decrease in molecular weight	260-280 nm	76
HDPE (with flame retardant)	Change in absorbance and decrease in molecular weight	260-320 nm	76
Lignocellulose (mechanical pulp)	Yellowing	280-340 nm	5

*The wavelength ranges over which light-induced damage was obtained from Hamid²⁴.

Additives (e.g., transition metal compounds that catalyse hydroperoxide decomposition) are sometimes used, especially in plastic packaging products, to enhance the solar UV-induced breakdown. In packaging plastics that tend to end up as litter causing an urban aesthetic problem the use of such additives deteriorate the plastic faster, disintegrating it to small fragments. Increased solar UV radiation and ambient temperatures will tend to disintegrate these at a slightly faster rate.

Natural fibres, such as wool, as well as synthetic fibres discolour on exposure to solar UV radiation. While naturally white in colour, these fibres are commonly dyed for use in fabric, apparel, or carpet applications and it is the breakdown of the dye (rather than polymer) that leads to discoloration. Thus, it is the action spectra of the dye that determines the UV-induced fading rates in such instances. The action spectrum for fading Disperse Blue dye was recently reported and showed a maximum colour difference (ΔE) in the wavelength 262 nm or 310 nm depending on the substrate fibre.²⁷ However, action spectra for textile dyes are sparse in the literature.

Light-induced degradation of materials

Polymer nanocomposites and UV stability

Reinforcing fillers are commonly used in polymer formulations to improve their stiffness (moduli) and other key mechanical properties. Interaction of the surface of filler particles with the plastic matrix defines an interfacial layer that contributes to these improvements in

properties of the composite. Therefore, a decrease in the average particle size of fillers (i.e., with high specific surface area) is generally desirable in designing composites. Commercial availability of bulk nanoscale fillers with average primary particle sizes in the hundreds of nanometres (nanoclays) to tens of nanometres (fumed silica, titania, and carbon nanofillers) has resulted in increased attention to nanocomposites. However, nanofillers generally exist as agglomerates that need to be broken down and dispersed to sizes that approach their primary particle size for best reinforcing performance. Promising results using nanofillers to improve the mechanical properties of composites have encouraged their use. In 2008, global use of polymer nanocomposites was 36 million kg with an annual growth rate of 20%.³⁶ Therefore, it is important to establish the effect of solar UV radiation on the lifetime of this new class of composite materials that will find application in construction. A recent valid concern is the potential for nanocomposites to release nanoparticles into the environment as the polymer matrix degrades due exposure to UV-B radiation outdoors.⁶⁰ Recent research suggests that inhalation of nanoparticles dispersed in air can result in negative health effects.⁸⁰ Whether the nanoscale filler in composites can over time be released as nanoparticles into the environment is not known.⁴⁷

The most cost-effective nanoscale fillers are the smectite clays such as montmorillonite (MMT). Dispersing clay nanoparticle agglomerates in melt processing of the polymers has been a challenge⁶³ but commercial master-batches with the MMT concentrate pre-dispersed in plastic are available on the market. However, recent studies on the UV-induced degradability of polymer composites based on MMT have been disappointing. Work on polypropylene/MMT^{11, 44, 57} and EPDM/MMT clay nanocomposites^{39, 73} show that, on exposure to UV radiation, the useful properties of the composites deteriorate faster than for the unfilled polymer. These results confirm similar findings reported earlier for polyethylene (PE) and polypropylene (PP) nanocomposites with MMT.³⁶ This is likely due to the effect of iron (Fe^{3+}) impurities present in the clay and their role in catalysing oxidation reactions. Hydroperoxides formed during the oxidation of the polymer, generate additional free radical species that promote further degradation. Also, the efficacy of light stabilizer additives was found to be greatly reduced in MMT-based composites, possibly due to adsorption of the stabilizer compound on the clay particle surface. An increase in photodegradability was reported for composites of polycarbonate/MMT (PC/MMT) and in Nylon/MMT.⁵⁸ The damage indicators used were yellowing and chemical degradation in the infra-red (IR) spectrum of the polymer, respectively. Other clay-like minerals such as talc (hydrated magnesium silicate) also catalysed the oxidative degradation in PP.⁸ To benefit from the advantages of clay-based plastic composite technologies in outdoor applications, better stabilization approaches need to be explored.

Composites based on oxide nanofillers in polymers show better promise.^{65, 82} Most recent studies have been on titanium dioxide (TiO_2), a material already used as an opacifier in rigid formulations of PVC intended for outdoor use. Commercial conventional grades of the pigment have surface modifications that optimize their UV absorbance. However, TiO_2 exists in three crystalline forms, brookite, rutile, and anatase. Only the rutile form, an excellent absorber of UV radiation, is able to protect polymer matrices from UV-induced damage. Rutile is commonly used in formulation of rigid PVC profiles (such as siding) to control light-induced degradation outdoors. Anatase, however, is a potent catalyst that promotes oxidation as opposed to being a stabilizer. Results from studies on photodegradation of composites therefore depend on the particular crystalline form of TiO_2 used in the experiments. Earlier results from solar-simulated radiation had already established that polypropylene/ TiO_2 (rutile) composites²⁸ and PMMA/ TiO_2 (rutile)⁸⁵ show better UV-stability compared to the polymer alone. The TiO_2 pigment transferred inadvertently from certain sunscreens used by

construction workers on to coatings on steel plates (by contact) has been reported to accelerate the deterioration of the surface characteristics of the product by as much as 100 fold.⁹

Zan et al.⁸⁶ recently studied nanocomposites based on either 98% anatase TiO₂ or a mixed oxide of TiO₂ (with 75% anatase and 25% rutile) grafted on to polystyrene [PS]⁸⁵. These were found to be highly photodegradable when exposed to UV radiation from a 30 W mercury vapour lamp. However, irradiation with wavelength of ca 254 nm UV radiation employed in the study is absent in terrestrial solar radiation. Accelerated photodegradability of anatase-filled nanocomposites under solar radiation occurred in nanocomposites of both epoxy/ TiO₂⁶⁵ as well as LDPE/TiO₂⁸⁴. Polyurethane nanocomposites compounded with rutile and anatase grades of TiO₂ resulted in either photostability or photosensitivity in the nanocomposites exposed to solar-simulated radiation, respectively.¹⁰

Zinc oxide (ZnO), another potent UV radiation absorber, has been evaluated for use as a nanoscale filler as well as in textile treatment.³³ Under solar-simulated UV-B radiation the photodegradation of nanocomposites of polypropylene/ZnO was markedly slower than that for the unfilled polymer.⁸⁸ Not only did the tensile properties deteriorate more slowly, but surface cracking was also better controlled in these nanocomposites. As the grades of nanoscale fillers are relatively higher in cost compared to conventional fillers, the minimum volume fractions needed to achieve the desired performance and level of stability are generally used. An experimental study on polyurethane clear-coat formulations investigated the filler levels needed in a thin coating film to block 99% of the incident UV-B radiation.⁴⁰ Such coatings can protect wood from light-induced damage. Not only was lacquer containing 4% by weight nanoscale ZnO reported to protect spruce and pine wood exposed to outdoor sunlight, but also the performance was superior to that afforded by conventional stabilizers such as UV absorbers and hindered-amine light stabilizers (HALS).⁸¹

UV degradation of wood and wood-plastic composites

Light-induced damaging effects in wood are generally localized at the surface layers defined by the UV radiation penetrating into the wood. It is mainly the lignin fraction in wood that carries chromophores that initiate the degradation process, as confirmed by Fabiyi and McDonald²⁰ and others.^{7, 51, 53} Degradation of lignin by solar UV radiation yields low molecular weight materials that support the growth of fungi and therefore helps initiate biodegradation that rapidly causes deterioration of the material. Controlling light-induced damage to the wood surface therefore has an impact on the bulk mechanical integrity of wood exposed outdoors. Recent use of sophisticated microscopic techniques with nanometre-scale resolution (Atomic Force Microscopy), has allowed a better understanding of structural changes due to photodegradation.⁴² The same technique has been employed very successfully to assess polymer photodegradation.^{22, 31}

X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) of pine wood show that the water-insoluble oxidized products generated at the surface by photodegradation shields the underlying wood from UV radiation.⁶² However, the light-stabilizing effect and mechanism of wood extractives, generally present in all wood, still remain unclear. While some studies show that extractives act as stabilizers against light-induced yellowing in several types of wood,^{48, 51} there is also evidence that extractives have little effect on early stages of light-induced yellowing.⁶⁶ These studies compared regular samples of wood with those where extractives had been removed by extraction with solvents or water prior to exposure. The difference reported might be attributable to the different solvents used which selectively extracted the relevant compounds (as well as to differences between species of wood). In some instances the extractives themselves undergo UV-induced reactions, contributing to discoloration of the wood.⁸³ Chromated copper arsenate used to

treat wood against biodeterioration can also control the light-induced yellowing of wood used outdoors.⁷² Copper ethanolamine treated pine wood showed reduced surface discoloration (and less damage to lignin) compared to untreated wood.⁸⁷ However, copper-based wood treatments have limited application because of their associated negative effects on freshwater and marine environments.

Most laboratory weathering studies on photodegradation of wood have used filtered xenon lamps with spectral distributions that simulate solar radiation.⁵⁰ However, work by Tolvaj and Mitsui^{74, 75} compared the colour change in several varieties of wood exposed to sunlight as well as to a xenon source, and showed differences in the levels of discoloration (hue angle and lightness measurements). Interpreting data on laboratory-accelerated discoloration of wood, especially drawing conclusions on natural weathering based on such data, must be undertaken with caution. Furthermore, the possibility of high intensity radiation causing reactions not typical of outdoor exposure must be taken into account in accelerated photodegradation of wood in laboratory tests. Irradiating with high intensity laser radiation has also been used in laboratory studies of photodegradation of wood but does not yield information on damage due to solar radiation. High energy, monochromatic radiation from an argon laser (244 nm), for instance, yields surface degradation products that are very different from those obtained on exposure to simulated solar radiation.^{35, 52} A positive correlation exists between the depth of penetration and the wavelength of radiation in the range 246-496 nm.³² The more damaging UV-B radiation affects the surface layers (but is rapidly attenuated) and radiation around 400 nm is the most effective in photodegradation of sub-surface bulk wood.

Wood plastic composites have increased in popularity in recent years, because they are viewed as a 'green' recyclable product (in the USA, the growth rate is projected to be >9% annually). Although often more expensive than lumber, the material does not require routine maintenance during use.⁴⁹ Previous research has shown that wood-derived fillers in plastic-wood composites act mainly as light stabilizers. This is expected due to shielding of light by the opaque wood particles. However, these composites are susceptible to moisture damage. The swelling of wood particles due to absorption of water results in micro-cracking of the matrix at the wood/plastic interface,² a phenomenon that depends on the type of polymer used (see Fig. 7-1). A comparison of wood/polymer composites (58-59% wood) made of polypropylene (PP) and high-density polyethylene (HDPE), showed UV-induced discoloration of the latter to be lower by ca 34%.²⁰ Similar results were found for PP/wood flour composites (30 and 60% filler) using the more fundamental molecular weight data that yield direct evidence of stability at a molecular level.³⁸ However, HDPE/wood showed a deterioration of mechanical properties of the composite^{68, 69} upon water/UV radiation exposure. This could be controlled to an extent using commercial UV stabilizers. Relatively less damage was observed on injection moulded surfaces than on planed surfaces where some wood filler granules are exposed.

UV degradation and stabilization of polycarbonates

Because of their unique combination of toughness and high clarity, polycarbonates (PC) are widely used in glazing applications in building construction (replacing glass) and automotive manufacture. The material, while more expensive than glass, has the advantage of being lighter and is increasingly employed also in non-glazing uses in automobiles, since it reduces the weight of the vehicle. Exposure of polycarbonate to solar UV radiation results in yellowing and loss in mechanical integrity.¹⁴ Yellowing in polycarbonate is due to two types of photodegradation reactions, the Photo-Fries reaction and oxidative degradation. The latter reaction is dominant in outdoor exposure and is confirmed to be initiated via the formation of charge-transfer complexes between polymer and oxygen.¹⁵

Pickett et al.⁵⁴ recently reported wavelength sensitivity data for yellowing of bisphenol-A polycarbonate and its blends with other thermoplastics on exposure to simulated solar radiation (a xenon source) at 35° to 45°C. In addition to demonstrating the effective wavelength ranges responsible for yellowing in the sunlight spectrum, the study also provided verification of the reciprocity rule for the materials. The reciprocity rule requires the relative rate of the degradation process, k , to be a linear function of the intensity, I , of light incident on the sample. Thus, for systems where the reciprocity rule applies: $\log_e k = \log_e A + p \log_e I$, with a constant p equal to unity. For the yellowing degradation in polycarbonate and poly(butylene terephthalate) [PBT], the value of p was close to unity but for styrene-acrylonitrile co-polymer [SAN] and acrylonitrile-butadiene-styrene copolymer [ABS], the values were 0.63 and 0.34. Accelerated test methods that rely on higher intensities of light therefore should not be used with the latter polymers. The applicability of the reciprocity rule for polycarbonates reported here is in agreement with two previous studies on stabilized PC, one carried out using a solar concentrator to increase the intensity³⁰ and another using a xenon source.¹⁶ The results emphasize the critical need to match the spectral characteristics of the source used in accelerated tests to that of sunlight to ensure meaningful and predictive quantification of photodamage. In accelerated testing of polymers in general, the distribution of degradation products was characteristically heterogeneous, affecting the degradation mechanism and complicating lifetime prediction.⁵⁶ Virtually no work has been reported on the applicability of the reciprocity rule in photodegradation of wood species of interest.

Compounds that absorb UV-B radiation, such as hydroxybenzophenones, are commonly used light stabilizers in bisphenol A polycarbonate (PC). However, qualitative data on a superior light absorber additive, a novel block co-polymer, has been reported.¹⁷ On exposure to UV-B radiation the block copolymer additive itself undergoes a rearrangement reaction and is converted within hours into an efficient UV-absorbing top layer. Being a polymer it is not easily leached out when the polycarbonate formulation is used outdoors. Other copolymers of polycarbonate that generate a protective UV-absorbing surface coating on initial

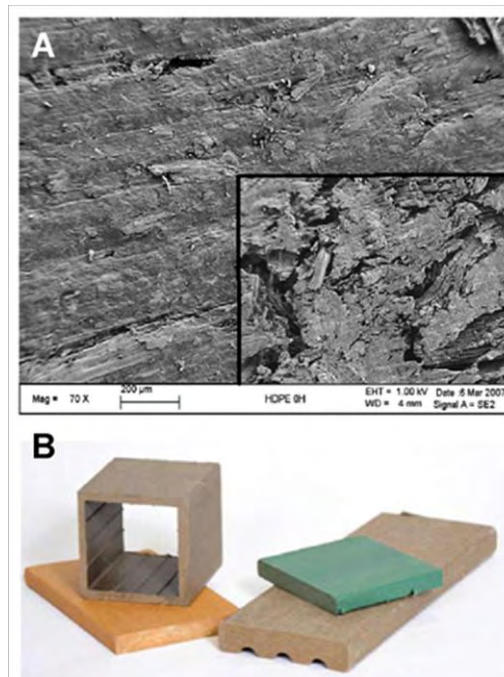


Fig. 7-1. (A) Magnified image (electron micrograph) of HDPE/pine wood composite with an inset at the same magnification, showing the surface after two years of outdoor exposure in Idaho (USA). Adapted with permission from Fabiyi et al.²⁰ (B) Processed wood plastic composite product. Reproduced with permission from Taylor et al.⁷¹

exposure to sunlight were also reported.⁶¹ A novel thin ceramic oxide (ZnO and Al₂O₃) coating on polycarbonate also effectively stabilizes the material.⁴⁵ However, the approach is not likely to be cost-effective for use in high-volume applications. The use of hybrid organic-inorganic polymers (ceramers) as a surface coating can impart light stability as well as enhance surface hardness in polycarbonates.¹⁹ Organic surface coatings can also be used for the same purpose.³⁴ These different approaches may allow low-cost alternative light-stabilization to be achieved in commercial polycarbonate glazing materials.

Effect of increased temperature and humidity on photodegradation

Projected increases in future average ambient temperatures due to global climate change in certain regions are likely to accelerate the light-induced degradation of materials outdoors. The oxidative reactions in wood and polymers can be initiated by UV-B radiation or thermal exposure. Once the photoinitiated oxidative degradation of a material is underway, the rate of the process increases with increasing ambient temperature. The magnitude of this acceleration depends on the activation energy of the reactions and varies with the chemical nature of the material. In the case of polymers, the presence of additives may also influence the activation energy. Increases in the ambient temperatures in some regions due to climate change will therefore accelerate light-induced degradation of materials. In mulch films made from polyethylene stabilized with conventional hindered amine light stabilizers (HALS), for instance, the useful lifetime (based on tensile property measurements) can be decreased by 40% when the temperature in the accelerated weathering chamber increases from 30° to 40°C.¹⁸ The same phenomenon was mostly responsible for the different rates of outdoor weathering of polypropylene (PP) in South India, obtained in summer *versus* in the winter.⁵⁹

The effect of temperature is also illustrated on rigid poly(vinyl chloride) siding material exposed outdoors with and without an insulating backing material. Samples with the backing reached a relatively higher temperature on exposure to sunlight and underwent more severe discoloration on exposure to the same dosage of UV-B radiation. Difference in discoloration between the backed and unbacked poly(vinyl chloride) samples showed a high positive correlation ($r = 0.96$) with the difference in temperatures achieved by the two sets of samples.²⁵ In assessing the reduced lifetimes of materials due to increased solar UV radiation levels, the contribution due to increased thermal oxidation and possible synergism between the two processes also needs to be taken into account.

The magnitude of the thermal acceleration of degradation depends on the activation energy for the process. Accelerated weathering carried out in the laboratory on polycarbonates with a UV-absorbing coating showed that the activation energy for changes in gloss and yellowing is less than ca 5 kcal/mole.⁵⁵ This translates to about a 33% increase in rate of degradation for each 10°C increase in temperature. For polycarbonates, temperature is not an overwhelming factor that controls the rate of yellowing. This is, however, not true of all common polymers in general. The activation energies for photodegradation of other common polymers tend to be much higher.

Increased humidity is well-known to accelerate the photothermal breakdown of polymers, including the coatings.²³ Although plastics are hydrophobic materials, they absorb moisture and are stressed due to the swell/shrink or freeze/thaw cycles. The evaporation of the absorbed water initially dries the surface layer resulting in stress at the interface with underlying hydrated layers. Beyond the physical impacts such as matrix swelling, erosion, and stabilizer extraction, humidity can also play a chemical role in chalking of materials such as titania-filled poly(vinyl chloride) (PVC) used in building applications.

Approaches to UV-stabilization of materials

Unlike for biota, engineers have stabilization technologies that can be used to mitigate the acceleration of degradation due to increases in the UV-B component of solar radiation. Better understanding of the mechanisms of photooxidation is critical to developing new stabilizer compounds that can protect materials against light-induced damage. This is particularly important for plastics used in outdoor applications. The general chemical pathways in the photooxidation of common polyolefins (PP and PE) are summarized in Fig. 7-2. The polymer RH is photo-excited into a species $[RH]^*$ that reacts with oxygen. The ROOH signifies the resulting unstable polymer peroxide intermediate in the reaction. The oxidation itself is a free-radical process where the polymer radical, $R\cdot$, reacts with molecular oxygen to yield a polymer peroxy radical $ROO\cdot$. This radical species is converted to ROOH, which can reform radicals, making this an autocatalytic process. Five different possible stabilization mechanisms are shown in boxes with the points at which each of these can act in the reactions scheme indicated in broken lines. Hindered amine light stabilizers (HALS) for instance, can act as a radical scavenger for $R\cdot$ and $ROO\cdot$ radicals. Novel research techniques are being used to better understand the changes in the structure of polymers due to photodegradation.^{1, 37}

Blending light stabilizers (UV absorbers with HALS) to obtain synergistic effects is of considerable research interest.⁶⁴ Polyester-polyurethane clear-coat formulations that contained both HALS and UV absorbers, for instance, show a synergistic light-stabilizing effect. However, this is not a general observation. Mixed stabilizer pairs may not be compatible with all types of coatings and not all pairs of stabilizers show synergism. Recent work suggests that it is the UV absorbers with a phenolic moiety in their structure that are likely to show synergy with HALS.⁷⁰

Stabilizers with a chemical structure that includes a phenolic moiety as well as a cyclic amine moiety (typical of HALS) in the same molecule were commercialized by the additives industry. A new light stabilizer for plasticized PVC with superior weathering performance compared to conventional stabilizers was introduced in 2005.⁴¹ In some formulations of PVC containing the additive, a doubling of the outdoor lifetime compared to conventional stabilizers was claimed. Yet another new stabilizer commercialized in 2007 is intended to control light-induced discoloration of thermoplastic polyurethanes.¹³ The additive itself does not impart any initial colour to the plastic material, a particular advantage in white or light-coloured formulations. These recently introduced UV-stabilizers show great promise in low-cost stabilization of common polymers against UV radiation -initiated degradation.

This approach of combining HALS stabilizers with a UV absorber has been reported for protection of wood as well. With wood plastic composites (40% wood) the synergistic stabilizing effect of diester-based HALS in combination with benzotriazole UV absorbers,

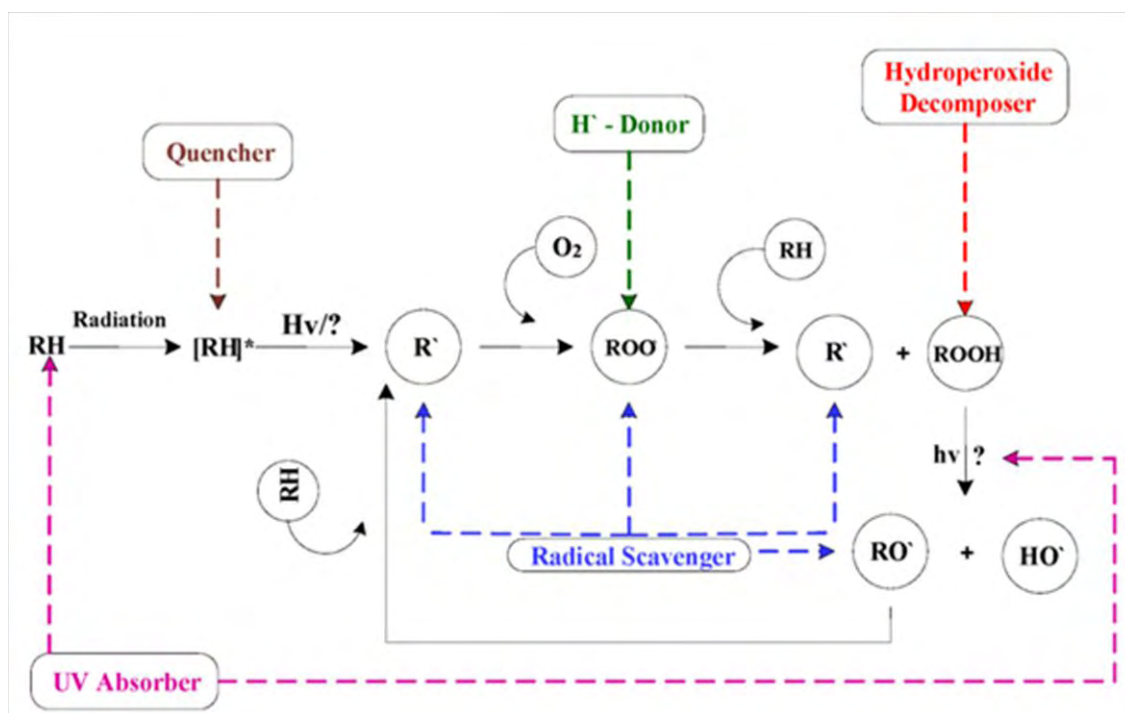


Fig. 7-2. A schematic diagram of the various reaction pathways involved in the UV radiation-initiated oxidative degradation of polyolefins.

was shown in an outdoor exposure study.⁴⁶ Wood is typically protected from elements using surface coatings. Nanocomposite coatings of zinc oxide (ZnO) can be used to protect wood from sunlight-induced damage.⁸¹ However, commonly used paints such as acrylic-urethane paints lose their surface gloss and pliability on natural and artificial weathering.⁴³ Using protective polyurethane (PU) clear coats based on either aliphatic or aromatic chemical structure can also deter such damage. Discoloration of clear-coated wood may be caused by the yellowing of both the clear coating itself and the underlying wood. While the aliphatic PU coatings increase transmission of UV-B radiation upon aging of the coating, resulting in damage of the underlying wood, the aromatic PU coatings are much more effective in protecting the wood from damage by UV-B radiation.¹²

Conclusions

Composites of thermoplastic polymers with nanoscale inorganic fillers show improved strength and durability as materials of construction. These can act as absorbers or screeners of UV radiation and are more efficient light stabilizers of the polymer matrix compared to conventional fillers. Initial findings suggest that metal oxide nanofillers impart photostability as expected, unless oxides such as anatase TiO₂, which catalytically promote oxidation of the polymer, are used. Clay nanofiller materials, however, unexpectedly decrease the photostability of the polymer matrix because of associated contaminants. The wood-polymer composites show better UV stability relative to the polymer matrix alone due to the same UV-shielding mechanism, but tend to be more humidity-sensitive. Based on the limited available data, polymer nanocomposites based on oxide nanofillers are likely to be more stable compared to comparable conventional composites under increased UV-B radiation in sunlight.

Estimating the impact of an increased solar UV-B component on the photodegradation of wood is complicated. In wood, photodegradation is limited to the surface layer defined by the depth of penetration of the UV radiation. Accelerated testing of wood in the laboratory therefore needs to use light sources that achieve similar depths of penetration. Even then, applicability of the reciprocity rule to the wood species may limit the use of the laboratory approach to simulate outdoor exposure. The naturally present extractives in some species of wood may also modify their photostability.

Polycarbonates, widely used in glazing and other applications, undergo light-induced yellowing and are mostly affected by solar wavelengths < 300 nm. Studies on intensity-dependence of the process show that the reciprocity rule is obeyed, suggesting that laboratory-accelerated testing provides a reliable means of estimating lifetimes outdoors. New approaches to photostabilizing polycarbonates as well as other common polymers are emerging. The use of novel stabilizers that combine the structural features of the effective UV absorbers and radical scavengers show particular promise. While stabilizer technology is able to mitigate the effects of any potential increase in solar UV radiation, particularly in polycarbonates, the associated increase in cost remains less clear.

References

- 1 Abel ML and Coppitters C, 2008, Conservation of polymers: A view to the future, *Surf. Interface Anal.*, **40**, 445-449.
- 2 Adhikary KB, Pang S and Staiger MP, 2009, Accelerated UV weathering of recycled polypropylene-sawdust composite, *J. Thermoplast. Compos. Mater.*, **22**, 661-679.
- 3 Andrady AL and Neal MA, 2009, Applications and societal benefits of plastics, *Philos. Trans. Roy. Soc. Lond. B. Biol. Sci.*, **364**, 1977-1984.
- 4 Andrady AL, Searle ND and Crewdson LFE, 1992, Wavelength sensitivity of unstabilized and UV stabilized polycarbonate to solar simulated radiation, *Polymer Deg. Stab.*, **35**, 235-247.
- 5 Andrady AL, Song Y, Parthasarathy VR, Fueki K and Torikai A, 1991, Photoyellowing of mechanical pulp. Part I: Examining the wavelength sensitivity of light-induced yellowing using monochromatic radiation, *TAPPI Journal*, **74**, 162-168.
- 6 Andrady AL, Torikai A and Fueki K, 1989, Photodegradation of rigid PVC formulations I. Wavelength sensitivity to light-induced yellowing by monochromatic light, *J. Appl. Polymer. Sci.*, **37**, 935-946.
- 7 Azadfallah M, Mirshokrati SA, Latibari AJ and Parsapajouh D, 2008, Analysis of photodegraded lignin on cellulose matrix by means of FTIR spectroscopy and high pressure size exclusion chromatography, *Iran. Polymer. J.*, **17**, 73-80.
- 8 Azuma Y, Takeda H, Watanabe S and Nakatani H, 2009, Outdoor accelerated weathering tests for polypropylene and polypropylene/talc composites, *Polymer Deg. Stab.*, **94**, 2267-2274.
- 9 Barker P and Branch A, 2008, The interaction of modern sunscreen formulations with surface coatings, *Prog. Org. Coat.*, **62**, 313-320.
- 10 Chen XD, Wang Z, Liao ZF, Mai YL and Zhang MQ, 2007, Roles of anatase and rutile TiO₂ nanoparticles in photooxidation of polyurethane, *Polymer Test.*, **26**, 206-208.
- 11 Chmela S, Kleinová A, Fiedlerová A, Borsig E, Kaempfer D, Thomann R and Mülhaupt R, 2005, Photo-oxidation of sPP/organoclay nanocomposites, *J. Macromol. Sci. A: Pure Appl. Chem.*, **42**, 821-829.

- 12 Chou P, Chang H, Yeh T and Chang S, 2008, Characterizing the conservation effect of clear coatings on photodegradation of wood, *Biores. Technol.*, **99**, 1073-1079.
- 13 CIBA, 2007, Ciba presents new light stabilizer for TPU resins, *Additives for Polymers*, **2007**, 2-3.
- 14 Diepens M and Gijsman P, 2007, Photodegradation of bisphenol A polycarbonate, *Polymer Deg. Stab.*, **92**, 397-406.
- 15 Diepens M and Gijsman P, 2008, Photo-oxidative degradation of bisphenol A polycarbonate and its possible initiation processes, *Polymer Deg. Stab.*, **93**, 1383–1388.
- 16 Diepens M and Gijsman P, 2009, Influence of light intensity on the photodegradation of bisphenol A polycarbonate, *Polymer Deg. Stab.*, **94**, 34-38.
- 17 Diepens M and Gijsman P, 2009a, Photostabilizing of bisphenol A polycarbonate by using UV-absorbers and self protective block copolymers based on resorcinol polyarylate blocks, *Polymer Deg. Stab.*, **94**, 1808–1813.
- 18 Espí E, Salmerón A, Fontecha A, García Y and Real AI, 2007, The effect of different variables on the accelerated and natural weathering of agricultural films, *Polymer Deg. Stab.*, **92**, 2150-2154.
- 19 Fabbri P, Leonelli C, Messori M, Pilati F, Toselli M, Veronesi P, Molat-Therias S, Rivaton A and Gardette JL, 2008, Improvement of the surface properties of polycarbonate by organic-inorganic hybrid coatings, *J. Appl. Polymer. Sci.*, **108**, 1426-1436.
- 20 Fabiyi JS, Armando A, McDonald G, Michael P, P. W, Peter R and Griffiths R, 2008, Wood plastic composites weathering: Visual appearance and chemical changes, *Polymer Deg. Stab.*, 1405-1414.
- 21 FAO, 2009, State of the World's Forests 2009, Food and Agricultural Organization of the United Nations Report No. I0350/E, Rome, Italy, p. 144. <http://www.fao.org/docrep/011/i0350e/i0350e00.HTM>
- 22 Germinari LT and Shang PP, 2008, Advances in nano and thermal analysis of coatings, *J. Therm. Anal. Calomet.*, **93**, 207–211
- 23 Gu X, Zhe D, Watson SS, Chen GN, Zhao M, Stutzman PE, Stanley D, Nguyen T, Chin J and Martin JW, 2009, Studying Long-term Performance of a Nano-ZnO filled Waterborne Polyurethane Coating using Spectroscopies and Microscopies in *Coatings Science International* Noordwijk, The Netherlands.
- 24 Hamid SH, 2000, *Handbook of Polymer Degradation, Revised and Expanded Second Edition*, Marcel Dekker, New York, NY, USA.
- 25 Hardcastle HK, III, 2008, Influence of backing on weathering induced color change of two rigid vinyl building materials in *Proceedings of the Society of Plastics Engineers - Color and Appearance Division Regional Technical Conference 2008. CAD RETEC 2008*, San Antonio, TX, pp. 184-188.
- 26 Howard JL, 1999, Timber Production, Trade, Consumption, and Price Statistics 1965-1997, USDA, Forest Service, Forest Products Laboratory Report No. FPL–GTR–116, Maddison, WI, USA, p. 82. <http://www.fpl.fs.fed.us/documnts/fplgtr/fplgtr116.pdf>
- 27 Imaizumi A and Yoshizumi K, 2006, Effect of substrate on action spectra of fading of a selected disperse dyestuff under light radiation, *Textile Res. J.*, **76**, 757-764.
- 28 Jianjun C, 2004, Preparation of PP/TiO₂ nanocomposite and analysis for its mechanisms of aging resistance, *Gongcheng Suliao Yingyong*, **32**, 43–46.
- 29 Jirous-Rajkovic V, Turkulin H and Miller ER, 2004, Depth profile of UV-induced surface degradation, *Surf. Coat. Int. B: Coat. Trans.*, **87**, 241-247.
- 30 Jorgensen G, Bingham C, King D, Lewandowski A, Netter J and Terwilliger K, 2000, Use of uniformly distributed concentrated sunlight for highly accelerated testing of

- coatings, in *Service life prediction, methodology and metrologies. ACS Symposium Series 802* (Eds.: Martin JW and Bauer DR), American Chemical Society, Washington, DC, USA, p. 115.
- 31 Kaczmarek K and Chaberska H, 2009, AFM and XPS study of UV-irradiated poly(methyl methacrylate) films on glass and aluminum support *Appl. Sur. Sci.*, **255**, 6729-6735.
 - 32 Kataoka Y, Kiguchi M, Williams RS and Evans PD, 2007, Violet light causes photodegradation of wood beyond the zone affected by ultraviolet radiation, *Holzforschung.*, **61**, 23-27.
 - 33 Kathirvelu S, D'Souza L and Dhurai B, 2009, UV protection finishing of textiles using ZnO nanoparticles, *Ind. J. Fibre Textile Res.*, **34**, 267-273.
 - 34 Kirwan K and Taylor A, 2007, Improving environmental performance of polymer glazing through novel material hybrids, *Plast. Rubber Composites*, **36**, 85-90.
 - 35 Krishna K, Pandey KK and Tapani VT, 2008, Comparative study of photodegradation of wood by a UV laser and a xenon light source, *Polymer Deg. Stab.*, **93**, 2138-2146.
 - 36 Kumar AP, Depan D, Tomer NS and Singh RP, 2009, Nanoscale particles for polymer degradation and stabilization—Trends and future perspectives, *Prog. Polymer Sci.*, **34**, 479–515.
 - 37 Kusakabe D, Takayama T and Kuriyama T, 2009, Degradation of surface structure and mechanical properties in plastics after outdoor exposure test, in *Proceedings of 20th Symposium of Materials Life Society Japan*, Kyoto, Japan, pp. 47-48.
 - 38 La Mantia FP and Morreale M, 2008, Accelerated weathering of polypropylene/wood flour composites, *Polymer Deg. Stab.*, **92**, 1252-1258.
 - 39 Lonkar SP, Kumar AP and Singh RP, 2007, Photo-stabilization of EPDM–clay nanocomposites: effect of antioxidant on the preparation and durability, *Polym. Adv. Technol.*, **18**, 891-900.
 - 40 Lowry MS, Hubble DR, Wressell AL, Vratsanos MS, Pepe FR and Hegedus CR, 2008, Assessment of UV-permeability in nano-ZnO filled coatings via high throughput experimentation, *J. Coat. Technol. Res.*, **5**, 233-239.
 - 41 Markarian J, 2004, Advances in PVC heat and light stabilization, *Plastics, Addit. Compounding*, **6**, 46-49.
 - 42 Meincken M and Evans PD, 2009, Nanoscale characterization of wood photodegradation using atomic force microscopy, *Europ. J. Wood. Wood. Prod.*, **67**, 227-231.
 - 43 Merlatti C, Perrin FX, Aragon E and Margaillan A, 2008, Natural and artificial weathering characteristics of stabilized acrylic-urethane paints, *Polymer Deg. Stab.*, **93**, 896-903.
 - 44 Morlat-Therias S, Mailhot B, Gonzalez D and Gardette J-L, 2005, Photooxidation of polypropylene /montmorillonite nanocomposites. 2. Interactions with antioxidants, *Chem. Material.*, **17**, 1072-1078.
 - 45 Moustaghfir A, Tomasella E, Jacquet M, Rivaton A, Mailhot B, Gardette JL and Bêche E, 2006, ZnO/Al₂O₃ coatings for the photoprotection of polycarbonate, *Thin Solid Films* **515**, 662-665.
 - 46 Muasher M and Sain M, 2006, The efficacy of photostabilizers on the color change of wood filled plastic composites, *Polymer Deg. Stab.*, **91**, 1156–1165.
 - 47 Nguyen P, Pellegrin B, Mermet C, Gu X, Shapiro A and Chin J, 2009, Degradation and Nanoparticle Release of Polymer Nanocomposites Exposed to UV, in *Paper Presented at the 4th European Weathering Symposium*, Budapest, Hungary.

- 48 Nzokou P and Kamdem DP, 2006, Influence of wood extractives on the photo-discoloration of wood surface exposed to artificial weathering, *Col. Res. Applic.*, **31**, 425-434.
- 49 Oksman K and Sain M, 2008, Wood-polymers Composites, Woodhead Publishing Ltd, Sawston, UK, p. 384.
- 50 Oltean L, Teischinger A and Hansmann C, 2008, Wood surface discolouration due to simulated indoor sunlight exposure, *Europ. J. Wood. Wood. Prod.*, **66**, 51-56.
- 51 Pandey KK, 2005, Study of the effect of photo-irradiation on the surface chemistry of wood, *Polymer Deg. Stab.*, **90**, 9-20.
- 52 Pandey KK and Vuorinen T, 2008, Comparative study of photodegradation of wood by a UV laser and Xenon light source, *Polymer Deg. Stab.*, **93**, 2138-2146.
- 53 Pastore TCM, Oliveira CC, Rubim JC and Santos KD, 2008, Effect of artificial weathering on tropical woods monitored by infrared spectroscopy *Quimica Nova*, **31**, 2071-2075.
- 54 Pickett JE, Gibson DA and Gardner MM, 2008, Effects of irradiation conditions on the weathering of engineering thermoplastics, *Polymer Deg. Stab.*, **93**, 1597-1606.
- 55 Pickett JE, Sargent JR, Blaydes HA and Babbie N, 2009, The effect of temperature on the weathering lifetime of coated polycarbonate, *Polymer Deg. Stab.*, **94**, 1085-1091.
- 56 Pospíšil J, Pilař J, N.C B, Marek A, Horák C and Nešpůrek S, 2009, Factors affecting accelerated testing of polymer photostability, *Polymer Deg. Stab.*, **91**, 417-422.
- 57 Qin H, Zhang S, Liu H, Xie S, Yang M and Shen D, 2005, Photo-oxidative degradation of polypropylene/montmorillonite nanocomposites, *Polymer*, **46**, 3149–3156.
- 58 Qin HL, 2004, UV photo aging of polyamide 6/montmorillonite nanocomposite, *Gaodeng Xuexiao Huaxue Xuebao*, **25**, 197–198.
- 59 Rajakumar K, Sarasvathy V, Chelvan AT and Vijayakumar CT, 2009, Natural weathering studies of polypropylene, *J. Polymner. Env.*, **17**, 191-202.
- 60 Reijnders L, 2008, Hazard reduction for the application of titania nanoparticles in environmental technology, *J. Haz. Matter.*, **142**, 440–445.
- 61 Ros M, 2007, Resisting the elements, *Materials World*, **15**, 20-21.
- 62 Salaita GN, Ma FMS, Parker TC and Hoflund GB, 2008, Weathering properties of treated southern yellow pine wood examined by X-ray photoelectron spectroscopy, scanning electron microscopy and physical characterization, *Appl. Sur. Sci.*, **254**, 3925–3934.
- 63 Sanchez-Valdes S, Martinez Colunga JG, Lopez-Quintanilla ML, Yanez Flores I, Garcia-Salazar ML and Gonzalez Cantu C, 2008, Preparation and weathering of polymer nanocomposites, *Polymer Bull.*, **60**, 829-836
- 64 Santos R, Botelho G and Machado AV, 2010, Role of ultraviolet absorbers (UVA) and hindered amine light stabilizers (HALS) in ABS stabilization, *Materials Sci. Forum*, **636-637**, 772-778.
- 65 Scierka S, Drzal PL, Forster AL and Svetlik S, 2005, Nanomechanical Properties of UV Degraded TiO₂/Epoxy Nanocomposites, in *Proceedings of the 28th Annual Meeting of the Adhesion Society*, Adhesion Society, Mobile. AL, USA, p. 524.
- 66 Sharratt V, Hill CAS and Kint DPR, 2009, A study of early colour change due to simulated accelerated sunlight exposure in Scots pine (*Pinus sylvestris*), *Polymer Deg. Stab.*, **94**, 1589–1594.
- 67 Shih Y and Wang C, 2009, Photolytic degradation of polybromodiphenyl ether under UV lamp and solar radiation,, *J. Haz. Matter.*, **165**, 34-38.

- 68 Stark NM and Matuana LM, 2006, Influence of photostabilizers on wood flour HDPE composites exposed to xenon-arc radiation with and without water spray, *Polymer Deg. Stab.*, **91**, 3048-3056.
- 69 Stark NM and Matuana LM, 2007, Characterization of weathered wood-plastic composite surfaces using FTIR spectroscopy, contact angle, and XPS, *Polymer Deg. Stab.*, **92**, 1883-1890.
- 70 Takenaka H, Mizokawa S and Ohkatsu Y, 2007, Interaction of hindered amine light stabilizers and UV absorbers, *J. Jap. Petrol. Inst.*, **50**, 8-15.
- 71 Taylor A, Yadama V, Englund KR and Harper D, 2009, Wood Plastic Composites: A Primer, University of Tennessee Report No. PB1779-500-1/09, p. 12. <http://www.utextension.utk.edu/publications/pbfiles/PB1779.pdf>
- 72 Temiz A, Terziev N, Eikenes M and Hafren J, 2006, Effect of accelerated weathering on surface chemistry of modified wood, *Appl. Sur. Sci.*, **253**, 5355-5362.
- 73 Therias SM, Mailhot B, Gardette J-L, Da Silva C, Haidar B and Vidal A, 2005, Photooxidation of ethylene-propylene-diene/montmorillonite nanocomposites, *Polymer Deg. Stab.*, **90**, 78-85.
- 74 Tolvaj L and Mitsui K, 2005, Light source dependence of the photodegradation of wood, *J. Wood. Sci.*, **51**, 468-473.
- 75 Tolvaj L and Mitsui K, 2010, Correlation between hue angle and lightness of light irradiated wood, *Polymer Deg. Stab.*, **95**, 638-642.
- 76 Torikai A, Chigita K, Okisaki F and Nagata M, 1995, Photo-oxidative degradation of polyethylene containing flame-retardant agents by monochromatic light, *J. Appl. Polymer. Sci.*, **58**, 685-690.
- 77 Torikai A, Geetha R, Nagaya R and Fueki K, 1990, Radiation-Induced degradation of polyethylene: Polymer structure and stability, *J. Polymer Sci. A-Chem.*, **28**, 36-39.
- 78 Torikai A, Kobatake T and Okisaki F, 1998, Photodegradation of polystyrene containing flame retardants, *J. Appl. Polymer. Sci.*, **67**, 1293-1300.
- 79 Torikai A, Mitsuoka T and Fueki K, 1993, Wavelength sensitivity of the photo-induced reactions in polycarbonate, *J. Polymer Sci. A-Chem.*, **31**, 2785-2788.
- 80 Wang J, Sun W and Ali SF, 2009, Nanoparticles: Is Neurotoxicity a Concern?, in *Nanotoxicity* eds.: Sahu SC and D.A.Casciano., John Wiley Sons New York, NY, USA, p. doi: 10.1002/9780470747803.ch9780470747809.
- 81 Weichelt F, Emmler R, Flyunt R, Beyer B, Buchmeiser MR and Beyer M, 2009, ZnO-based UV nanocomposites for wood coatings in outdoor applications, *Macromol. Mat. Engin.*, **295**, 130-136.
- 82 Yang R, Li Y and Yu J, 2005, Photo-stabilization of linear low density polyethylene by inorganic nano-particles, *Polymer Deg. Stab.*, **88**, 168-174.
- 83 Zahri S, Belloncle C, Charrier F, Pardon P, Quideau S and Charrier B, 2007, UV light impact on ellagitannins and wood surface color of European oaks (*Quercus petraea* and *Quercus robur*), *Appl. Sur. Sci.*, **253**, 4985-4989.
- 84 Zan L, Fa W and Wang S, 2006, Novel photodegradable low-density polyethylene-TiO₂ nanocomposite film, *Environ. Sci. Technol.*, **40**, 1681-1685.
- 85 Zan L, Liu Z, Fa W and Peng T, 2006, A novel polymethyl methacrylate (PMMA)-TiO₂ nanocomposite and its thermal and photic stability, *Wuhan University Journal of Natural Sciences*, **1**, 415-418.
- 86 Zan L, Tian L, Liu Z and Peng Z, 2004, A new polystyrene-TiO₂ nanocomposite film and its photocatalytic degradation, *Appl. Catal. A*, **264**, 237-242.
- 87 Zhang J, D, Kamdema DP and Temiz A, 2009, Weathering of copper-amine treated wood, *Appl. Sur. Sci.*, **256**, 842-846.

- 88 Zhao H and Li R, 2006, A study on the photo-degradation of zinc oxide (ZnO)-filled polypropylene nanocomposites, *Polymer*, **47**, 3207–3217.

Members of the 2010 Environmental Effects Assessment Panel and UNEP representatives

Dr. Anthony L. Andrady
Department of Chemical and
Biomolecular Engineering
North Carolina State University
Raleigh, NC Raleigh, NC 27695-7901,
USA
andrady@andrady.com
Andradyncsu@gmail.com

Dr. Pieter J. Aucamp
Ptersa Environmental Consultants
P.O. Box 915751
Faerie Glen, 0043, South Africa
Email: pjaucamp@iafrica.com

Prof. Alkiviadis F. Bais
Aristotle University of Thessaloniki
Laboratory of Atmospheric Physics
Campus Box 149
54124 Thessaloniki, Greece
Email: abais@auth.gr

Prof. Carlos L. Ballaré
IFEVA, Facultad de Agronomía,
CONICET and Universidad de Buenos
Aires
Avda. San Martin 4453
C1417DSE Buenos Aires, Argentina
Email: ballare@ifeva.edu.ar

Prof. Lars Olof Björn
School of Life Science
South China Normal University
Guangzhou 510631, China, and
Lund University
Department of Biology
SE-223 62 Lund, Sweden
Email: Lars_Olof.Bjorn@cob.lu.se
Lars_Olof.Bjorn@scnu.edu.cn

Prof. Janet F. Bornman (Co-Chair)
International Global Change Centre,
IGCC
University of Waikato
Private Bag 3105
Hamilton 3240, New Zealand
Email: jbornman@waikato.ac.nz

Prof. Martyn Caldwell
2126 Connecticut Ave.,
NW #61
Washington
DC, 20008, USA
Email: martyn.caldwell@usu.edu

Dr. Anthony P. Cullen
School of Optometry, University of
Waterloo
131 Briarcliffe Crescent
Waterloo
Ontario, Canada N2L 5T6
Email: acullen@uwaterloo.ca

Dr. Frank R. de Gruijl
Department of Dermatology
Leiden University Medical Centre
Bldg. 2 POSTAL Zone S2P
P.O. Box 9600
NL-2300 RC Leiden, The Netherlands
Email: F.R.de_Gruijl@Lumc.nl

Dr. David J. Erickson III
Computational Earth Sciences Group
Computer Science and Mathematics
Division
Oak Ridge National Laboratory
TN 37831-6016, USA
Email: ericksondj@ornl.gov

Prof. D.-P. Häder
Neue Str. 9
91096 Möhrendorf, Germany
Email: donat@dphaeder.de

Dr. E. Walter Helbling
Estación de Fotobiología Playa Unión
Casilla de Correo 15
(9103) Rawson, Chubut, Argentina
Emails whelbling@efpu.org.ar

Members of the UNEP Environmental Effects Assessment Panel

Dr. Mohammad Ilyas
Albiruni Environment and Science
Development Centre (EnviSC)
9 Hilir Pemancar
11700 Gelugor, Malaysia
Email: drmij9@yahoo.com

Dr. Janice Longstreth
TIGRR
911 Kirkdale Rd, Ste 200
Bethesda, MD 20817, USA
Email: janicel@tigrr.com

Dr. Robyn Lucas
National Centre for Epidemiology and
Population Health
The Australian National University
Cnr Mills and Eggleston Roads 0200
Canberra, Australia
Email: robyn.lucas@anu.edu.au

Dr. Sasha Madronich
Atmospheric Chemistry Division
National Center for Atmospheric
Research
Boulder, Colorado, 80307, USA
Email: sasha@ucar.edu

Dr. Richard L. McKenzie
National Institute of Water and
Atmospheric Research
NIWA, Lauder
Private Bag 50061 Omakau
Central Otago 9320, New Zealand
Email: r.mckenzie@niwa.co.nz

Prof. Mary Norval
Biomedical Science
University of Edinburgh Medical
School
Teviot Place, Edinburgh EH8 9AG, UK
Email: Mary.Norval@ed.ac.uk

Dr. Nigel D Paul (Co-Chair)
Lancaster Environment Centre,
Lancaster University,
Lancaster, LA1 4YQ, UK
Email: n.paul@lancaster.ac.uk

Dr. Halim Hamid Redhwi
King Fahd University of Petroleum &
Minerals (KFUPM)
Dhahran 31261, Saudi Arabia
Email: hhamid@kfupm.edu.sa

Prof. Sharon Robinson
Institute for Conservation Biology and
Environmental Management
School of Biological Sciences
University of Wollongong
Northfields Avenue
NSW 2522, Australia
Email: sharonr@uow.edu.au

Dr. Keith Solomon (Secretary)
Centre for Toxicology, School of
Environmental Sciences
University of Guelph
Guelph, ON, N1G 2W1 Canada
Email: ksolomon@uoguelph.ca

Dr. Barbara Sulzberger
Swiss Federal Institution of Aquatic
Science and Technology (Eawag)
Überlandstrasse 133
P.O. Box 611
CH-8600 Dübendorf, Switzerland
Email: sulzberger@eawag.ch

Prof (Emeritus). Yukio Takizawa
National Institute for Minimata Disease
2-34-9 Nakadai Itabashiku,
Tokyo 174-0064, Japan
Email: takizawa-y@sky.plala.or.jp

Dr. Xiaoyan Tang (Co-Chair)
Peking University
Center of Environmental Sciences
Beijing 100871, China
Email: xytang@pku.edu.cn

Dr. Ayako Torikai
Materials Life Society of Japan
2-6-8 Kayabacho Chuo-ku
Tokyo 103-0025, Japan
Email: torikaia@msj.biglobe.ne.jp

Members of the UNEP Environmental Effects Assessment Panel

Prof. Jan C. van der Leun
Ecofys Netherlands
Kanaalweg 16 G
NL-3526 KL Utrecht, The Netherlands
Email: j.vanderleun@ecofys.nl

Prof. Craig E. Williamson
Department of Zoology,
158 Pearson Hall
Miami University,
Oxford, Ohio 45056 USA
Email: craig.williamson@muohio.edu

Prof. Stephen Wilson
School of Chemistry
University of Wollongong
Northfields Ave.
Wollongong, NSW, 2522, Australia
Email: Stephen.Wilson@uow.edu.au

Dr. Robert C. Worrest
CIESIN, Columbia University
(Emeritus)
190 Turnbull Road
New Hartford, Connecticut 06057-
4139, USA
Email: rworrest@ciesin.columbia.edu

Dr. Richard G. Zepp
United States Environmental
Protection Agency
960 College Station Road
Athens, Georgia 30605-2700, USA
Email: zepp.richard@epa.gov

UNEP contact

Mr. Marco Gonzalez
Ozone Secretariat, UNEP
P.O. Box 30552
Nairobi, Kenya
Email: Marco.Gonzalez@unep.org

Co-Authors

Prof. Amy Austin
University of Buenos Aires,
Faculty of Agronomy and IFEVA-
CONICET,
Department of Ecology,
Avenida San Martín 4453,
(C1417DSE) Buenos Aires, Argentina
Email: austin@ifeva.edu.ar

Prof. Min Shao
College of Environmental Sciences
and Engineering,
Peking University
Beijing, 100871, China
Email: mshao@pku.edu.cn

Members of the UNEP Environmental Effects Assessment Panel



The UNEP Environmental Effects Assessment Panel Lancaster, UK, September 2010

Reviewers of the 2010 UNEP Environmental Effects Assessment Report

Dr. Pedro J. Aphalo,
University of Helsinki,
Helsinki, Finland

Dr. Amy T. Austin,
University of Buenos Aires,
Faculty of Agronomy and IFEVA-
CONICET,
Department of Ecology,
Avenida San Martín 4453,
(C1417DSE) Buenos Aires, Argentina

Dr. Germar Bernhard,
Biospherical Instruments,
San Diego, CA, 92110-2621 USA

Dr. Marianne Berwick,
Memorial Sloan-Kettering Cancer
Center,
Dept of Epidemiology and Biostatistics,
1275 York Avenue, Box 588,
New York, NY, 10021, USA

Prof. Wolfgang Bilger,
AG Ökophysiologie der Pflanzen,
Botanisches Institut,
Universität Kiel,
Olshausenstr. 40, 24098, Kiel,
Germany

"Dr. Natalia Chubarova,
Meteorological Observatory, Chair of
Meteorology and Climatology,
Faculty of Geography,
Moscow State University,
GSP-1, 119991, Moscow, Russia

Dr. Thomas P. Coohill,
Siena College,
515 Loudon Road,
Loudonville, NY, 12211, USA

Dr. Sandra L Cooke,
Duke University,
Department of Biology
Durham, NC 27708, USA

Dr. Susana Diaz,
CADIC-CONICET ,
Ruta 3 y Cap.Mutto,
C.C. 92,
9410 Ushuaia - Tierra del Fuego,
Argentina

Prof. Brian Diffey,
Emeritus Professor of Photobiology,
Dermatological Sciences,
Institute of Cellular Medicine,
Newcastle University NE2 4HH, UK

Prof. Nils Ekelund,
Department of Natural and
Environmental Sciences,
Mid-Sweden University,
851 70 Sundsvall, Sweden

Dr. Auroop R Ganguly,
Oak Ridge National Laboratory,
Oak Ridge, TN, 37831-6016, USA

Dr. Kunshan Gao,
State Key Laboratory of Marine
Environmental Science,
Xiamen University,
Daxue Road 182 (HAIYANG-LOU),
Xiamen, Fujian, 361005, China

Dr. W D Grant,
Sunlight, Nutrition and Health
Research Centre,
San Francisco, CA, USA

Dr. R Elizabeth M Griffin,
Department of Earth and Space
Sciences and Engineering,
4700 Keele Str.,
Toronto, ON M3J 1P3, Canada

Members of the UNEP Environmental Effects Assessment Panel

Prof. Michaela Hegglin,
University of Toronto,
Department of Physics,
60 St. George Street,
Toronto, ON M5S 1A7, Canada

Prof. Dag Hessen,
Section of Marine Biology and
Limnology,
Department of Biology,
University of Oslo,
Pb. 1064, Blindern, N-0316

Dr. Rainer Hofmann,
Faculty of Agriculture and Life
Sciences,
Lincoln University,
PO Box 84,
Lincoln 7647, New Zealand

Dr. Marcel A. K. Jansen,
University College Cork,
College Road, Cork, Ireland

Prof. Jennifer Y King,
Geography Department,
University of California,
Santa Barbara, CA, USA.

Dr. Margaret Kripke,
Department of Immunology,
Box 178,
The University of Texas, M.D.
Anderson Cancer Center,
1515 Holcombe Boulevard,
Houston, TX, 77030-4095, USA

Dr. G. Kulandaivelu,
Madurai Kamaraj University
Kothi No.-242/2,
Opp.Soraswati Hospital,
Old Delhi Road, Gurgaon, India

Dr. Shaoshan Li ,
School of Life Science,
South China Normal University,
Guangzhou 510631, China

Prof. Lawrence E Licht,
York University,
Department of Biology,
4700 Keele Street,
Toronto, ON, M3J 1P3, Canada

Mr Ben Liley
National Institute of Water and
Atmospheric Research
NIWA, Lauder
Private Bag 50061 Omakau
Central Otago 9320, New Zealand

Dr. Kevin K Newsham,
Biological Sciences Division,
British Antarctic Survey,
High Cross, Madingley Road,
Cambridge, CB3 0ET, UK

Dr. Madan Pal,
Senior Scientist,
Division of Plant Physiology,
Indian Agricultural Research Institute,
New Delhi-110012, India

Dr. Barrie M Peake,
University of Otago,
Chemistry Department,
Box 56, Dunedin, New Zealand

Dr. Norma D Searle,
114 Ventnor F,
Deerfield Beach, FL, 33442, USA

Prof. Günther Seckmeyer,
Institute for Meteorology and
Climatology,
University of Hannover ,
Herrenhaeuser Str. 2,
30419 Hannover, Germany

Dr. Anna Maria Siani,
Universita' di Roma "La Sapienza",
Dipartimento di Fisica,
Piazzale Aldo Moro, 5,
IT-00185 Roma, Italy

Reviewers of the UNEP Environmental Effects Assessment Report

Dr. Rajeshwar Sinha,
Department of Botany,
Banares Hindu University,
Varanasi, 221005, India

Dr. Harry Slaper,
Lab for Radiation Research,
RIVM, P.O. Box 1,
NL-3720 BA Bilthoven, The
Netherlands

Professor Ruben Sommaruga,
Head, Laboratory of Aquatic
Photobiology and Plankton Ecology,
Institute of Ecology,
University of Innsbruck,
Technikerstr. 25,
A-6020 Innsbruck, Austria

Dr. J. Richard Soulen,
5333 Hickory Bend,
Bloomfield Hills, MI 48304, USA

Dr. Johannes Stratmann,
University of South Carolina,
Columbia, SC 29208 USA

Dr. Åke Strid,
Department of Natural Sciences,
Örebro University,
701 82 Örebro, Sweden

Prof. Hugh R Taylor,
Centre for Eye Research Australia,
The University of Melbourne,
Department of Ophthalmology,
Locked Bag 8, East Melbourne 8002,
Australia

Dr. Anssi Vähätalo,
Department of Biological and
Environmental Sciences, P.O. Box 65,
FIN-00014 University of Helsinki,
Finland

Dr. John Wargent,
Institute of Natural Resources,
Massey University,
Private Bag 11222,
Palmerston North 4442, New Zealand

Dr. Ann R Webb,
University of Manchester,
Sackville Street,
P.O. Box 88,
Manchester, M60 1QD, UK

Prof. Huixiang Xie,
Institute of Marine Sciences,
University of Quebec at Rimouski,
Rimouski, QC G5L 3A1 Canada

Appendix 2-1: Health risks associated with the use of substitutes for ozone depleting substances

In committing themselves to the phase out of ozone depleting substances (ODSs), Parties to the Montreal Protocol also *de facto* committed themselves to identifying and using acceptable alternatives or replacements for the ODSs, many of which had enjoyed widespread use in a number of important industrial sectors. One of the issues that needed to be considered in the introduction of new chemicals or old chemicals for new uses was the potential health risks associated with the use of these substitutes. As a consequence, the substitutes needed to be evaluated not only for their ability to replace ODSs in terms of technical performance but also for their ability to do so within a framework of acceptable risk; that is, it would not be appropriate to replace an ODS with a substitute that poses a significant or unmanageable risk to humans or their environment.

In the United States (U.S.), the authority for identifying and assessing the risks of ODS substitutes resides with the U.S. Environmental Protection Agency (EPA) which established the Significant New Alternatives Policy (SNAP) programme to evaluate alternatives to ozone depleting substances.¹ The SNAP programme's mandate is to identify substitutes that lower the overall risks to human health and the environment. To the Environmental Effect Assessment Panel's (EEAP) knowledge, the U.S. is the only national authority to have created a programme specifically designed to evaluate substitutes for ODSs; other national authorities have chosen to conduct such evaluations under their extant programs for assessing and managing the risks of chemicals such as the Registration, Evaluation and Authorization of Chemicals (REACH) programme in the EU, the Act on the Evaluation of Chemical Substances and Regulation of Their Manufacture, etc in Japan and National Industrial Chemicals Notification and Assessment Scheme (NICNAS) in Australia.

Because the SNAP programme is the only programme the EEAP is aware of that specifically focuses on the evaluation of substitutes, it also represents the largest source of information that could be accessed rapidly. Thus this section focuses on the assessments made by the SNAP programme with a particular focus on those assessments made in the last decade. At some later date, should the assessment of the risks of substitutes become a permanent part of

¹ Section 612 Clean Air Act Amendments of 1990

its mandate, the EEAP would hope to include information from the assessments of ODS substitutes made by other programs.

A complete review of the SNAP programme, its legislative mandate, and the complete suite of regulatory activities it has undertaken since its inception is beyond the scope of this section. Some information critical to the decision-making process has been included; considerable additional information can be found at the SNAP website:

<http://www.epa.gov/ozone/snap/>, and in the notices and rules that document the acceptable and unacceptable or provisionally acceptable decisions, respectively (see <http://www.epa.gov/Ozone/snap/regulations.html>).

When the SNAP programme was created, its mandate was to not only evaluate the traditional human health and environmental effects associated with the use of the proposed substance or process but also to consider substitutes for their potential to mitigate ozone depletion, thereby reducing exposure to UV-B radiation and the associated health risks. This mandate permits the SNAP programme to evaluate substitutes in a comparative risk framework that is quite different from that required under other U.S. chemical review programs. Important elements of that framework and the SNAP programme mandate include the fact that 1) substitutes are not required to be risk-free to be found acceptable, 2) the SNAP programme is required to evaluate substitutes by use, so that resulting decisions as to whether a substitute is acceptable or not are context specific, i.e., decisions were specific to the ODS being replaced, the sector, and the specific end-use(s) within which the substitute would be deployed, and 3) the comparative framework involved the use of several models considering usage patterns and health risks. These models include the Atmospheric Health Effects Framework (AHEF) model to estimate the human health risks from ODS use and compare them to similar risks from substitutes, the Vintaging model to estimate the market penetration and turn-over rates of technologies, ODSs, and substitutes that replace them; and a box model used to estimate exposure concentrations for consumers and workers who might be exposed to the substitutes, generally under both typical and worst-case scenarios of exposure.

The SNAP programme's legislative mandate (detailed in §612 of the Clean Air Act and 40 CFR 82.180) encompasses the review and evaluation of substitutes in the following industrial use sectors: Refrigeration & Air Conditioning, Foam Blowing Agents, Cleaning Solvents, Fire Suppression and Explosion Protection, Aerosols, Sterilants, Tobacco Expansion, and Adhesives,

Coatings & Inks. Producers of substances they propose to introduce as substitutes within these sectors that meet certain reporting requirement are required to submit a notice of intent to introduce the substitute into interstate commerce along with a dossier² of information on the substance. To determine if a substitute is acceptable or not as a replacement for an ODS, the SNAP programme uses the information submitted in order to evaluate the following:

- Atmospheric effects and related human health and environmental impacts,
- General population risks from ambient exposure to compounds with direct toxicity and to increased ground-level ozone;
- Ecosystem risks;
- Occupational risks;
- Consumer risks;
- Flammability; and
- Cost and availability of the substitute³

Following this review, substitutes are listed in one of the following categories: acceptable, acceptable subject to use conditions, acceptable subject to narrow use limits, or unacceptable. The initial risk screens for acceptable and unacceptable substitutes were presented in individual technical background documents entitled “Risk Screen on the Use of Substitutes for Class I Ozone-Depleting Substances” for each use sector which are available for review in the public docket⁴ supporting the SNAP rulemaking. More recently, as new substitutes are evaluated, individual risk screens have been added as addenda to the original background documents. Many of these risks screens are also available for review in the public docket, although in a number of instances the documents made available lack information identified as confidential business information (CBI) under the Clean Air Act, and until EPA’s decision is complete, no version of the risk screen is made public. Furthermore, no compendium of risk screens conducted has yet been assembled, nor is there a single source that summarizes all resulting decisions although tables for each sector are available at the following URL:

² Name and description of the substitute, physical and chemical information, substitute applications, process description, ozone depletion potential, global warming impact, toxicity data, environmental fate and transport, flammability, exposure data, environmental release data, replacement ratio for a chemical substitute, required changes in use technology, cost of substitute, availability of substitute, anticipated market share, applicable regulations under other environmental statute, information already submitted to the agency, information already available in the literature.

³ It should be noted, however, that the SNAP programme is not charged with evaluating efficiency, or effectiveness

⁴ <http://www.regulations.gov/search/Regs/home.html#docketDetail?R=EPA-HQ-OAR-2003-0118>.

<http://www.epa.gov/ozone/snap/lists/index.html>. Table A2-1 provides a list of substitutes that in the past decade have received a SNAP determination involving information from a risk screen. Substitutes are identified by the chemical or trade name under which the submission was made, the sector and end-use under consideration, the decision, the use conditions or limits, and also provides certain other information, e.g., where additional SNAP recommendations can be found, the degree to which CBI has affected the information released. Because decisions are made in the context of specific end uses, chemicals frequently appear multiple times, particularly within the larger sectors.

Table A2-1 ODS Substitutes Evaluated by the SNAP Programme since 2000 with Publically Available Risk Screens

Chemical	Sector	Replacing	End Use	Decision	Use Conditions/Limits^a	Issues
HFE-7200 [1-ethoxy-1,1,2,2,3,3,4,4,4-nonafluorobutane]	Adhesives, Coatings & Inks	CFC-113, methyl chloroform, HCFC-141b		Acceptable		
N-propyl bromide ⁸ CAS RN: 000106-94-5	Adhesives, Coatings & Inks	CFC-113, methyl chloroform, HCFC-141b	Coatings	Proposed Acceptable, with use condition	Limited to one coatings facility which demonstrated ability to maintain acceptable workplace exposures	
N-propyl bromide ⁸ CAS RN: 000106-94-5	Adhesives, Coatings & Inks	CFC-113, methyl chloroform, HCFC-141b	Adhesives	Proposed Unacceptable		
N-propyl bromide ⁸ CAS RN: 000106-94-5	Aerosols	CFC-113, methyl chloroform, HCFC-141b	Aerosol Solvents	Proposed Unacceptable		
HFE-7000 ² [1,1,1,2,2,3,3-heptafluoro-3-methoxy-propane]	Aerosols & Solvents	CFC-11, methyl chloroform	Electronics	Acceptable	None	workplace exposure 75 ppm; observe recommendations in MSDSs.
N-propyl bromide CAS RN: 000106-94-5 ⁸	Cleaning Solvents	CFC-113, methyl chloroform	Metals, precision and electronics cleaning	Acceptable		Recommendation for personal protective equipment; compliance with

Table A2-1 ODS Substitutes Evaluated by the SNAP Programme since 2000 with Publically Available Risk Screens

Chemical	Sector	Replacing	End Use	Decision	Use Conditions/Limits ^a	Issues
NAF P-IV [HCFC-123, HFC-125, 4-isopropenyl-1-methylcyclohexene]	Fire Suppression and Explosion Protection	Halon 1211	Handheld & portable fire extinguisher	Acceptable	Non-residential applications	any future OSHA final PEL CBI restriction on % by weight information for components Additional EPA recommendations ^b Additional recommendations ^b
Powdered Aerosol C ⁷	Fire Suppression and Explosion Protection	Halon 1301	Total flooding agent	Acceptable	Unoccupied spaces only	
Halotron II	Fire Suppression and Explosion Protection	Halon 1301	Total flooding agent	Acceptable	Unoccupied spaces only	
HFC227BC (FM-200 NaHCO ₃) HFC 227ea plus bicarbonate	Fire Suppression and Explosion Protection	Halon 1301	Total flooding agent	Acceptable with use limits	NaHCO ₃ release should be targeted so that pH levels are not adversely affected in exposed individuals. Systems containing HFC227BC should be clearly labeled as to potential hazards and appropriate handling procedures. Individuals required to be in environments protected by these systems should receive special training	
Novec 1230 [C6-perfluoroketone]	Fire Suppression and Explosion Protection	Halon 1301	Total flooding agent	Acceptable		
Novec 1230	Fire Suppression and Explosion Protection	Halon 1211	Handheld & portable fire extinguisher	Acceptable		Non-residential applications
Envirogel [amorphous silica]	Fire Suppression and Explosion	Halon 1211	Handheld & portable fire	Acceptable		Residential use market

Table A2-1 ODS Substitutes Evaluated by the SNAP Programme since 2000 with Publically Available Risk Screens

Chemical	Sector	Replacing	End Use	Decision	Use Conditions/Limits ^a	Issues
gel]	Protection		extinguisher			
NAF S 125 [HFC-125 with 0.1% <i>d</i> -limonene]	Fire Suppression and Explosion Protection	Halon 1301	Total flooding agent	Acceptable		Additional recommendations ^b
NAF S 227[HFC-227ea with 0.1% <i>d</i> -limonene]	Fire Suppression and Explosion Protection	Halon 1301	Total flooding agent	Acceptable		Additional recommendations ^b
Carbon Dioxide	Fire Suppression and Explosion Protection	Halon 1301	Total flooding agent	Acceptable	System design must adhere to OSHA 1910.162(b)(5) and NFPA Standard 12	
PBr ₃ ⁷	Fire Suppression and Explosion Protection	Halon 1301	Total flooding agent	Acceptable with use conditions	For use only in aircraft engine nacelles	Additional recommendations ^b
Uni-Light Advance Fire Fighting Foam 1% water mist system ⁴	Fire Suppression and Explosion Protection	Halon 1301	Total flooding agent	Acceptable	This agent is intended for use onboard ships and in off-shore installations. It may be used both in normally occupied and unoccupied areas. Additional recommendations ^b	
Envirogel ⁶ [3 formulations: HFC-125, HFC-227ea, or HFC-236fa]	Fire Suppression and Explosion Protection	Halon 1301	Total flooding agent	Acceptable with use conditions	Use of HFC employed in the formulation (HFC-125, HFC-227ea, or HFC-236fa) must be in accordance with all requirements (i.e., narrowed use limits) of that HFC under EPA's SNAP programme.	Additional recommendations ^b
Aero-K (Stat-X) ⁵	Fire Suppression and Explosion Protection	Halon 1301	Total flooding agent	Acceptable with use conditions	For use in normally unoccupied areas	Additional recommendations ^b
FirePro	Fire Suppression	Halon	Total flooding	Acceptable		Additional

Table A2-1 ODS Substitutes Evaluated by the SNAP Programme since 2000 with Publically Available Risk Screens

Chemical	Sector	Replacing	End Use	Decision	Use Conditions/Limits ^a	Issues
	and Explosion Protection	1301	agent			recommendations ^b
Victaulic Vortex System ¹¹	Fire Suppression and Explosion Protection	Halon 1301	Total flooding agent	Acceptable with use conditions		Additional recommendations ^b
ATK OS-10 ¹⁰	Fire Suppression and Explosion Protection	Halon 1301	Total flooding agent	Acceptable		Additional recommendations ^b
H Galden [hydrofluoropolyethers]	Fire Suppression and Explosion Protection	Halons & HCFCs	Handheld & portable fire extinguisher	Acceptable with use limits	Non-residential applications	Additional recommendations ^b
Enovate 3000 ¹ (HFC-245fa) with HCFC 22	Foam Blowing Agents			Acceptable		
Transcend Additive Technology ⁹	Foam Blowing Agents			Acceptable		
HFC-365mfc ¹⁵ [1,1,1,3,3-pentafluorobutane; CAS RN. 405–58–6].	Foam Blowing Agents	HCFC-141b	Rigid polyurethane (PU) appliance foam, rigid PU commercial refrigerant and sandwich panels, flexible PU, integral skin PU, polystyrene (PS) extruded sheet, polyolefin (PO), rigid PU slabstock and other, PS extruded boardstock and	Acceptable		Mildly flammable

Table A2-1 ODS Substitutes Evaluated by the SNAP Programme since 2000 with Publically Available Risk Screens

Chemical	Sector	Replacing	End Use	Decision	Use Conditions/Limits ^a	Issues
Formacel TI ¹²	Foam Blowing Agents	HCFC-22 & HCFC-142b	billet, rigid PU and polyisocyanurate (PIC) laminated boardstock, phenolic insulation board and bunstock Rigid PU appliance foam, rigid PU spray, commercial refrigeration and sandwich panels, integral skin PU, PS extruded sheet, PO, rigid PU slabstock and other, PS extruded boardstock and billet, rigid PU and PIC laminated boardstock	Acceptable		
HFO-1234ze ¹⁸ [trans1,1,1,3, tetrafluoropropene; CAS RN: 1645-83-6]	Foam Blowing Agents	CFCs & HCFCs	Rigid PU appliance foam, rigid PU spray/commercial refrigeration/sand wich panels, PS extruded boardstock and	Acceptable		EPA recommends a preliminary acceptable exposure limit (8 hour TWA) of 375 ppm

Table A2-1 ODS Substitutes Evaluated by the SNAP Programme since 2000 with Publically Available Risk Screens

Chemical	Sector	Replacing	End Use	Decision	Use Conditions/Limits ^a	Issues
IKON 12 (IKON A)	Refrigeration & Air Conditioning ^c	CFC-12	billet Household refrig/freezers, retail food refrig, industrial process refrig & AC, chillers, cold storage warehouses, refrig transport, commercial ice machines, vending machines, water coolers	Acceptable		
HBr Refrigerants [HFC-134a + HBr (92/8% by weight)]	Refrigeration & Air Conditioning ^c	CFC-12 & 502	Retail food refrig, industrial process refrig, cold storage warehouses, refrig transport,	Acceptable		
FOR12A [a ternary blend of 85%R134a/4%R152 a/11%CF3I,]	Refrigeration & Air Conditioning ^c	CFC-12	Household refrig/freezers, retail food refrig, industrial process refrig & AC, chillers, cold storage warehouses, refrig transport, commercial ice machines, vending	Acceptable		

Table A2-1 ODS Substitutes Evaluated by the SNAP Programme since 2000 with Publically Available Risk Screens

Chemical	Sector	Replacing	End Use	Decision	Use Conditions/Limits ^a	Issues
FOR12B [ternary blend of 77%R134a; 2%DME, 21%CF3I]	Refrigeration & Air Conditioning ^c	CFC-12	machines, water coolers Household refrig/freezers, retail food refrig, industrial process refrig & AC, chillers, cold storage warehouses, refrig transport, commercial ice machines, vending machines, water coolers	Acceptable		
Polycold HCFC Blends [16]	Refrigeration & Air Conditioning ^c	CFC 113, CFC-114, CFC- 13 & Blends	Niche Industrial Applications	Acceptable		To protect CBI, redaction of all composition, concentration info, etc
ISCEON 39TC [52.5:47.5%, 1,1,1,2-Tetrafluoroethane CAS RN 811-97-2 & 1,1,1,2,3,3,3-Heptafluoropropane CAS RN 431-89-0]	Refrigeration & Air Conditioning ^c	CFC 12	Commercial comfort AC, industrial process refrig & AC, cold storage warehouse, ice skating rinks	Acceptable		
SUVA HP63 (R404A) [HFC	Refrigeration & Air Conditioning ^c	HCFC-22	Commercial refrig systems, ice	Acceptable		

Table A2-1 ODS Substitutes Evaluated by the SNAP Programme since 2000 with Publically Available Risk Screens

Chemical	Sector	Replacing	End Use	Decision	Use Conditions/Limits ^a	Issues
134a, HFC-125, HFC-143a]			machines, refrig transport, water coolers			
HFE-7000 (HFE 301) methoxyheptafluoro-propane CAS 375-03-1	Refrigeration & Air Conditioning ^c	HCFC-123, CFC-113, CFC-11	Autocascade refrig systems, industrial process refrig, heat transfer systems	Acceptable		
RS-44 (2003 formulation)	Refrigeration & Air Conditioning ^c	HCFC-22	Household refrig/freezers, retail food refrig, industrial process refrig & AC, chillers, residential dehumidifiers, ice skating rinks, cold storage warehouses, refrig transport, commercial ice machines	Acceptable		
ISCEON 89 [HFC-125, R218, propane] R-407C	Refrigeration & Air Conditioning ^c	R131B	Very low temperature refrig	Acceptable		
	Refrigeration & Air Conditioning ^c	HCFC-22 & blends	Most refrig & AC end uses	Acceptable		
RS-24 (2002 formulation)	Refrigeration & Air Conditioning ^c	CFC-12	Household refrig/freezers, retail food refrig, industrial process refrig & AC,	Acceptable		

Table A2-1 ODS Substitutes Evaluated by the SNAP Programme since 2000 with Publically Available Risk Screens

Chemical	Sector	Replacing	End Use	Decision	Use Conditions/Limits ^a	Issues
HFC-152a	Refrigeration & Air Conditioning ^c	CFC-12	residential dehumidifiers, bus and passenger train AC, ice skating rinks, cold storage warehouses, refrigeration transport, commercial ice machines, vending machines, water coolers Motor vehicle air-conditioning	Acceptable subject to use conditions	Engineering strategies and/or devices shall be incorporated into the system such that R-152a concentrations of 3.7% v/v or above do not occur in any of the free space of the passenger compartment for more than 15 seconds when the car ignition is on.	Only allowed for new equipment, i.e., MVAC equipment designed for this refrigerant.
Carbon dioxide	Refrigeration & Air Conditioning ^c	CFC-13, 13B1, 503	Industrial process refrigeration, very low temperature refrigeration	Acceptable		
HFC-245fa [1,1,1,3,3-pentafluoropropane; CAS RN. 460-73-6]	Refrigeration & Air Conditioning ^c	CFC-11, 114, 123	Centrifugal chillers	Acceptable		

Table A2-1 ODS Substitutes Evaluated by the SNAP Programme since 2000 with Publically Available Risk Screens

Chemical	Sector	Replacing	End Use	Decision	Use Conditions/Limits ^a	Issues
1]						
HFC-245fa	Refrigeration & Air Conditioning ^c	CFC 11, 114, 141b	Very low temp. refrigeration	Acceptable		
HFC-245fa	Refrigeration & Air Conditioning ^c	CFC 11, 113, 21, 141b	Non-mechanical heat transfer	Acceptable		
HFC-245fa	Refrigeration & Air Conditioning ^c	CFC 114	Industrial process refig & AC	Acceptable		
Carbon dioxide ¹⁴	Refrigeration & Air Conditioning ^c	HCFC-22 & blends, CFC-12,502	Retail food refig	Acceptable		
Carbon Dioxide ¹³	Refrigeration & Air Conditioning ^c	CFC- 11, 12, 113, 114, 115	Cold storage warehouses	Acceptable		
C6 perfluoroketone; ¹⁶ Novec 649	Refrigeration & Air Conditioning ^c	CFC-113	Non-mechanical heat transfer	Acceptable		
HFO 1234yf ¹⁷ [2,3,3,3-tetrafluoropropene; CAS RN 754-12-1]	Refrigeration & Air Conditioning ^c	CFC-12	Motor vehicle air-conditioning	Proposed Acceptable, subject to use conditions	Engineering strategies and/or devices must be incorporated into the system such that HFO– 1234yf concentrations of 6.2% v/v or above do not occur in 1) the free space of the passenger compartment for more than 15 seconds; 2) the engine compartment or vehicle electric power source storage areas, or 3) proximity to exhaust manifold surfaces and hybrid/electric vehicle electric power sources. Manufacturers must adhere to all the safety requirements listed in the SAE 2009 Standard J639 and must conduct and keep on file, a failure mode and effect	

Table A2-1 ODS Substitutes Evaluated by the SNAP Programme since 2000 with Publically Available Risk Screens

Chemical	Sector	Replacing	End Use	Decision	Use Conditions/Limits ^a	Issues
IoGas Blends 1, 3, and 6 ³ (blends of CF ₃ I/CO ₂ /EtO)	Sterilants	HCFC-22 or blends of HCFC-22 and HCFC-124		Acceptable	analysis of the MVAC per SAE J1739.	

^aParaphrased to shorten; ^b <http://www.epa.gov/ozone/snap/fire/halon.pdf>; ^cUnless indicated decisions apply both to new and retrofit applications.
PU=polyurethane, PS=polystyrene, PO=polyolefin, PIC=polyisocyanurate, refig = refrigeration/refrigerated/refrigerators, AC= air conditioning, MVAC=motor vehicle AC; refig = refrigeration/refrigerated/refrigerator; TWA = time weighted average; SAE = Society of Automotive Engineers; CAS RN = Chemical abstract service registry number

The information provided above is a compendium of substitutes that have at a minimum undergone a risk screen under the SNAP programme. In addition to the risk screens that the SNAP programme conducts, frequently more in depth evaluations are completed to address specific issues identified in the risk screen. Most of these in-depth assessments have involved issues related to human health effects, e.g., for new chemicals, the need to develop exposure limits for occupationally exposed populations or the general public may be identified. In the case of foam-blowing agents or fire suppression agents, there may be a need to assess the toxicity of break-down products, and for substitutes with a wide variety of consumer end-uses such as refrigerants, worst-case exposure scenario modeling may be used to assess the risks of toxicity or asphyxiation to consumers and workers following catastrophic release, or the likelihood of explosion or fire for substitutes identified as being flammable.

However, it should also be noted that the evaluations and assessments that the SNAP programme conducts are those conventionally used to evaluate the risks of chemicals which have had to evolve over time in order to assess an ever enlarging list of potential threats, e.g., ozone depletion, biomagnification, endocrine disruption, and persistence in the environment, and it seems likely that these methods will need to continue to evolve as additional threats are identified. Furthermore, as demonstrated in the examples discussed below, the SNAP programme evaluations are iterative, and the programme's decisions as presented in rules or notices may reflect additional information not present in the risk screen.

Discussion of the detailed results for two sample risk screens, one for HFO 1234yf which was recently proposed to be listed as acceptable, subject to use conditions, and the other for MT-31, which was initially listed as acceptable and subsequently listed as unacceptable, are provided below.

Example 1: HFO 1234yf

Proposed as a substitute for: CFC-12 in Motor Vehicle Air Conditioning

Atmospheric Assessment: The environmental impacts resulting from use are generally in the range of other substitutes previously examined.

Flammability Assessment: Flammable at a concentration in the range of 65000 ppm to 123,000 ppm; within these concentrations, an ignition source (spark, static electric) an explosion or fire could result. Worst case modeling of releases during end-use (into automobile passenger compartment) produced concentration above the lower flammability limit (LFL), i.e., >65,000 ppm); however, field testing found concentrations equal to about 46% of the LFL. During manufacture and servicing of air condition units, catastrophic releases of large quantities could result in an explosion.

Flammability Recommendations: (1) automobile air conditioning systems using HFO-1234yf should be designed to avoid occupant exposure concentrations above 65,000 ppm in the passenger compartment for more than 15 seconds under any conditions (2) during manufacturing and servicing, OSHA requirements (29 CFR 1910) with regard to the proper ventilation and storage practices needed to prevent fire and explosion should be followed. If refrigerant air concentrations surrounding the equipment exceed one-fourth the lower flammability limit, the space should be evacuated and remain vacant until the space has been properly ventilated.

Asphyxiation Assessment: a series of worst-case scenario analyses were used to evaluate how much HFO-1234yf would need to be released in order to achieve oxygen to concentrations below the no observed adverse effect level (NOAEL) for hypoxia (120,000 ppm) in representative compartments of various classes of automobiles. None of the scenarios modeled resulted in releases likely to pose a risk of asphyxiation or impaired coordination. Furthermore, as the NOAEL for hypoxia (120,000 ppm) is greater than the LFL for HFO-1234yf, the recommendation made above to that concentrations in automobile compartments not exceed the LFL should protect against the limited risk of asphyxiation.

Toxicity Assessment: EPA compared toxicity threshold values, e.g., occupational long term exposure limit, to modeled exposure concentrations for a variety of scenarios (e.g., short-term (15 minute) and longer term (8 hours) worker, short term vehicle passenger) and concluded that HFO-1234yf was unlikely to be a toxicity threat to trained professionals involved in a manufacturing facility but that consumers involved in “do-it-yourself” car repair could be exposed to concentrations far in excess of the occupational exposure limit. For vehicle passengers, the risk screen concluded that the worst case concentration to which passengers would be exposed was nearly 20-fold lower than the most relevant toxicity value, an acute LOAEL in rats.

Toxicity Recommendation: Based on the “do-it yourself” car repair scenario, the Agency recommended that HFO-1234yf not be made available to untrained workers such as those involved in “do-it-yourself” car repair.

Volatile Organic Compound Analysis: Non-attainment resulting from HFO-1234yf emissions is not likely to be a major concern for local air quality in most locations.

Additional Environmental Impacts Analysis: Trifluoroacetic acid production resulting from HFO-1234yf emissions is not expected to pose significant harm to aquatic communities.

Example 2: MT-31

Proposed as a substitute for: CFC 12 used as a refrigerant in a variety of systems, e.g., chillers, refrigerated transport, ice machines, water coolers, household refrigerators and freezers, cold storage warehouses, as well as for HCFC22 in retrofitted end-uses.

Initially (62 FR 30275), the SNAP programme concluded that this blend of components (the exact composition of which was considered to be CBI) did not contain any flammable components and that all components were low in toxicity so that this was an acceptable substitute for the end uses specified.

Subsequently (64CFR 3861) the SNAP programme received and reviewed additional toxicity information on one of the components and upon completing a risk screen (which could not be made publically available due to the CBI concerns) determined that the presence of this unspecified chemical in MT-31 meant that the use of MT-31 as a refrigerant in the manufacture or servicing of refrigeration or air conditioning equipment was unacceptably high in risk.

These two examples provide insights into the iterative nature of the SNAP programme's evaluations. For example, the information in Table A2-1 for HFO1234yf is somewhat different from that summarized above from the risk screen: the latter indicated that concentrations above 65,000 ppm (6.5%) should be avoided whereas the published use limit was 6.2%. Furthermore while the risk screen included a recommendation that HFO-1234yf not be made available to untrained workers, that recommendation was not part of the final acceptability decision. While the rationale for these changes is not immediately obvious, it seems likely that it is documented in the EPA docket, probably via the Agency's interactions with various stakeholders in this decision. The ultimate MT-31 decision was driven by consideration of information that was not initially available to the Agency at the time of its first decision and demonstrates the SNAP programme's quick response to address a serious issue. Unfortunately, the exact nature of that issue was protected by the producers CBI claim.

References

- 1 USEPA, 2003, Risk Screen for Blends of Enovate3000 (HFC-245fa) and HCFC-22 in foam blowing, United States Environmental Protection Agency Report No., Washington DC, USA.
<http://www.regulations.gov/search/Regs/home.html#documentDetail?R=09000064800bb031>
- 2 USEPA, 2003, Risk Screen on the Use of Substitutes for Ozone-Depleting Substances: Aerosols and Solvents; HFE-7000, United States Environmental Protection Agency Report No. EPA-HQ-OAR-2003-0118-0023, Washington DC, USA, August 21, 2003, p. 15.
<http://www.regulations.gov/search/Regs/home.html#docketDetail?R=EPA-HQ-OAR-2003-0118>
- 3 USEPA, 2004, Risk Screen for IoGas Sterilants 1, 3, and 6, United States Environmental Protection Agency Report No. EPA-HQ-OAR-2003-0118-0053, Washington DC, USA, September 15, 2004, p. 14.
<http://www.regulations.gov/search/Regs/home.html#docketDetail?R=EPA-HQ-OAR-2003-0118>
- 4 USEPA, 2006, Risk Screen On Substitutes For Halon 1301--Total Flooding Fire Extinguishers In Occupied Spaces--Uni-light, United States Environmental Protection Agency Report No., Washington DC, USA.

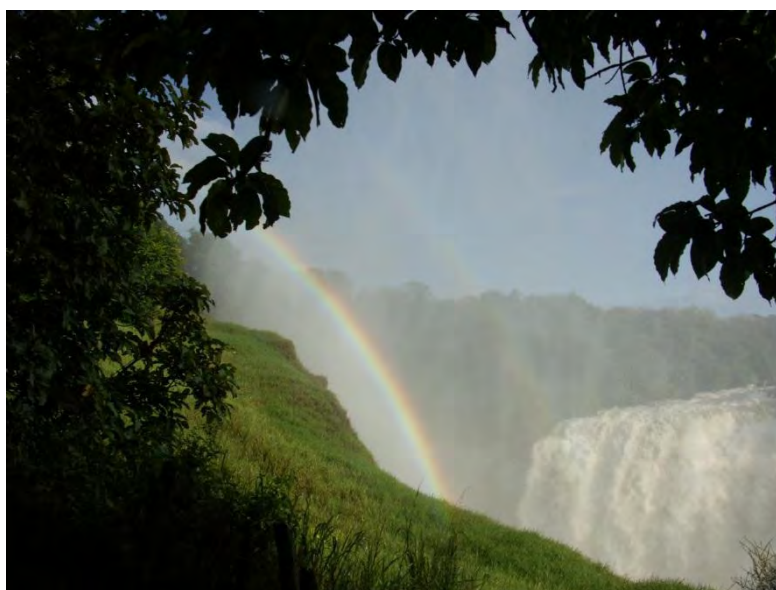
- <http://www.regulations.gov/search/Regs/home.html#documentDetail?R=09000064801837cd>
- 5 USEPA, 2006, Risk Screen on Substitutes for Halon 1301 Fire Suppression and Explosion Protection Applications Proposed Substitute: Aero-K[®] United States Environmental Protection Agency Report No., Washington DC, USA.
<http://www.regulations.gov/search/Regs/home.html#documentDetail?R=09000064801cd03c>
- 6 USEPA, 2006, Risk Screen on Substitutes for Halon 1301 Fire Suppression and Explosion Protection Applications; Proposed Substitute: Envirolgel B25 + 36, United States Environmental Protection Agency Report No., Washington DC, USA.
<http://www.regulations.gov/search/Regs/home.html#documentDetail?R=09000064801cca82>
- 7 USEPA, 2006, Risk Screen on Substitutes for Halon 1301 in Fire Suppression and Explosion Protection Applications Proposed Substitute: Phosphorus Tribromide (PBr₃) Total Flooding Applications in Unoccupied Spaces, United States Environmental Protection Agency Report No. EPA-HQ-OAR-2005-0087-0007, Washington, DC, USA, April 3, 2006, p. 7. <http://www.regulations.gov/search/Regs/home.html#docketDetail?R=EPA-HQ-OAR-2005-0087>
- 8 USEPA, 2006, Risk Screen on Substitutes for Ozone-Depleting Substances for Adhesive, Aerosol Solvent, and Solvent Cleaning Applications Proposed Substitute:n-Propyl Bromide (nPB risk screen), United States Environmental Protection Agency Report No. EPA-HQ-OAR-2002-0009-0149, Washington DC, USA, April 23, 2006, p. 73.
<http://www.regulations.gov/search/Regs/home.html#docketDetail?R=EPA-HQ-OAR-2002-0009>
- 9 USEPA, 2006, Risk Screen On Substitutes For Ozone-Depleting Substances: Foam-Blowing Sector--Transcend[®] Additive Technology United States Environmental Protection Agency Report No. EPA-HQ-OAR-2003-0118-0146, Washington DC, USA, March 29, 2006, p. 8.
<http://www.regulations.gov/search/Regs/home.html#docketDetail?R=EPA-HQ-OAR-2003-0118>
- 10 USEPA, 2008, Risk Screen for ATK OS-10 as a Fire Suppressant, United States Environmental Protection Agency Report No. EPA-HQ-OAR-2003-0118-0199, Washington DC, USA, December 23, 2008, p. 9.
<http://www.regulations.gov/search/Regs/home.html#docketDetail?R=EPA-HQ-OAR-2003-0118>
- 11 USEPA, 2008, Risk Screen for Victaulic Vortex System in Fire Suppression, United States Environmental Protection Agency Report No. EPA-HQ-OAR-2003-0118-0200, Washington DC, USA, January 23, 2008, p. 5.
<http://www.regulations.gov/search/Regs/home.html#docketDetail?R=EPA-HQ-OAR-2003-0118>
- 12 USEPA, 2009, Foam-Blowing Sector (Risk Screen for Formacel TI), United States Environmental Protection Agency Report No. EPA-HQ-OAR-2003-0118-0230, Washington DC, USA, September 21, 2009, p. 5.
<http://www.regulations.gov/search/Regs/home.html#docketDetail?R=EPA-HQ-OAR-2008-0664>
- 13 USEPA, 2009, Risk Screen for Carbon Dioxide (CO₂) in Cold Storage Warehouses, United States Environmental Protection Agency Report No. EPA-HQ-OAR-2003-0118-0232, Washington DC, USA, July 2, 2009.
<http://www.regulations.gov/search/Regs/home.html#docketDetail?R=EPA-HQ-OAR-2003-0118>
- 14 USEPA, 2009, Risk Screen for Carbon Dioxide (CO₂) in Retail Food Refrigeration, United States Environmental Protection Agency Report No. EPA-HQ-OAR-2003-0118-0231, Washington DC, USA, July 2, 2009, p. 7.

- <http://www.regulations.gov/search/Regs/home.html#docketDetail?R=EPA-HQ-OAR-2003-0118>
- 15 USEPA, 2009, Risk Screen for HFC-365mfc in Foam Blowing, United States Environmental Protection Agency Report No. EPA-HQ-OAR-2003-0118-0235, Washington DC, USA, August 12, 2009, p. 14.
<http://www.regulations.gov/search/Regs/home.html#docketDetail?R=EPA-HQ-OAR-2003-0118>
- 16 USEPA, 2009, Risk Screen for Novec 649 Heat Transfer, United States Environmental Protection Agency Report No. EPA-HQ-OAR-2003-0118-0229, Washington DC, USA, September 17, 2009, p. 14.
<http://www.regulations.gov/search/Regs/home.html#docketDetail?R=EPA-HQ-OAR-2003-0118>
- 17 USEPA, 2009, Risk Screen on Substitutes for CFC-12 in Motor Vehicle Air Conditioning: Substitute: HFO-1234yf. , United States Environmental Protection Agency Report No. EPA-HQ-OAR-2008-0664-0038, Washington DC, USA, October 19, 2009, p. 9.
<http://www.regulations.gov/search/Regs/home.html#docketDetail?R=EPA-HQ-OAR-2008-0664>
- 18 USEPA, 2009, Risk Screen on Substitutes in the Foam Blowing Sector for HFO-1234ze, United States Environmental Protection Agency Report No. EPA-HQ-OAR-2003-0118-0237, Washington DC, USA, 28 September 2009.
<http://www.regulations.gov/search/Regs/home.html#docketDetail?R=EPA-HQ-OAR-2003-0118>

Questions and Answers about the Environmental Effects of the Ozone Layer Depletion and Climate Change: 2010 Update

Environmental Effects Assessment Panel: 2010

United Nations Environmental Programme



Pieter J Aucamp & Lars Olof Björn

Coordinating Authors

This document provides some answers to commonly asked questions about the environmental effects of ozone depletion

Table of Contents

Introduction	4
I. Ozone and UV.....	5
Q1. How is ozone produced and destroyed.....	5
Q2. What is the relationship between ozone and solar ultraviolet radiation?	7
Q3. How and why has the situation regarding the ozone layer changed over the past 30 years?	9
Q4. What determines the level of solar UV-B radiation at a specific place?	11
Q5. What is the solar UV Index?	13
Q6. How does the UV index vary with location and time?	15
Q7. What is the effect of the interaction between UV-B radiation, climate change, and human activity on air pollution?	16
II. Effect on humans and on the environment	17
Q8. Can human activities have any effects on worldwide phenomena such as depletion of the ozone layer and climate change?.....	17
Q9. Effects on Human Health	19
a. What are the effects of exposure to solar UV radiation on the human eye and how can the eye be protected?	19
b. What are the adverse effects of exposure to solar UV-B on human skin?	20
c. How does UV-B radiation affect the immune system?.....	22
d. Are there any beneficial health effects of solar UV-B radiation?	24
e. What risks do the breakdown products of HFCs and HCFCs present to humans and the environment?	25
f. How can I protect myself from the adverse effects of solar UV-B radiation on the skin?	26
g. How much time should I spend in the sun in order to produce sufficient vitamin D but avoiding sunburn and minimising the risk of skin cancer?	27
h. Will global climate change alter the effects of UV radiation on human health?	28
Q10. Effects on the Environment	29
a. What are the major impacts of UV-B radiation on natural terrestrial ecosystems, crops and forests?	29
b. Does exposure to UV-B radiation affect aquatic life?	33
c. Does climate change alter the effect of UV radiation on aquatic ecosystems?	35
d. Do increasing atmospheric CO ₂ concentrations influence the sensitivity of aquatic organisms to solar UV-B radiation?	37
e. What effects does the depletion of ozone have on environmental processes and cycles?	38

Q11. Can the increased temperature due to global warming increase the deleterious effects of UV-B radiation on plastics and wood products used outdoors?	39
Q12. Ozone and Climate.....	41
a. Do ozone depleting gases and their substitutes have an effect on climate"?	41
b. Is ozone depletion affected by climate change?	43
Q13. Are the control measures in the Montreal Protocol working? What is the world we avoided?.....	45
a. Phase-out of ODS	45
b. UV Radiation changes	46
c. Effect on the climate.....	47
Q14. Where can I get more information about the science and effects of ozone depletion?	49

Introduction

In the mid-1970s it was discovered that some man-made products destroy ozone molecules in the stratosphere. This destruction leads to higher ultraviolet (UV) radiation levels at the surface of the Earth and can cause damage to ecosystems and to materials such as plastics. It may cause an increase in human diseases such as 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 in this field. 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 Meetings 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 2010 report of this Panel, but also on information from previous assessments and from the report of the Scientific Assessment Panel. Readers who need further details on any question should consult the full reports for a more complete scientific discussion. All these reports can be found on the UNEP website: (<http://ozone.unep.org>).

The update of this component of the Assessment was discussed by the 24 scientists who attended the Panel Review Meeting for the 2010 Environmental Effects Assessment (Lancaster, England, 29 Augustus – 7 September 2010). In addition, subsequent contributions, reviews or comments were provided by the following individuals: Alkiviadis F. Bais, Lars Olof Björn, Anthony P. Cullen, David J. Erickson, Donat-P. Häder, Walter Helbling, Robyn Lucas, Richard L. McKenzie, Mary Norval, Sharon Robinson, Keith R. Solomon.

I .Ozone and UV

Q1. How is ozone produced and destroyed

The ozone molecule (O_3) contains three atoms of oxygen and is mainly formed by the action of the UV rays of 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 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 10-16 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.

Ozone is a very tiny fraction of the air, which consists mainly of nitrogen (N_2) and oxygen (O_2) molecules. In the stratosphere, near the peak of the ozone layer, there are up to 12 ozone molecules for every million air molecules. In the troposphere near Earth's surface, ozone is even less abundant, with a typical range of 0.02 to 0.1 ozone molecules for each million air molecules.

Ozone is destroyed naturally in the upper stratosphere by the UV radiation from the sun. These reactions are most important in the stratosphere of tropical and middle latitudes, where this 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.

Other, non-natural, mechanisms for the destruction of ozone involve halogen atoms. Emissions from human activities and natural processes include large sources of chlorine (Cl), bromine (Br) and fluorine (F) containing gases that eventually reach the stratosphere. When exposed to UV radiation from the Sun, these halogen-containing gases are converted to more reactive gases, also containing chlorine and bromine, for example, chlorine monoxide (ClO) and bromine monoxide (BrO). These reactive gases participate in "catalytic" reaction cycles that efficiently destroy ozone in the stratosphere.

Atomic oxygen (O) is formed when UV radiation in sunlight interacts with ozone and oxygen molecules. The destruction of ozone involves two separate chemical reactions. The net or overall reaction is that of atomic oxygen (O) with ozone (O_3), forming two oxygen molecules (O_2). The cycle can be considered to begin with either ClO or Cl. Cl reacts with (and thereby destroys) ozone and reforms ClO. The cycle then is repeated with another reaction of ClO with O. Because Cl or ClO is reformed each time an ozone molecule is destroyed, chlorine is considered a catalyst for ozone destruction (Figure 1). Similar reactions occur with bromine derivatives. The relative potency of the different halogens depends a great deal on the stability of the compounds. Hydrogen fluoride (HF) is so very stable that fluorocarbons have relatively 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.

Volcanoes can emit some chlorine-containing gases, but these gases are dissolved in rainwater and ice and are usually “washed out”

of the atmosphere before they can reach the stratosphere.



Figure 1a: Formation of atomic oxygen

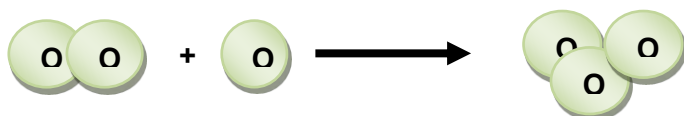


Figure 1b: Production of ozone

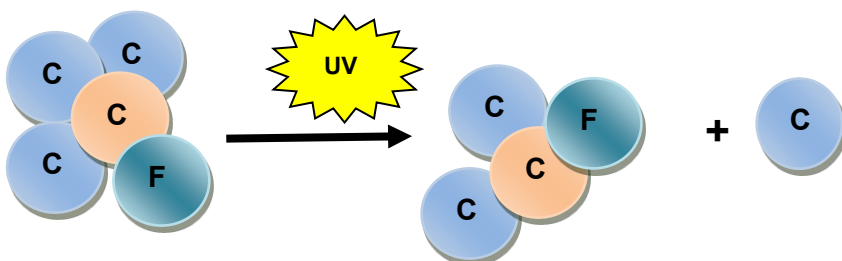


Figure 1c: Formation of atomic chlorine

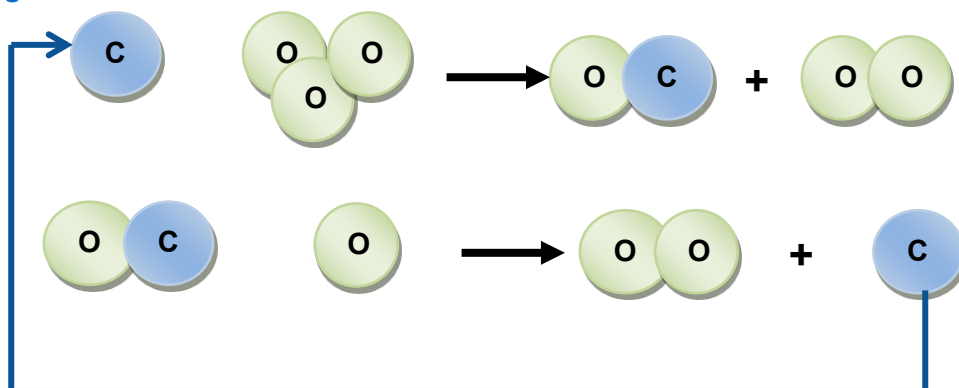


Figure 1d: Destruction of Ozone – The last two reactions are repeated many times. Figure 1 presents only one of the chemical processes responsible for the destruction of Ozone in the Stratosphere. In the example CFC 11 (CCl_3F) is used. (Figure provided by Dr P J Aucamp, Ptersa)

Q2. What is the relationship between ozone and solar ultraviolet radiation?

There is an inverse relationship between the concentration of ozone and the amount of harmful UV radiation transmitted through the atmosphere since ozone absorbs some of the UV radiation.

A small fraction of the radiation emitted by the Sun resides in the ultraviolet range. This range extends from 100 to 400 nm and is divided into three bands: UV-A (315 – 400 nm), UV-B (280 – 315 nm) and UV-C (100 – 280 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. 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 (Figure 2 - also Figure 5). 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 biologically much more 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 humans.

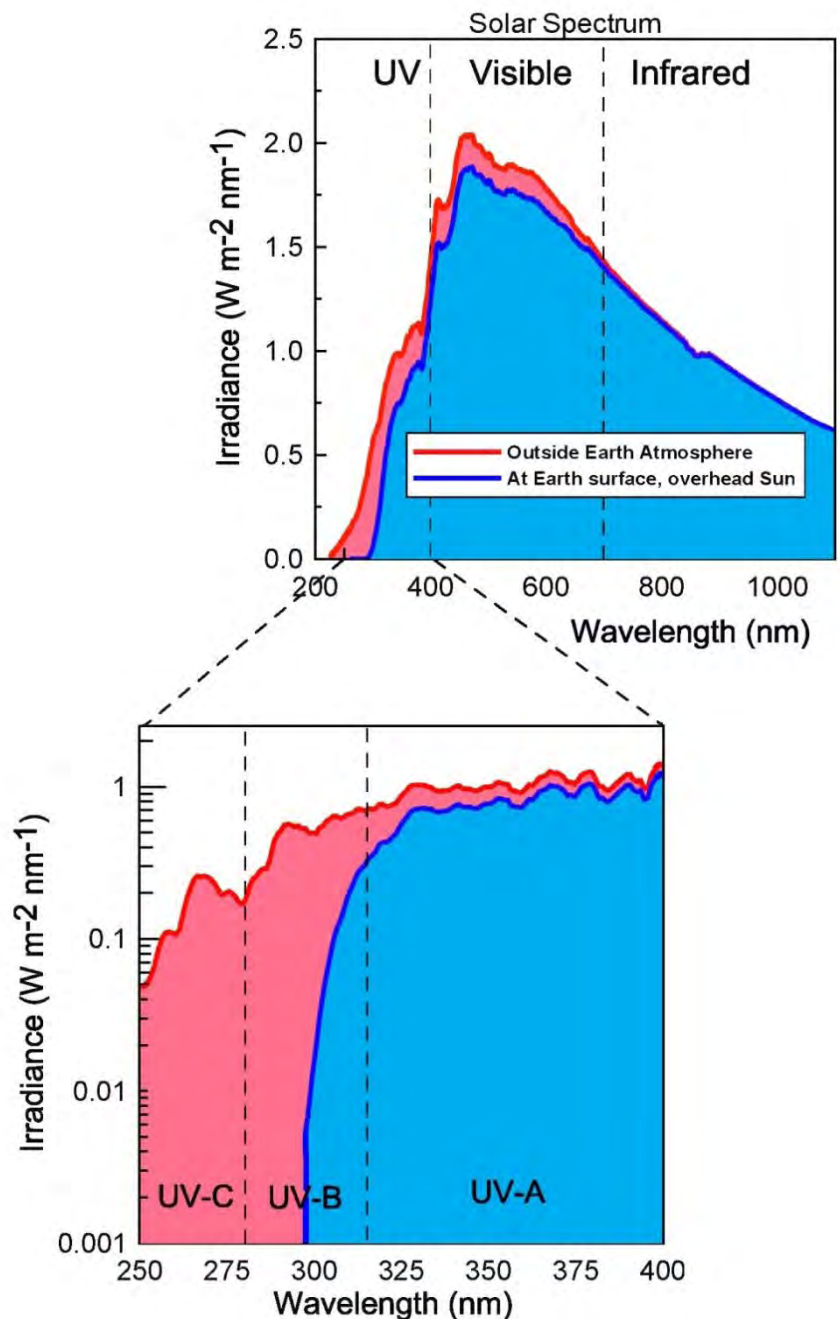


Figure 2: The spectrum of UV radiation as part of the solar spectrum. Note the log scale on the y-axis in the bottom panel. The blue area shows that ozone absorption increases rapidly at shorter wavelengths so that at wavelengths less than 300 nm, less than 1% of the radiation is transmitted. Figure provided by Dr R L McKenzie, NIWA.

Q3. How and why has the situation regarding the ozone layer changed over the past 30 years?

Stratospheric ozone has decreased over the globe since the 1980s. Averaged over the globe, ozone in the period 1996-2009 is about 4% lower than before 1980. Much larger depletion, up to 40%, occurs over the high latitudes of the Southern Hemisphere in October.

The increase in reactive halogen gases in the stratosphere is considered to be the primary cause of the average ozone depletion. The lowest ozone values in recent years occurred after the eruption of Mt. Pinatubo volcano in 1991, which increased the number of sulphur-containing particles in the stratosphere. These particles remained in the stratosphere for several years and increased the effectiveness of reactive halogen gases in destroying ozone. Observed ozone depletion varies significantly with latitude on the globe. The largest losses occur at the highest southern latitudes as a result of the severe ozone loss over Antarctica that occurs every year during winter and early spring. The next largest ozone losses are observed in the high latitudes of the Northern Hemisphere, caused in part by late winter/early spring

losses over the Arctic. Ozone-depleted air over both Polar regions is dispersed away from the poles during and after each winter/spring period. Ozone depletion also occurs directly at latitudes between the Equator and Polar regions but is much smaller. Figure 3 shows the average measured and predicted amounts of equivalent effective stratospheric chlorine (EESC) concentration based on the findings of the latest Scientific Assessment Report. EESC is used as an indicator of the amount of ozone depleting substances in the atmosphere. This figure shows that the amounts of these substances in the stratosphere have already reached a maximum and now are decreasing. The concentration of the ozone is inversely proportional to the concentration of the EESC.

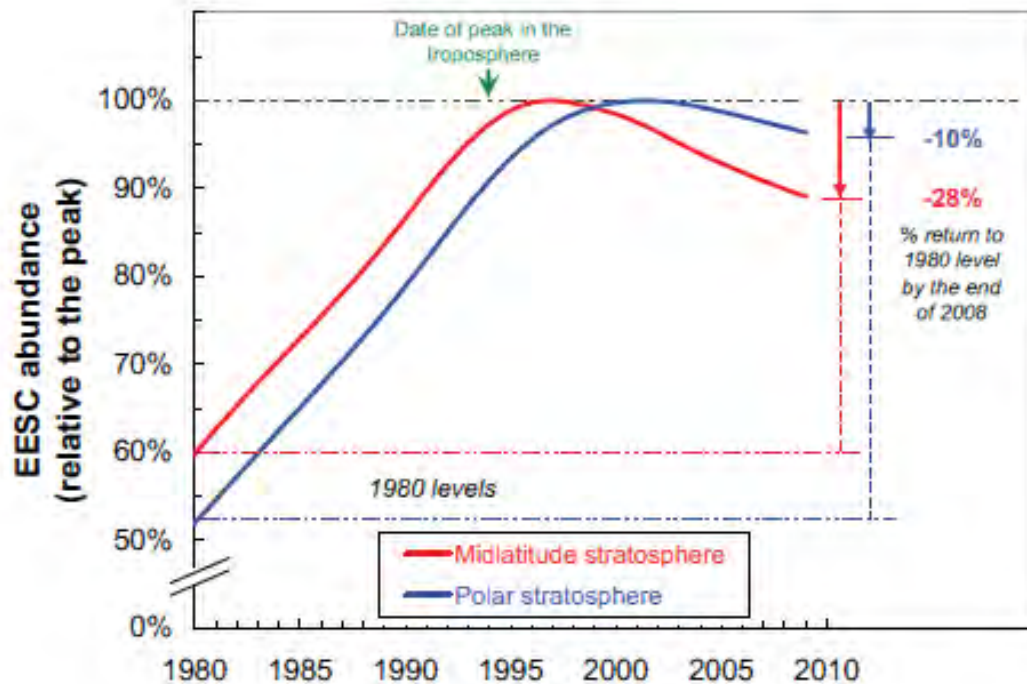


Figure 3: Stratospheric EESC derived for the mid latitude and polar stratospheric regions relative to peak abundances, plotted as a function of time. (Reproduced from Figure ESA-1 in the executive summary of the Scientific Assessment 2010)

http://us-cdn.creamermedia.co.za/assets/articles/attachments/29653_898_executivesummary_emb.pdf

Q4. What determines the level of solar UV-B radiation at a specific place?

The Sun is the source of the UV radiation reaching Earth. UV radiation is partly absorbed by the components of Earth's atmosphere. The amount of UV radiation that is absorbed depends mainly on the length of the path of the sunlight through the atmosphere.

The UV-B levels at Earth's surface vary with the time of day, geographic location and season. UV radiation is highest in the tropics, because the sun is higher in the sky, and decreases towards the poles where the Sun is lower. The height of the Sun above the horizon (the solar elevation angle) has an influence on the UV radiation, since the lower elevation mean longer pathways and more opportunity for the radiation to be absorbed. For the same reason, UV radiation is more intense near noon hours and least near sunrise or sunset, and is more in the summer and less in the winter. Clouds, particulate matter, aerosols and air pollutants absorb and scatter some of the UV radiation and thereby reduce the amount reaching Earth's surface.

Locations at higher altitudes (Figure 4) have thinner atmosphere overhead, therefore the radiation from the Sun is less attenuated. This increase in UV radiation varies between 5% and 20% for each kilometre of

height, depending on the specific wavelength, solar angle, atmospheric pollution and other local conditions. Frequently, other factors cause even larger differences in UV radiation between different altitudes. Surface reflections, especially from snow, ice and sand, increase the UV radiation levels at a particular location, because the reflected radiation is redirected towards the surface through scattering by particles and molecules in the atmosphere. Snow reflects as much as 90% and dry beach sand and sea foam about 25% of UV radiation. Clouds also reflect an appreciable amount of radiation towards the surface, Thus while areas that are not shaded by clouds usually receive more radiation, under certain cloud conditions levels of UV radiation at Earth's surface can actually be higher under these conditions than under clear-sky conditions.



Figure 4: The quantity of solar UV-B received by an object is affected by the surroundings. UV radiation is both absorbed and reflected from clouds and water, and is reflected by snow and shiny surfaces in town. (Photo provided by Dr P J Aucamp, Ptersa).

Q5. What is the solar UV Index?

The solar UV Index (UVI) describes the level of solar UV radiation relevant to human sunburn (erythema).

The UVI was originally used in Canada. The maximum value in the South of the country is 10 at midday in the summer, and about 1 at midday in the winter. In other locations and under different conditions the UVI can be higher or lower. In the tropics at sea level the UVI can exceed 16 and peak terrestrial values of 25 can occur at high altitudes. 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 skin damage (erythema) from an exposure of about 15 minutes. Outside the protective layer of Earth's atmosphere (altitude > 50 km), the UVI can exceed 300.

Information about UV intensities 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 sunburning UV radiation. For clear sky conditions, the UVI can be calculated approximately from knowledge of the ozone and the solar elevation angle (Figure 5). 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, atmospheric pollution, and surface reflection. When the surface is snow-covered, the UVI can be up to 90% greater than for snow-free surfaces. Several countries provide forecasts of 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: Colours used in the UV Index

Exposure Category	Colour	UVI Range
Low		< 2
Moderate		3 - 5
High		6 - 7
Very High		8 – 10
Extreme		11+

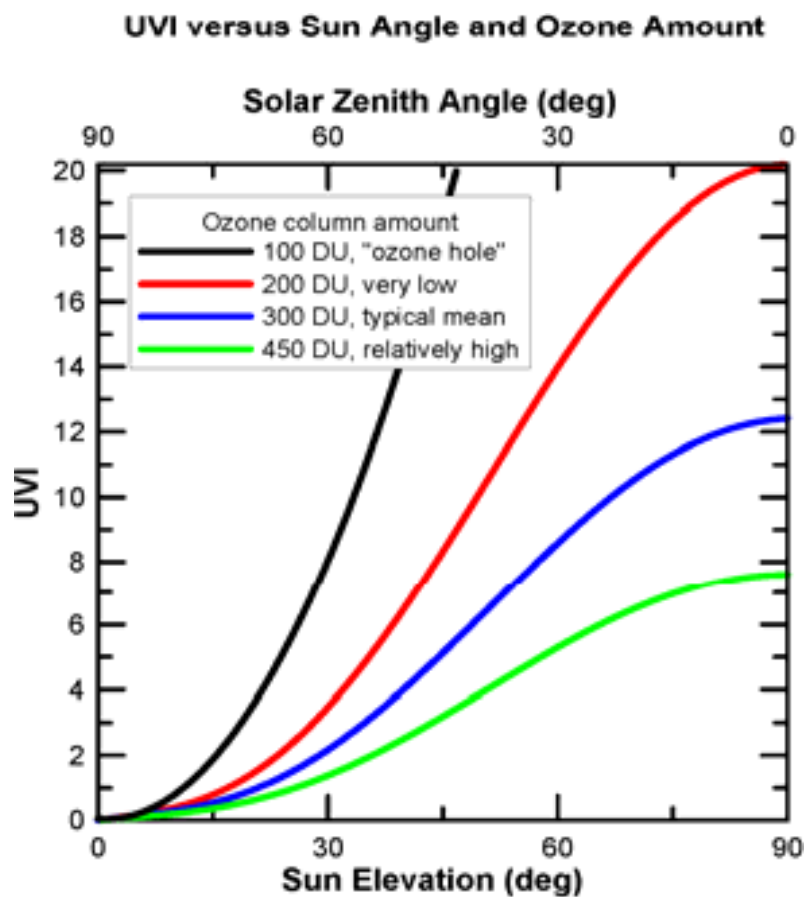


Figure 5: A figure indicating the variation of the UVI with the solar elevation. The coloured lines represent different Ozone concentrations measured in Dobson Units (DU), Figure provided by Dr R L McKenzie, NIWA.

Q6. How does the UV index vary with location and time?

The combination of total ozone, aerosols, clouds, airpollution, altitude, surface reflectivity and solar zenith angle (that is determined by the geographical position, season and time of the day) are the main factors resulting in variation in the UV Index.

A global picture of the UVI can be derived from measurements with instruments on satellites. UVI varies with latitude and time of year, as can be seen from the example for 3 September 2010 presented in Figure 6. UV levels increase with altitude, and therefore the UVI is higher at mountainous locations (as seen, for example, in the Andes and Tibet).

The presence of “patchy clouds” or snow-covered ground can result in larger UV Index values. A combination of small solar zenith angle near noon, high altitude, a naturally low total ozone column and a very clean atmosphere can lead to exceptionally high values of the UVI. A good example is the high altitude desert *Puna de Atacama* in Argentina, where a UV index of 18 is common in January and December, with a maximum of 20 and even more on occasional days.

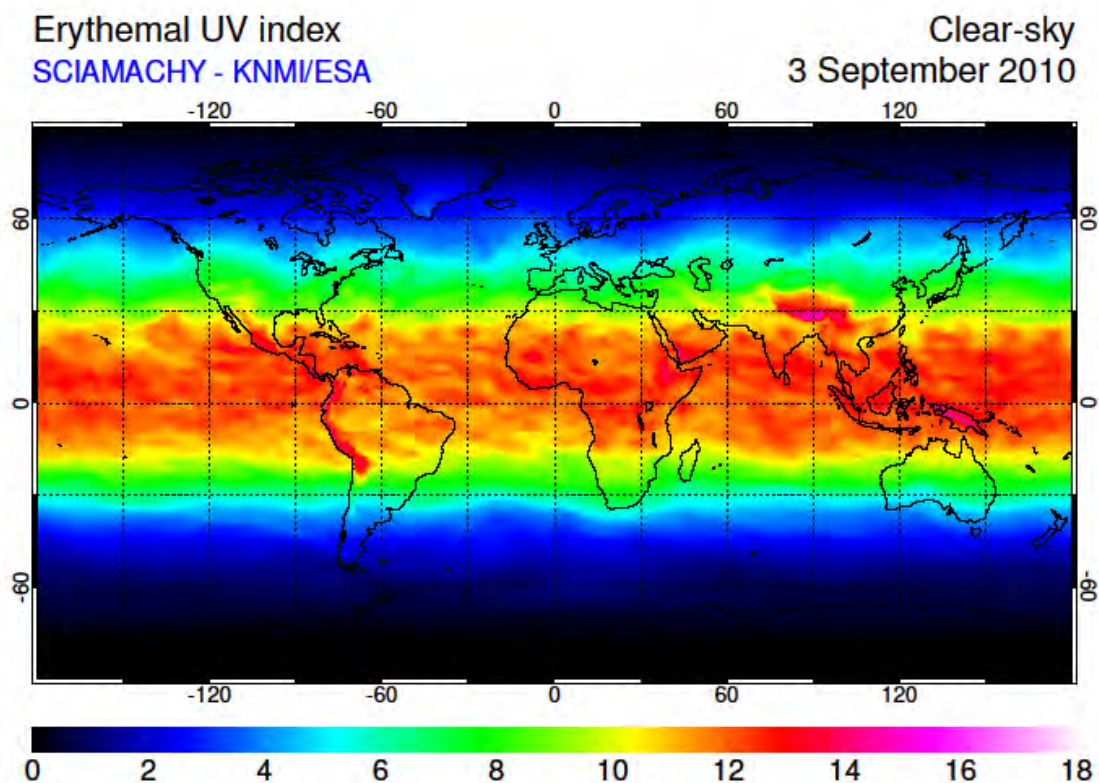


Figure 6: UV Index for 3 September 2010 derived from Sciamachy instrument on Envisat satellite.

Q7. What is the effect of the interaction between UV-B radiation, climate change, and human activity on air pollution?

Pollutants emitted by human activities can reduce UV-B radiation near the surface, while particles may lead to enhancement by scattering. These processes decrease some exposures to UV radiation while enhancing others. Interactions between UV radiation and pollutants resulting from changes in climate and burning of fossil and plant fuels will worsen the effects of ozone on humans and plants in the lower atmosphere.

While most of the atmospheric ozone is formed in the stratosphere, ozone is also produced in the lower atmosphere (troposphere) by the chemical reactions between pollutants such as nitrogen oxides and hydrocarbons and UV radiation. This ground-level ozone is a significant component of photochemical smog found in many polluted areas and has important adverse effects on human health and the environment.

Some estimates indicate that increases of this type of air pollution will result in more human deaths than other effects of climate change, such as increased intensity of storms and flooding.

Climate change will likely increase circulation of gases in the atmosphere but cause only small increases in ozone in the lower atmosphere in areas where there is little pollution. These increases will be less significant for the health of humans than those caused by tropospheric ozone in polluted areas.

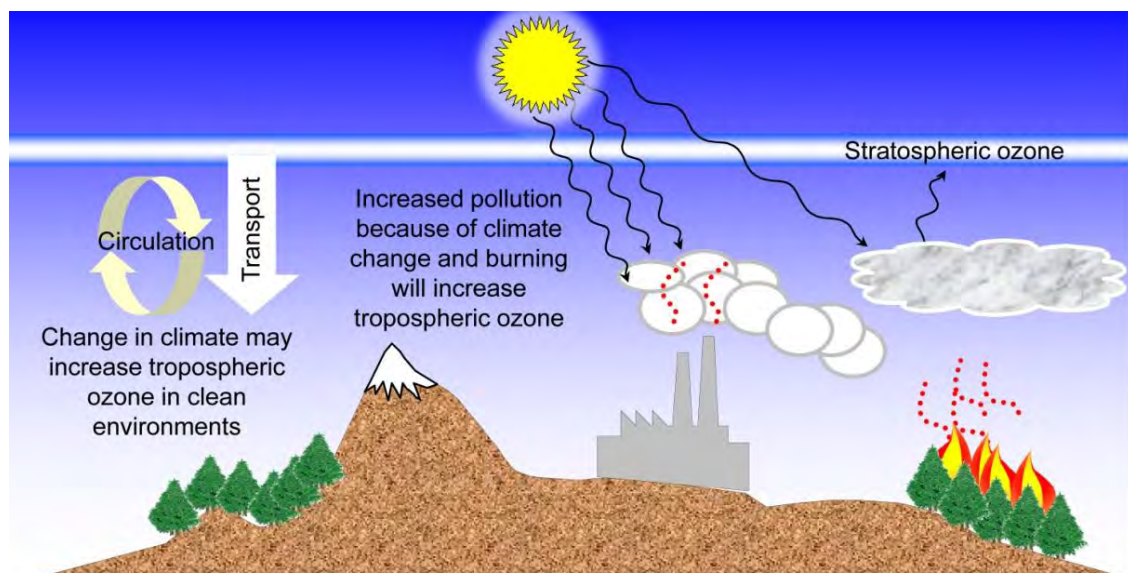


Figure 7: Concentration of ozone at different altitudes in the atmosphere. Figure provided by Prof K Solomon, Guelph University.

II. Effect on humans and on the environment

Q8. Can human activities have any effects on worldwide phenomena such as depletion of the ozone layer and climate change?

There is overwhelming evidence that human activities are influencing global phenomena.

Natural environmental cycles often span thousands of years but most scientific measurements are only available for the past one to three centuries. It is not easy to accurately determine the influence of humans on any natural activity. In the case of the ozone layer, the depletion of the ozone over Antarctica cannot be explained by natural cycles alone but is caused by the increase of man-made chemicals in the stratosphere. The relationship between these chemicals (e.g. chlorofluorocarbons, also known as CFCs) and ozone depletion has been shown by experiments in laboratories, numerical modelling studies and by direct measurements in the atmosphere (see Figure 8a).

By absorbing the infrared radiation emitted by Earth, some substances influence the natural energy flows through the atmosphere. The greenhouse gases, such as carbon dioxide, although only a tiny fraction of the atmosphere, play an important role in this process. Carbon dioxide (CO₂) is produced when fossil fuels are used to generate energy

and when forests are burned. Measurements show that its concentration has increased by almost 30% over the past 250 years. In the mid-20th century, the concentration of CO₂ was 280 ppmv, and it is currently 390 ppmv, and increasing at about 3% per decade. Methane and nitrous oxide emitted from agricultural activities, changes in land use, and other sources are also important (see Figure 8b).

The increase in greenhouse gases contributes to climate change in the form of increased temperatures (about 0.6°C near Earth's surface over the past 150 years) and a rise in sea level. Models of the climate change induced by emission of greenhouse gases predict that the global temperature will rise between 2 and 6°C in the next century. If this happens, the change would be much larger than any temperature change experienced over at least the last 10,000 years.

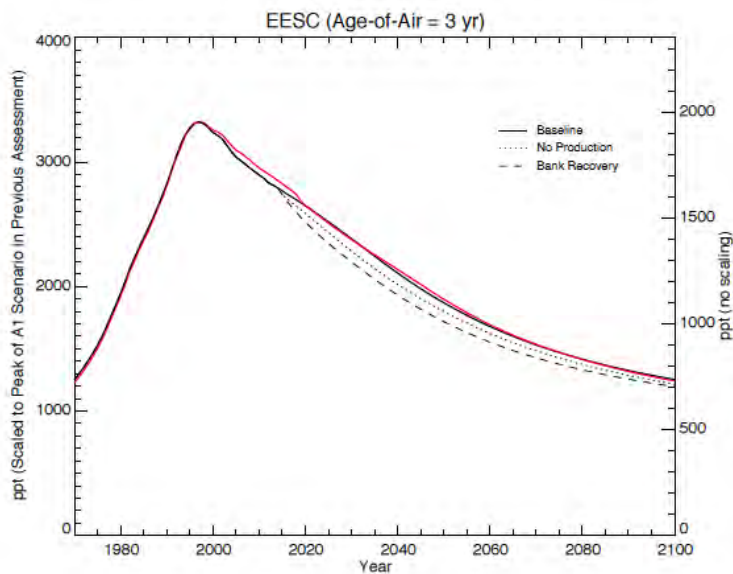


Figure 8a: Changes in EESC values and prediction of future values (Reproduction of Fig. 5.2 in the Scientific Assessment of Ozone Depletion: 2010 http://us-cdn.creamermedia.co.za/assets/articles/attachments/29653_898_executivesummary_emb.pdf)

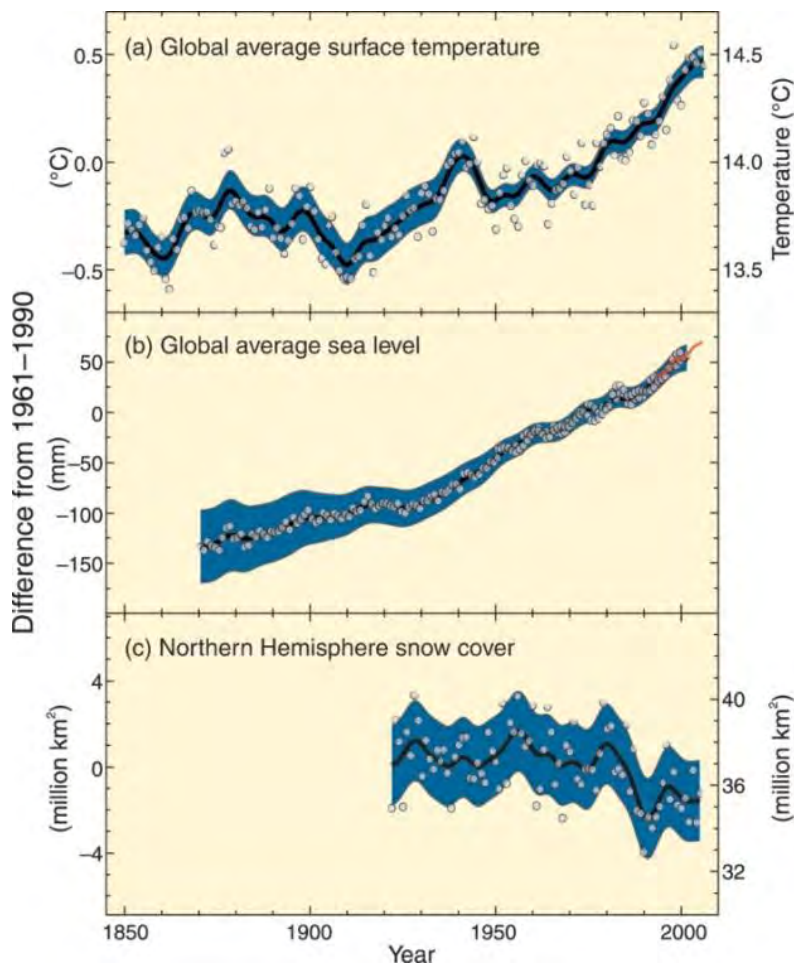


Figure 8b: Effects of climate change on average surface temperature, sea level and snow cover over time (From the IPCC 2007 report).

Q9. Effects on Human Health

a. What are the effects of exposure to solar UV radiation on the human eye and how can the eye be protected?

The effects of UV radiation on the eye can be almost immediate (acute) occurring several hours after a short, intense exposure. They can also be long-term (chronic), following exposure of the eye to levels of UV radiation below those required for the acute effects but occurring repeatedly over a long period of time. The commonest acute effect, photokeratitis (snow blindness), leaves few or no permanent effects, whereas cataract due to chronic exposure is irreversible and ultimately leads to severe loss of vision requiring surgery.

Avoidance of the sun is an effective but impractical means of avoiding exposure of the eyes to UV radiation. Although the eyes rarely receive direct sunlight, protection is frequently needed under conditions of high ambient UV radiation and/or where there are reflective surfaces.

Appropriate glass and plastic lenses absorb all UV-B radiation and much of the UV-A radiation. Even clear spectacle lenses provide protection from UV-B. However, in the case of

non-wrap-around sunglasses, there is potential for ambient UV radiation to enter the eye from the side. This effect can be exacerbated by tinted sunglass lenses which encourage a wider opening of the eyelids. UV radiation-blocking soft contact lenses (Figure 9a), that cover the entire cornea, effectively shield the cornea and ocular lens against UV radiation incident from all angles. They offer a UV protection alternative in those situations where the wearing of sunglasses is not practical or convenient.

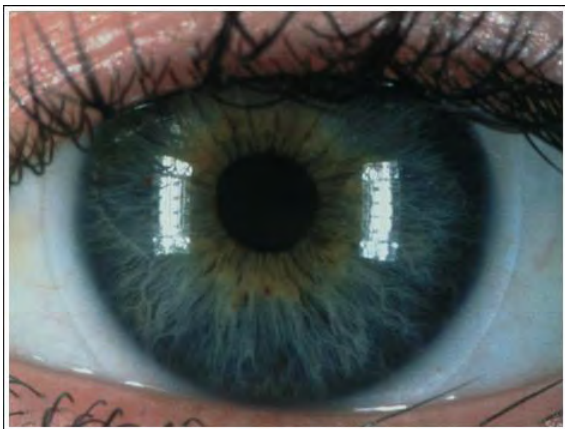


Figure 9a. Soft UV radiation-absorbing contact lens covering the entire cornea. Photograph provided by Dr A. Cullen (University of Waterloo, Canada).

b. What are the adverse effects of exposure to solar UV-B on human skin?

Acute overexposure of the skin to solar UV radiation causes sunburn; chronic sunlight exposure can lead to the development of skin cancers.

Sunburn is the major acute outcome in the skin of overexposure 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. People are frequently divided into 6 categories of skin type (Table 9b).

The major harmful effect of chronic exposure to sunlight, and/or intermittent episodes of sunburning, is the induction of skin cancers. Such tumours are divided into melanomas and the non-melanoma skin cancers, i.e., basal cell carcinoma and squamous cell carcinoma

(Figure 9b). Basal cell carcinomas are most common, followed by squamous cell carcinomas and both are found at highest frequency in fair-skinned individuals living in sunny climates. They can be readily treated and are rarely fatal. Cutaneous melanoma, on the other hand, is rarer but much more dangerous and the number of new cases has increased significantly each year in many countries over the past 40 years or so. The number of cases of melanoma in dark-skinned individuals is fewer than in fair-skinned individuals and it is also uncommon in people under the age of 20.

Table 9b: Skin types.

Phototype/Ethnicity	UV-sensitivity	Sunburn/tan
I/White Caucasian	Extremely sensitive	Always burns, never tans
II/White Caucasian	Very sensitive	Burns readily, tans slowly and with difficulty
III/White Caucasian	Moderately sensitive	Can burn after high exposure, tans slowly
IV/White Caucasian, often south Mediterranean	Relatively tolerant	Burns rarely, tans easily
V/Brown, Asian/Middle Eastern	Variable	Can burn easily, difficult to assess as pigment is already present
VI/Black, Afro-Caribbean	Relatively insensitive	Rarely burns

Solar UV-B exposure is the major environmental risk factor in skin cancers



Squamous cell carcinoma



Cutaneous melanoma



Basal cell carcinoma

Figure 9b. Examples of the 3 major types of skin cancer. Photograph supplied by Professor M. Norval (University of Edinburgh, Scotland).

c. How does UV-B radiation affect the immune system?

The immune system can be suppressed by exposure of the skin and eyes to UV-B radiation leading to reduced immune responses to infectious agents and skin cancers, but a potentially beneficial effect for some autoimmune diseases.

UV radiation is absorbed by specific molecules called chromophores in the skin. These initiate a cascade of events affecting the immune system: decreasing the ability of specialised cells to recognise foreign challenges such as invading microorganisms or tumour proteins, altering the production of a range of immune mediators, and inducing the generation of particular lymphocytes called T regulatory cells. All of these changes lead to suppression of immune responses following the exposure.

Numerous animal models of infection have demonstrated that exposure to UV radiation at a critical time during infection can increase the severity of symptoms and duration of the disease. In addition, UV radiation before (and possibly immediately after) immunisation can reduce the immune response generated and therefore the effectiveness of the vaccination. How these observations relate to human diseases is currently not clear and remains a subject of intense interest and research. The results from a limited range of studies in humans indicate that exposure to UV radiation around the time of vaccination can decrease

the immune response generated, at least in some groups of individuals.

Some examples in humans where UV exposure before or during infection suppresses immunity are recognised. In the case of cold sores caused by herpes simplex virus (Figure 9c), solar UV radiation is a common trigger for the reactivation of latent virus and the reappearance of the vesicles in the skin. Some immunological effects of UV radiation are also involved in the interaction between certain human papillomavirus types (these viruses typically cause warts) and the many viruses that promote formation of squamous cell carcinomas. The involvement of T regulatory cells in squamous and basal cell carcinomas indicate that UV-induced immunosuppression is an important factor in their development. In contrast, this down regulation in immunity is of potential benefit in protection against the development of some autoimmune diseases, such as multiple sclerosis, where there is an over-activity of T cells directed against specific elements of the body's own tissues.



Figure 9c. 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).

d. Are there any beneficial health effects of solar UV-B radiation?

A major benefit to human health of exposure to UV-B radiation is the production of vitamin D.

Although the diet of humans contains some items rich in vitamin D, such as oily fish and eggs, more than 90% of the vitamin D in most people is produced by exposure of the skin to solar UV radiation (Figure 9d). Vitamin D is synthesised most effectively when the sun is at its height in the summer months and little or none is synthesised in the winter at mid to high latitudes. Individuals with dark skin 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 subjects. 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) in the blood: a minimal cut-off value is recommended for optimal health benefits, below which some adverse effects could occur.

Vitamin D is required for the growth, development and maintenance of bone. Those individuals deficient in vitamin D can develop bone defects, resulting in an increased risk of osteoporosis and fractures in adults, and of rickets in children. Vitamin D has also been implicated in protection against a range of non-skeletal disorders. These include some internal cancers such as colorectal cancer, autoimmune diseases such as multiple sclerosis and insulin-dependent diabetes, infections such as tuberculosis and influenza, and cardiovascular diseases such as hypertension. The most convincing evidence to date for these protective roles has come from clinical trials involving dietary vitamin D supplementation, and it has yet to be confirmed that increased solar UV-B exposure, affecting vitamin D status, can modulate the risk of the disease.

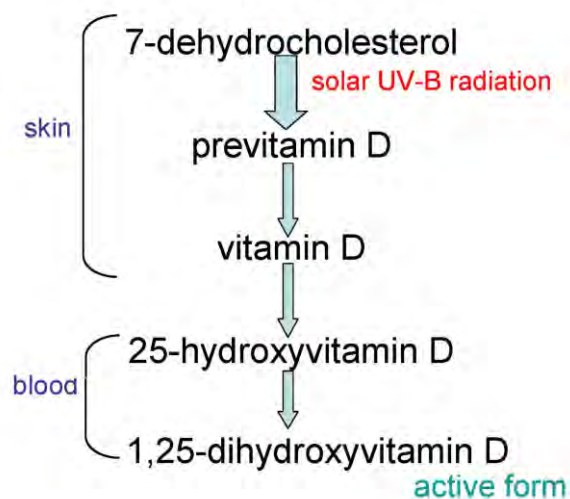


Figure 9d. Simplified metabolic pathway leading to the active form of vitamin D (1,25-dihydroxyvitamin D).

e. What risks do the breakdown products of HFCs and HCFCs present to humans and the environment?

The main breakdown product, trifluoroacetic acid (TFA) and other related short-chain fluorinated acids are presently judged to present a negligible risk to human health or the environment.

The hydrofluorocarbons (HFCs) and hydrochlorofluorocarbons (HCFCs) are replacements for the chlorofluorocarbons (CFCs) as they have a smaller effect on the ozone layer. The HFCs and HCFCs are largely degraded before reaching the stratosphere (Figure 9e).

HFCs and HCFCs break down relatively rapidly into several products including persistent substances such as trifluoroacetic acid (TFA) and chlorodifluoroacetic acid (CDFA). The compounds are soluble and are washed from the atmosphere by precipitation and reach surface waters, along with other chemicals washed from the soil. Microbiological degradation slowly removes these substances from the water. In locations

where there is little or no outflow and high evaporation (seasonal wetlands and salt lakes), these products are expected to increase in concentration over time.

The effects of increased concentrations of naturally occurring mineral salts (from natural sources such as undersea vents and volcanic activity) and other materials would be greater and more biologically significant than those of breakdown products of the HFCs and HCFCs. TFA is very resistant to breakdown, and amounts deposited in flowing surface water will ultimately accumulate in the oceans. However, 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.

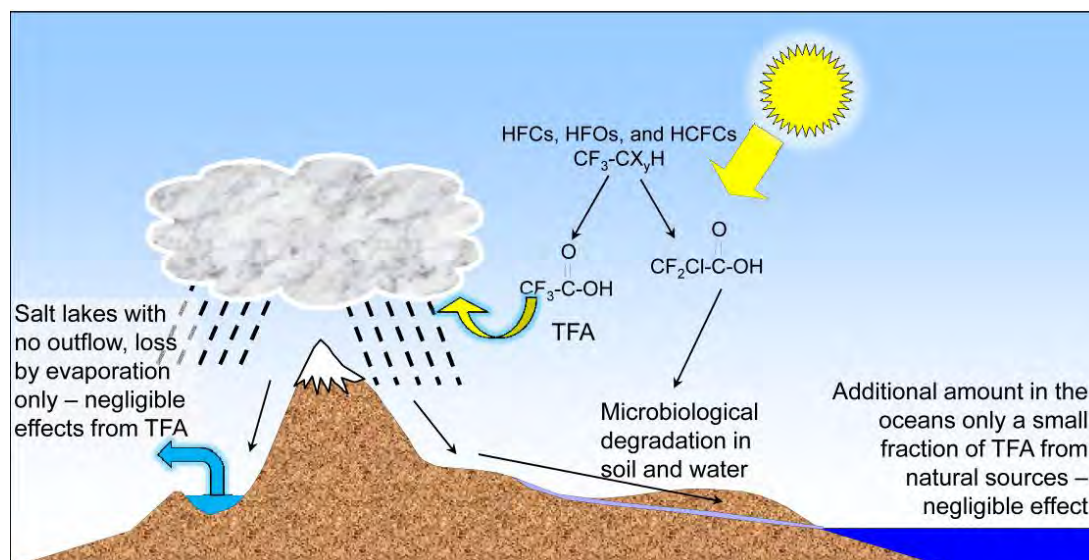


Figure 9e: The breakdown of CFC replacements into TFA. (Figure provided by Prof K Solomon.)

f. How can I protect myself from the adverse effects of solar UV-B radiation on the skin?

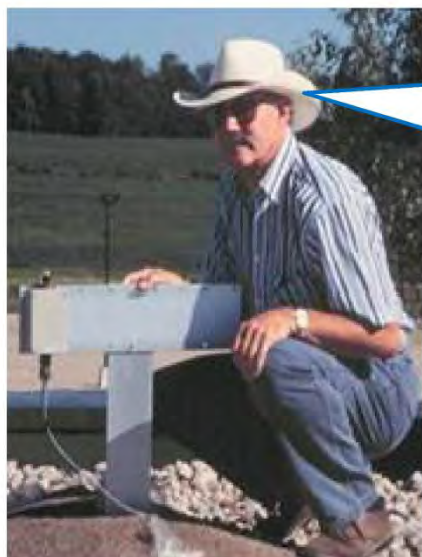
Many protective strategies against excessive exposure to sunlight have been developed, particularly to avoid sunburn.

The intensity of UV-B radiation from the sun is usually highest during the central hours of the day (about 10 am until 2 pm) or later in periods of daylight savings). Many news outlets and government websites report the daily UV Index, and issue alerts when high values are predicted (see question 5).

If you are outside, it is most important to avoid sunburn. The time taken to reach this point depends on many variables including your ability to tan in response to sunlight. The popular advice “to slip (on a shirt), slap (on a hat), slop (on some sunscreen)” and wrap (add wrap-around sunglasses), is useful (Figure 9f). 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 side UV-B irradiation. Wrap-around sunglasses are better at protecting the entire eye than conventional sunglasses with open sides.

Protection of the body with suitable clothing is recommended when outside during the central hours. Some textiles are highly effective in this regard while others are less so. Sunscreens are also effective and ones with a sun protection factor of 30 are generally recommended. They need to be applied at the stated concentration and to be frequently re-applied, especially when swimming. It is particularly important to protect children from sunburn, episodes of which could lead to an increased risk of skin cancer development in adulthood. The use of sun protection is recommended when the UV Index is forecast to be 3 or greater.



Note the wide brimmed hat, wrap-around glasses and textile clothes. The face and exposed arms should be protected by the use of the correct sunscreen.

Figure 9f: Wearing the correct clothing and the use of sunscreen can protect against UV radiation. (Photograph supplied by Dr A. Cullen, University of Waterloo, Canada.)

g. How much time should I spend in the sun in order to produce sufficient vitamin D but avoiding sunburn and minimising the risk of skin cancer?

There is no short and simple answer to this question but some guidance is given below.

The time will depend on the latitude, season, time of day, weather conditions, the amount of skin exposed and whether your skin is accustomed to exposure. You should also know your skin type (see question 9b) and recognise how readily you burn or tan as a result of sun exposure. Most importantly, sunburn should be avoided, particularly in children. One useful guide is to find out the daily forecast for the noon UV Index (see question 5) for your location. In many countries the UV Index is reported in weather forecasts on the radio and TV and in newspapers, and can also be found on various websites. The UV Index at times other than noon is lower unless there is a big change in cloudiness.

Estimates of the daily variations in sun-burning UV radiation and in the UV radiation needed to make vitamin D at mid-latitudes are shown in Table 9g.

Some calculations have been made giving an indication of the number of minutes in the sun required to cause sunburn, and the number required for adequate vitamin D production for various UV Indices at various latitudes in the summer and winter. The values below should be taken as a rough guide only, and are for times around noon and for (previously unexposed) skin type II. They should be multiplied by 2 for skin type IV and by 5 for skin type VI.

Table 9g: Estimates of daily variations in sun-burning UV radiation and in the UV radiation needed to make vitamin D at mid-latitudes.

	Minutes to sunburn	Minutes for sufficient vitamin D, full body exposure	Minutes for sufficient vitamin D, 10% body exposure
Mid-latitude, summer UV Index 12	15	1	10
Mid-latitude, winter UV Index 1	180	20	200
Tropics UV Index 16	10	<1	7

(Data from R.L. McKenzie, J.B. Liley and L.O. Björn. UV radiation: balancing risks and benefits. Photochem. Photobiol. 2009, 85, 88-98)

h. Will global climate change alter the effects of UV radiation on human health?

While there are clear concerns about the health effects of global climate change through, for example, increasing temperatures and changes in the distribution of some vector-borne diseases, it is not possible at the present time to predict whether climate change will affect UV-related health issues.

In trying to assess possible interactions between climate change and solar UV radiation, the major uncertainty for human health is whether people will spend more or less time outdoors in sunlight as temperatures rise, but humidity, storms, floods and droughts also increase. One animal study suggests that the risk of skin cancer is greater for the same level of UV radiation exposure if the ambient temperature increases; there is some support for a similar finding in human populations living in different regions (Figure 9h). Exposure to UV radiation in sunlight can be important for disinfection of waterborne pathogens, which may grow and survive better in warmer conditions.

If warmer temperatures encourage people to spend more time outside, it will be important to ensure adequate sun protection. In contrast, if more time is spent indoors, vitamin D may need to be provided as a dietary supplement.

Climate change may alter the effects of UV radiation on terrestrial and aquatic ecosystems to change the availability or quality of human food supplies, with resulting effects on human health. In addition, climate-induced changes in air pollution have potential health effects, but these remain highly uncertain.

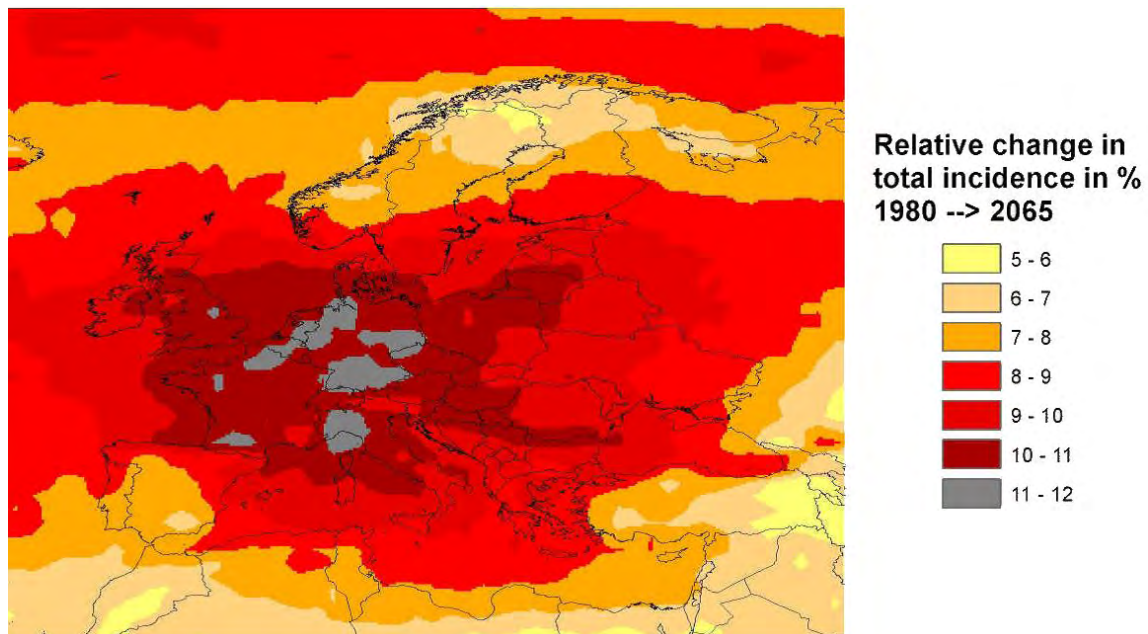


Figure 9h: The predicted relative change in total skin cancer incidence from 1980 to 2065 in Europe. (From: Figure 5.16. Relative change in total skin cancer incidence from 1980 to 2065 for the A1 scenario, based on the AMOUR2.0 assessment model, RIVM in <http://www.rivm.nl/bibliotheek/rapporten/610002001.html>).

Q10. Effects on the Environment

a. What are the major impacts of UV-B radiation on natural terrestrial ecosystems, crops and forests?

-
- i) *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 crop and forest species) have mechanisms that provide some UV shielding.*
-

Vital biomolecules, including DNA, proteins, and lipids, are potentially vulnerable to UV-B radiation. However, only a small portion of the UV-B radiation striking a leaf penetrates into the inner tissues. 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. Other adaptations include increased thickness of leaves, thereby reducing the proportion of inner tissues exposed to UV-B radiation, and changes in the protective waxy layer of the leaves. Plants also have several mechanisms for repairing damage to DNA.

Some protective molecules produced by plants, in response to natural UV-B radiation, are important in our food, enhancing colours, flavours, antioxidant activity and fibre production (see Figure 10a-1). Some of the changes in plant biochemistry induced by UV-B radiation influence the interactions between crop plants and herbivorous insects. The change in biochemical composition can make the leaves less attractive as food for herbivores (including for insect pests) and alter the speed with which leaf litter is broken down in the soil. At an ecosystem level, these effects on palatability and decomposition can be substantial, since they have an impact on the food supply of animals and the recycling of nutrients in the soil.

-
- ii) *UV radiation has impacts that go beyond the individual plant and can affect ecosystem processes. Changes to plant composition, induced by UV-B radiation, can flow through to the animals and microbes (bacteria and fungi) that rely on plant matter for food.*
-

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 changes in plant tissues induced by the UV-B radiation. 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). This means that if UV-B radiation is higher, insects generally eat less plant material. By contrast, higher atmospheric CO₂ leads to increased herbivory, so future levels of UV-B irradiance and CO₂ will be important in controlling both plant production and the food supply for insects.

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 light-induced breakdown (photodegradation).

Sunscreen compounds and structural alterations, which allow leaves to withstand UV-B radiation while attached to the plant, can make leaves 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). Changes

to both microbial and photodegradation breakdown processes have important consequences for future carbon sequestration and nutrient cycling.

iii) *Some types of crops and wild plants may show detrimental effects from increased UV-B radiation.*

It is possible to breed and genetically engineer UV-B tolerant crops. While many forest tree species appear to be UV-B tolerant, there is some evidence that detrimental UV-B effects accumulate slowly from year to year in certain species.

The present rate of global change is so rapid 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 10a-2). Although the negative impact of UV-B radiation on plant growth 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 10a-1: Other examples of protective molecules produced by plants, in response to UV radiation include the red pigments seen in lettuces (left panel), while those shielded from UV are mostly green. Similarly, Antarctic mosses (right panel) shielded by small stones are green (centre), while the plants around them produce protective red pigments. These protective 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).

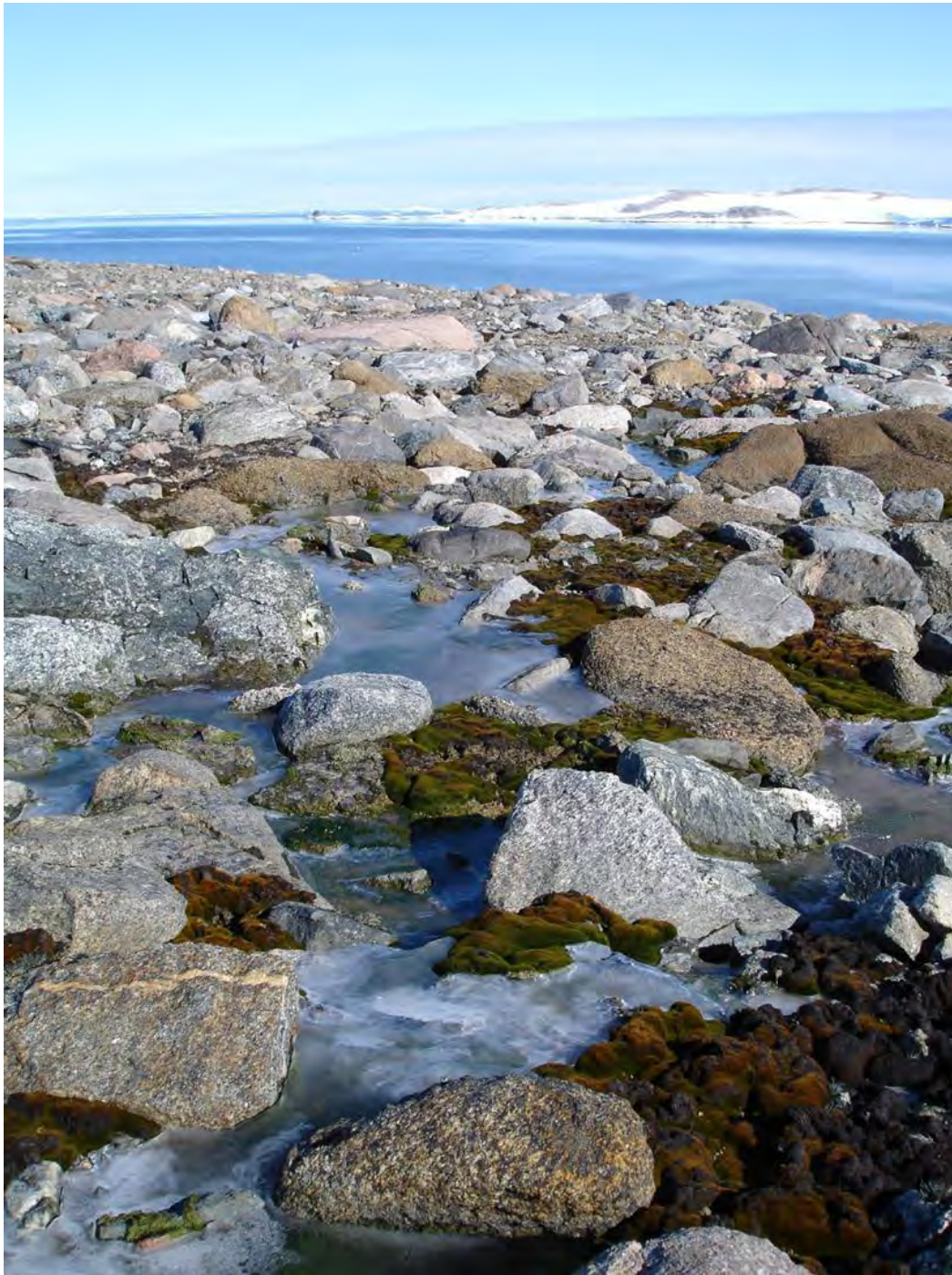


Figure 10a-2: Impacts of UV-B radiation on terrestrial ecosystems. Ozone depletion has led to higher UV fluxes over Antarctica with negative effects on some species of Antarctic plants, such as the mosses seen growing along this icy stream. (Photograph from Prof. S. Robinson, University of Wollongong, Australia)

b. Does exposure to UV-B radiation affect aquatic life?

UV-B radiation can penetrate to ecologically significant depths in the clearest natural waters and have an effect on the aquatic life.

In clear ocean and lake waters, UV-B radiation can penetrate to tens of metres. In turbid rivers and wetlands, however, UV-B radiation may be completely absorbed within the top few centimetres. In aquatic ecosystems, most organisms, such as phytoplankton, live in the illuminated upper layer of a body of water that allows the penetration of enough light (and UV-B radiation) to support photosynthetic, or green, plants. In particular, UV-B radiation may damage those organisms that live at the surface of the water during their early life stages.

Detrimental effects of UV-B radiation have been shown for phytoplankton, fish eggs and larvae, zooplankton and other primary and secondary consumers. Most adult fish are well protected from excessive solar UV radiation, since they inhabit deep waters. Some shallow-water fish can develop skin cancer and other UV-related diseases.

UV-B radiation reaches different depths in ocean water depending on water chemistry, the density of phytoplankton, and the presence of dissolved and particulate matter. Figure 10b shows the average depth that UV-B radiation

penetrates into ocean water. At the depth indicated, only 10 per cent of the UV-B radiation that was present at the water's surface remains. The rest was absorbed or scattered back towards the ocean surface.

In the Gulf of Maine, UV radiation penetrates to considerable depth where the embryos and larvae of the Atlantic cod develop. Exposure to UV radiation equivalent to that present at 10 m depth results in a significant mortality of developing embryos and a significant decrease in the length of the larvae. Such radiation levels occur at many temperate latitudes where these ecologically and commercially important fish spawn. In freshwater lakes and ponds, amphibian embryos are protected from UV-B radiation by the enzyme photolyase, melanin pigmentation of eggs, jelly surrounding the eggs, the water depth and dissolved organic matter in the water. Larvae can seek shelter from sunlight by swimming into shaded areas and vegetation in ponds. In contrast, lobster larvae seem to be tolerant to UV radiation even though they develop in the surface layers of the water column.

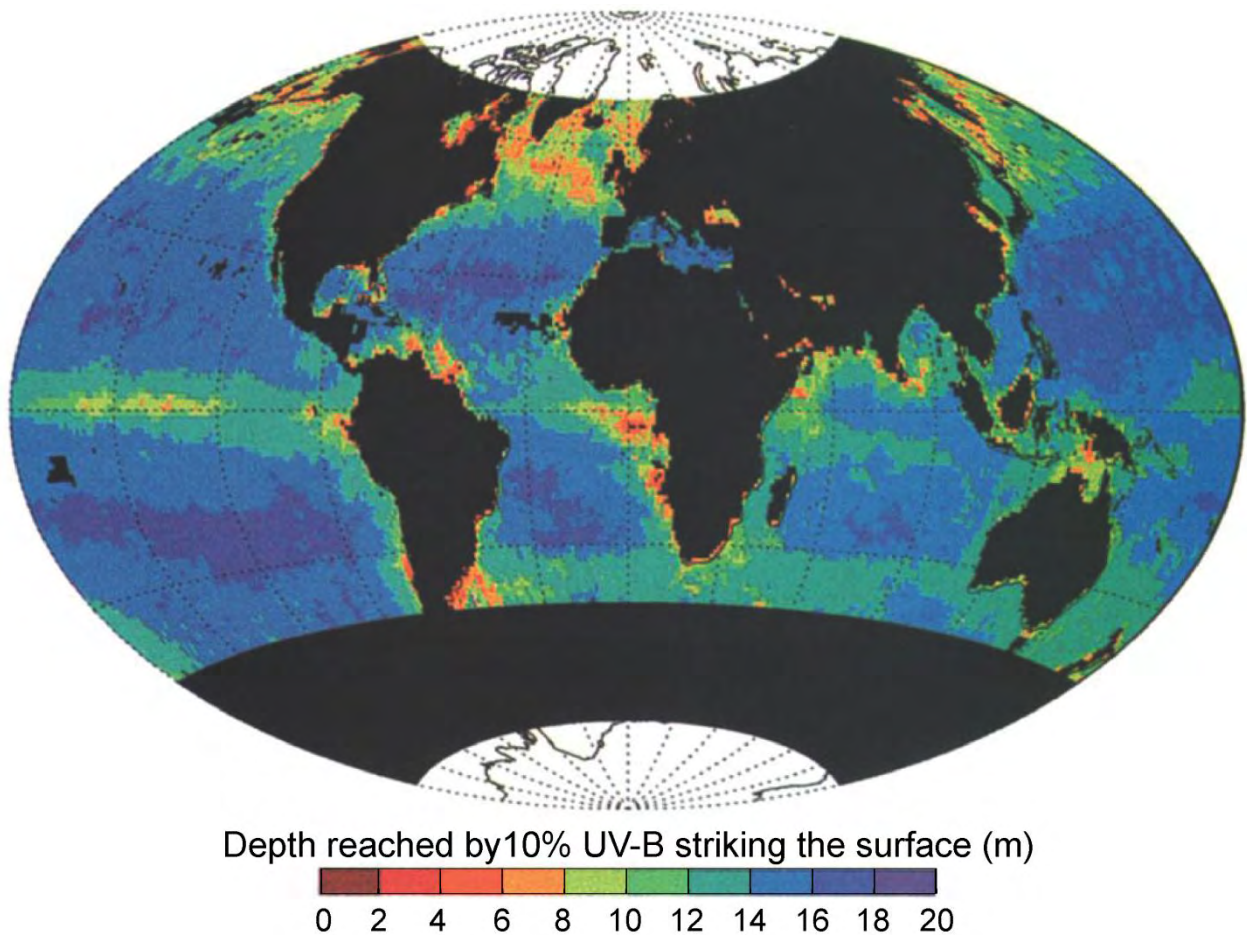


Figure 10b: The penetration of UV-B radiation into the global oceans by indicating the depth to which 10% of surface irradiance penetrates. (Image courtesy of Vasilkov et al. *J. Geophys. Res. Oceans*, 2001106, 205-227).

c. Does climate change alter the effect of UV radiation on aquatic ecosystems?

Climate change will influence various aspects of how UV-B radiation affects aquatic ecosystems, such as through changes in temperature and sea-level, shifts in the timing and extent of sea-ice cover, changes in the wave climate, ocean circulation and salinity and alterations in the stratification of the water column.

These complex changes are likely to have significant effects on ecosystems, including biological production as well as changes in the global hydrological cycle, vertical mixing and efficiency of carbon dioxide uptake by the ocean (Figure 10c). Such effects will vary over time and between different locations. Changes in temperature and the intensity and frequency of rainfall may alter the input of terrestrially-derived coloured dissolved organic matter (CDOM) to inland and coastal aquatic ecosystems. For example, decreased rainfall and increased temperature cause reductions in CDOM inputs and consequent increases in the depth to which UV radiation penetrates. In addition, the dissolved and suspended material in the water column changes the ratio of UV-A to UV-B to photosynthetically active radiation (PAR) in the penetrating UV radiation. These changing ratios, in turn, have various influences on decomposers, producers and consumers.

Climate change influences the amount of ice and snow cover in polar and sub polar areas. Ice and snow strongly attenuate the penetration of solar radiation into the water column. Any substantial decrease in ice and snow cover will alter the exposure of aquatic ecosystems to solar UV radiation.

Shifts in atmospheric circulation will change wind fields, influencing mixing and the depth of the upper mixed layer of the ocean. Such changes, and increases in temperature, affect the stratification of the surface layer of the ocean and the potential impact of UV-B radiation on near-surface organisms. Changing winds will also influence coastal upwelling systems and the potential for possible influence of these systems on UV radiation. Additionally, many physiological responses are dependent on temperature, providing another route whereby climate change may interact with the effects of UV radiation.

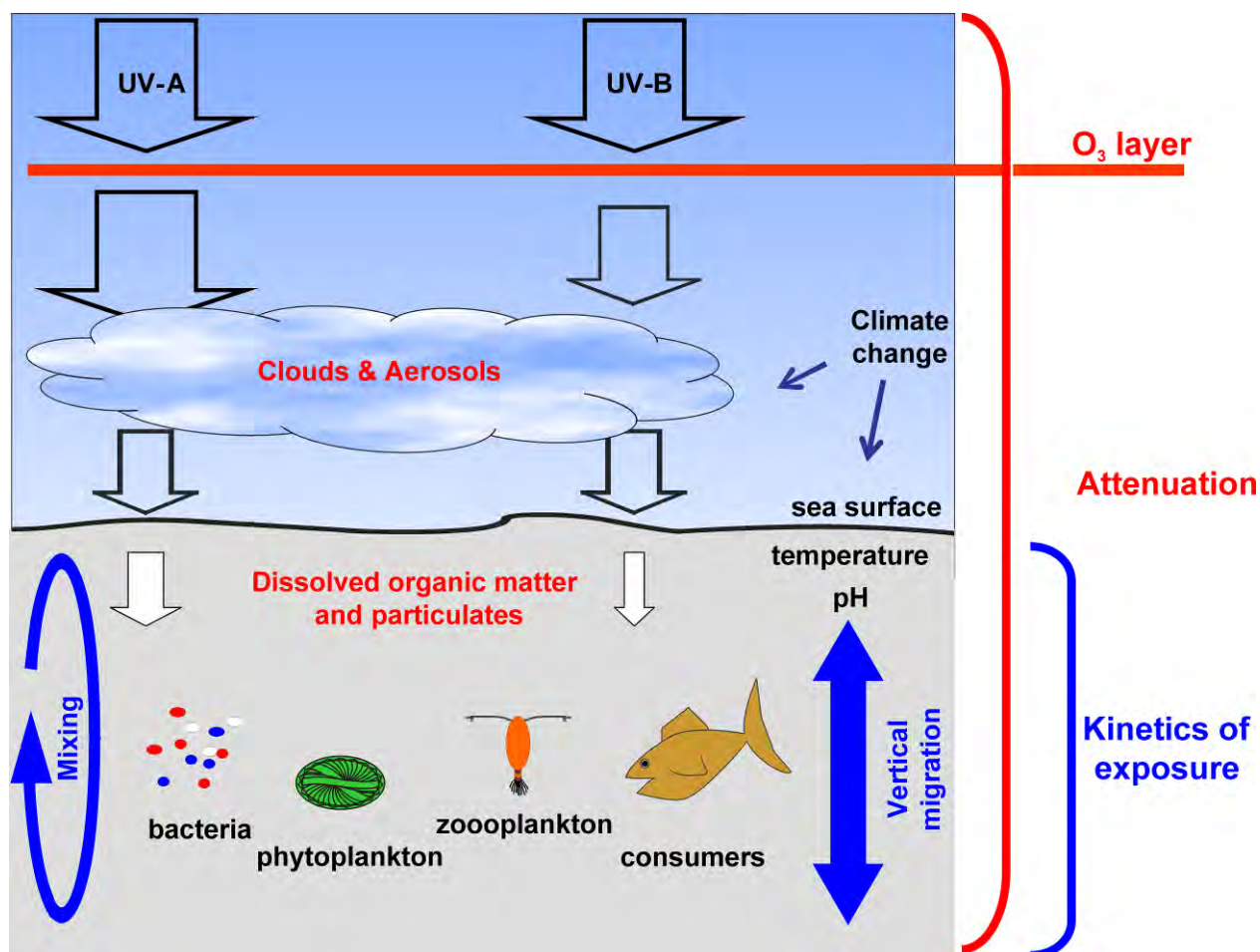


Figure 10c: Main factors affecting the quantity and quality of UV radiation received by aquatic organisms (Diagram modified from Gonçalves et al. *Ecología Austral.*, 2010, 20, 129-153).

d. Do increasing atmospheric CO₂ concentrations influence the sensitivity of aquatic organisms to solar UV-B radiation?

Several marine organisms protect themselves from solar UV-B radiation by producing a calcified outer layer; the increasing acidification of lakes and marine habitats impairs the calcification process.

Acidification of lakes and oceans is a major stress factor closely related to climate change and solar UV-B radiation. Increasing acidification of marine waters due to increased atmospheric CO₂ concentrations hampers carbonate incorporation in many calcified marine organisms and makes them more vulnerable to solar UV-B radiation. Before industrialization, the concentration of CO₂ in the atmosphere was about 280 ppmv (parts per million by volume). This corresponded to an average pH in the oceans of about 8.2. The current level of 390 ppmv CO₂ has lowered the pH of the water by about 0.1 units, which corresponds to a 26% increase in acidity. A further pH decrease of 0.3 – 0.4 units is expected by the year 2100. This acidification is expected to adversely affect the uptake and incorporation of calcium carbonate in

molluscs, phytoplankton and some seaweeds. Encrustations of calcium carbonate efficiently absorb UV radiation. At lower pH values, increased UV transmission will expose the vulnerable organisms to higher levels of solar UV-B radiation. Experiments have shown that UV radiation significantly inhibits growth, photosynthetic oxygen evolution and calcification rates in the seaweed *Corallina* at high CO₂ concentrations (1000 ppmv as compared to 390 ppmv). In one of the major biomass producers in the ocean (the coccolithophore, *Emiliania huxleyi*, Figure 10d), calcification rates are diminished by increased acidity, resulting in thinner protective scales (coccoliths) on the surface. The transmission of UV radiation is significantly higher because of the acidification (by 0.1 pH units).

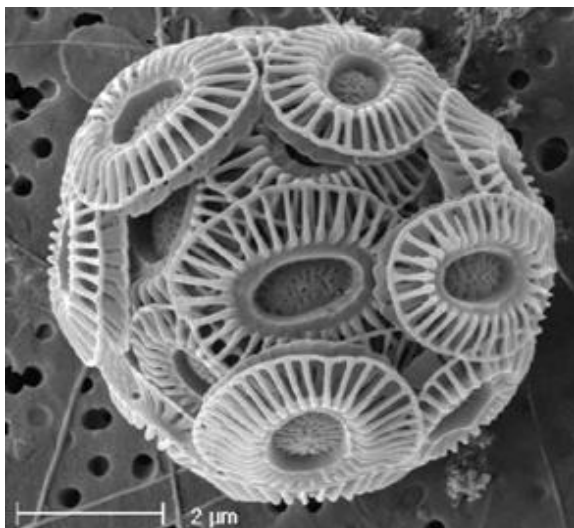


Figure 10d: Scanning electron micrograph of the phytoplankton coccolithophore *Emiliania huxleyi* covered with coccoliths. Courtesy of Kunshan Gao, Xiamen, China.

e. What effects does the depletion of ozone have on environmental processes and cycles?

Changes in UV-B radiation cause complex alterations to atmospheric chemistry, and thus affects the entire biosphere, with consequences for all organisms on Earth, including humans.

UV radiation influences the biological productivity of oceans, including the production of gases at their surfaces and their subsequent transfer to the atmosphere. Once in the atmosphere, gases such as carbon dioxide (CO₂) interact with the physical climate system resulting in alterations to climate and feedbacks in the global biogeochemical system (Figure 10e). Since atmospheric CO₂ plays a central role in the distribution of heat in the atmosphere, its increasing concentrations may affect

many components of the physical climate system, such as wind, precipitation and the exchange of heat and energy between the air and the oceans.

There are also similarly complex interactions between biogeochemical cycles on land and the integrated climate system that may have important implications for organisms on Earth. At this stage, it is not possible to predict the overall environmental effects of these complex interactions between changes in climate and UV radiation.

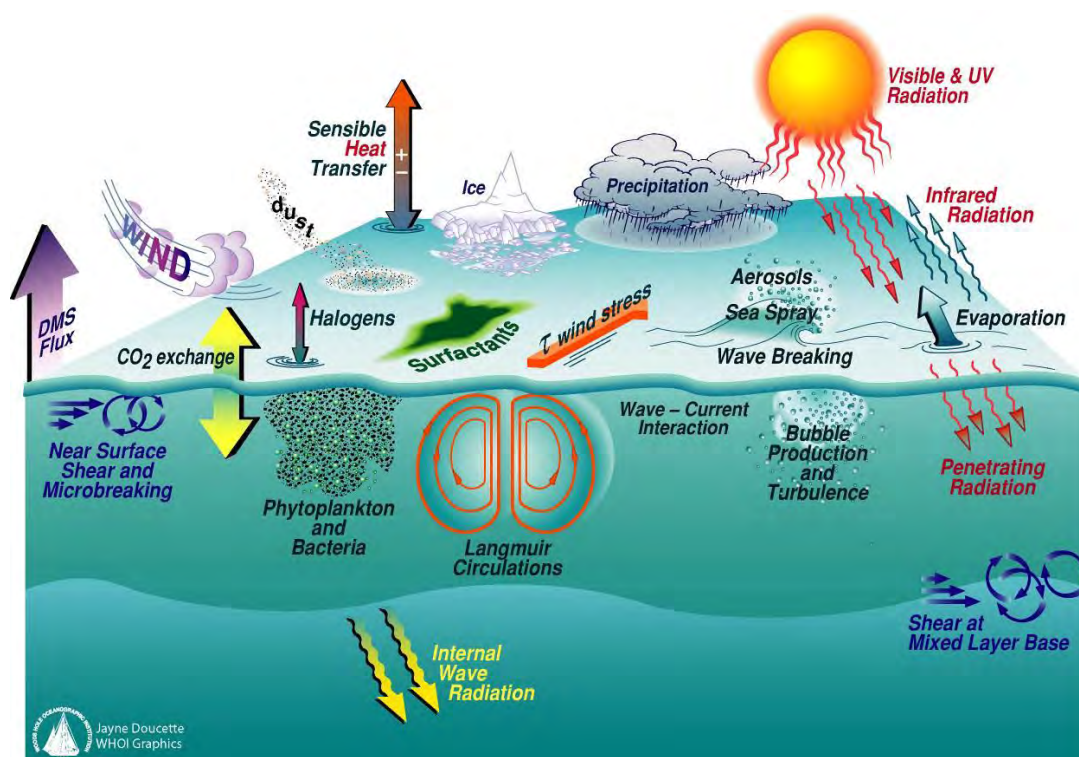


Figure 10e: Interactions between environmental processes and cycles. (Figure provided by the US Surface Ocean Lower Atmosphere Study (SOLAS) and the Woods Hole Oceanographic Institute).

Q11. Can the increased temperature due to global warming increase the deleterious effects of UV-B radiation on plastics and wood products used outdoors?


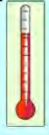


Yes, climate change can have a detrimental effect on plastics and wood products used outdoors.

Useful lifetimes of plastic and wood products are determined to a large extent by degradation due to the action of solar UV radiation (Table 11). A partial depletion of the stratospheric ozone layer results in increased terrestrial UV-B flux, affecting organic materials used in construction. Plastics materials undergo oxidation and chemical breakdown when exposed to UV-B radiation in the atmosphere. This is well known to result in discolouration, surface cracking and loss of strength or stiffness in the product, limiting its useful lifetime. Additives called light stabilizers are used to partly mitigate the deleterious effects of UV-B radiation in plastics used outdoors. Similar degradation and breakdown occurs in wood products, although here biodegradation also contributes to the deterioration very significantly. The action of UV-B radiation on the surface of wood also renders it hydrophilic; rainwater is better absorbed by the surface, leading to the growth of wood-rot fungi that biodegrade the wood. Photodamage by UV-B radiation facilitating fungal biodegradation is seen in wood-plastic composites (or plastic lumber) that are essentially plastics mixed with large amounts of wood flour.

Climate models suggest that near-surface air temperatures will rise anywhere from 2°C to 6°C during the 21st century due to accumulation of greenhouse gases. The rates of chemical reactions that cause the UV-initiated oxidative degradation of plastics or wood are increased at higher temperatures. Thus the useful lifetimes of these materials outdoors will shorten as the ambient air temperature increases. The extent to which this happens depends on the temperature sensitivity of the reaction and varies from material to material. The change can be significant for plastics exposed in geographic locations with already high UV-B radiation that experience higher ambient temperatures.

The change of a few degrees in temperature is already found in seasonal variations. Plastics with a deeper colour exposed to sunlight reach bulk temperatures higher than those of light-coloured products of the same plastic. While the oxidative breakdown will indeed be faster, the available light-stabilizer technologies are likely to control this, thus maintaining the useful lifetimes at the present levels. Because of the need to use higher levels of conventional stabilizers or coatings, the cost of preservation may be higher in some locations.

Table 11: Several environmental factors affect the outdoor degradation of materials

	UV-B radiation 	Temperature 	Humidity 	Pollutants 
Plastics	+++++	+++	+	+
Wood	+++	++	+++++	+

++++ Very susceptible, +++ Moderately Susceptible, ++ Susceptible, + Likely to be susceptible (illustration from Dr. A. Andrady, North Carolina State University).

Q12. Ozone and Climate

a. Do ozone depleting gases and their substitutes have an effect on climate?

Stratospheric ozone depletion has an influence on climate change since both ozone and the compounds responsible for its depletion are active greenhouse gases.

Ozone depleting substances (ODSs) such as the CFCs have contributed to increases in global average surface temperature. On the other hand, ozone depletion itself has a cooling effect. Warming due to 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 less to warming than to cooling, whereas CFCs and HCFCs contribute more to warming than to cooling. HFCs and PFCs contribute only to warming.

Actions taken under the Montreal Protocol have led to the replacement of CFCs with HCFCs, HFCs, and other substances. Because replacement species (with the exception of HFCs) generally have lower global warming potentials (GWPs) and because total halocarbon emissions have decreased, their contribution to climate

change has been reduced (Figure 12a). Ammonia and hydrocarbons used as halocarbon substitutes will have a negligible effect on global climate. The relative future warming and cooling effects of emissions of CFCs, HCFCs, HFCs, PFCs and halons vary. The indirect cooling effect of ODSs is projected to cease upon ozone layer recovery, so that GWPs associated with the indirect cooling effect depend on the year of emission, compliance with the Montreal Protocol and gas lifetimes.

Substitutions for ODSs in air conditioning, refrigeration, and foam blowing by HFCs, PFCs, and other gases such as hydrocarbons are not expected to have a significant effect on global tropospheric chemistry.

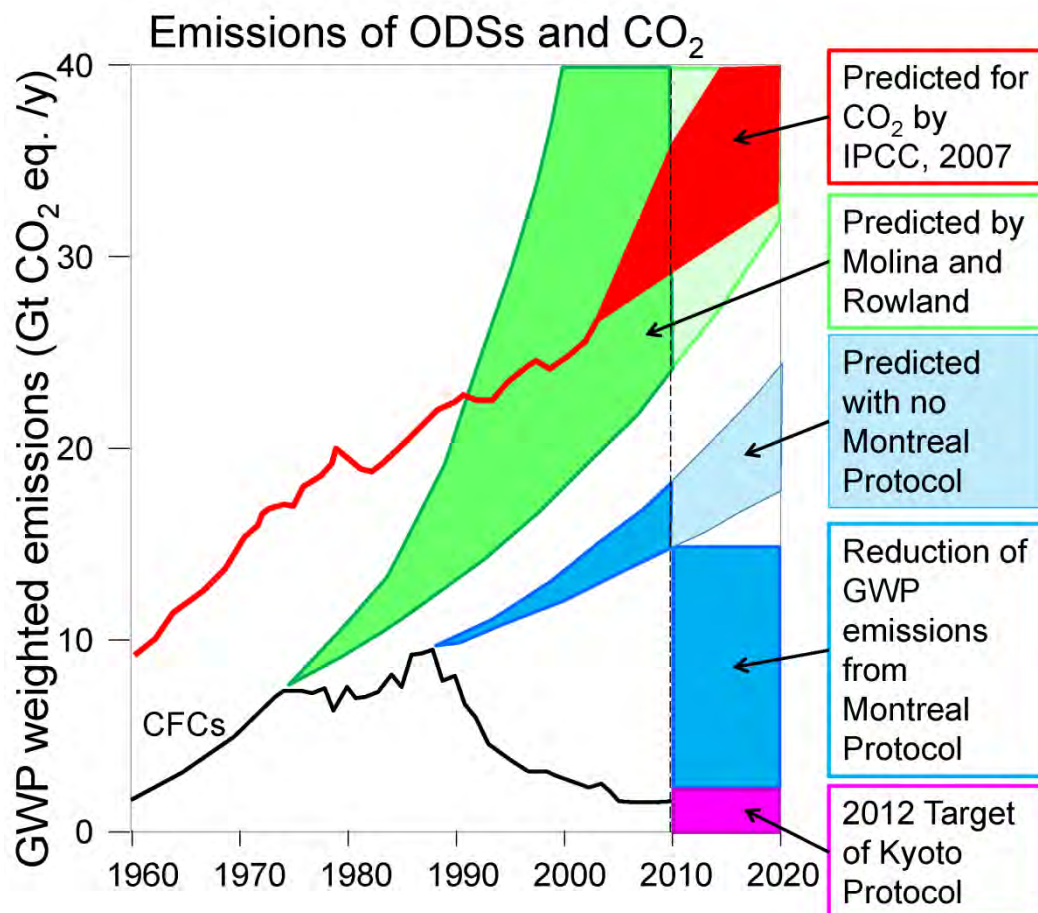


Figure 12a: An illustration of the reduction in global warming by the Montreal Protocol compared with what was expected by the Kyoto Protocol on Climate Change (Based on a figure provided by Dr Mack McFarland based on Velders, et al. *Proc. Nat. Acad. Sci. USA.*, 2007, 104, 4814–4819).

b. Is ozone depletion affected by climate change?

Climate change affects ozone depletion through changes in atmospheric conditions that affect the chemical production and loss of stratospheric ozone. The interactions are complex (see Figure 11b). Climate change is expected to decrease temperatures and water vapour abundances in the stratosphere. This will tend to speed up ozone recovery outside Polar Regions, but slow down the recovery in Polar Regions

Ozone, the CFCs and their substitutes are minor greenhouse gases with a relatively small ($\pm 13\%$) contribution to climate change. Several other gases involved in the chemistry of ozone depletion are also active greenhouse gases. They include water vapour, methane, and nitrous oxide. Increases in those will ultimately lead to increases in stratospheric gases that destroy ozone. Changes in solar output and future volcanic eruptions will influence both climate change and ozone depletion.

While current ozone depletion compared with periods prior to the 1980s is dominated by chlorine and bromine in the stratosphere, in the longer term (~100 years) the impact of climate change will dominate through the effects of changes in atmospheric circulation and chemistry (Figure 12b). The result is that over the first half of the current century, increases in greenhouse gases may contribute to a colder stratosphere. This will lead to a decrease in the rate of destruction

of ozone outside Polar Regions. In Polar Regions, however, the lower temperatures may lead to increased polar stratospheric clouds, thus exacerbating ozone depletion. The temperature changes will also lead to changes in atmospheric circulation. These changes may aid the mixing of long-lived CFCs from the troposphere to the stratosphere, which will increase their rate of photochemical destruction. This will lead to more severe ozone depletion in the short term but will contribute to a faster ultimate recovery of ozone. Changes in polar ozone also can 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 thus indirectly affect UV radiation), and those that depend on changes in other variables (such as clouds, aerosols or snow cover that influence solar UV radiation directly).

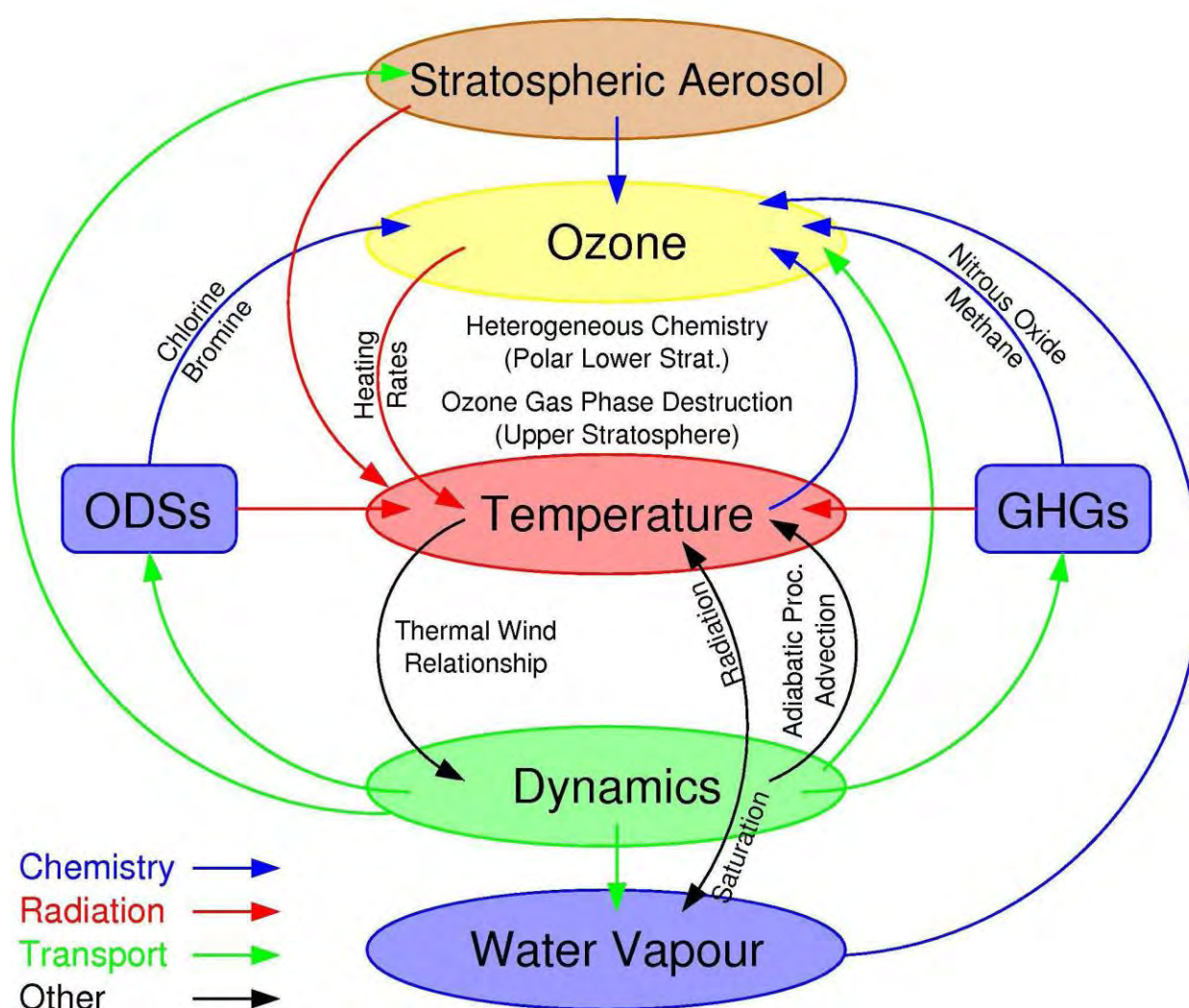


Figure 12b: Schematic of ozone focused stratospheric chemistry-climate interactions (as explained in the 2011 Scientific Assessment Panel report). Links between components of the chemistry-climate system are indicated with arrows representing chemistry (blue), radiation (red), transport (green) and other mechanisms (black). A simple example is ozone depletion in the upper stratosphere leading to lower temperatures. Lower temperatures slow down the gas phase destruction of ozone, thus reducing the amount of ozone depletion. Feedback cycles not originating from ozone, but e.g. dynamics, are possible as well: “Dynamics” moderates the distribution of GHGs (e.g. the meridional gradient of N_2O , nitrous oxide), this changes temperature directly (radiation) and indirectly (chemistry, via a change in ozone) and the changing temperature will alter the dynamics (e.g. via the thermal wind relationship) and ozone (e.g. in a colder upper stratosphere ozone gas phase destruction will slow down leading to increased ozone values). The feedback loops involving volcanic aerosol in the stratosphere are sporadic and currently not important.

Q13. Are the control measures in the Montreal Protocol working? What is the world we avoided?

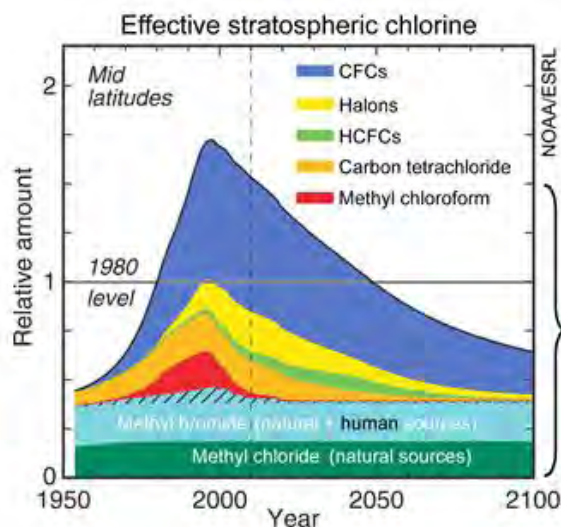
a. Phase-out of ODS

Yes 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 196 countries of the world. 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 2010 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 ozone depleting substances have been decreasing for over ten years, and are expected to continue to decrease in the future (Figure 13a).



The Montreal Protocol has **slowed and reversed** the accumulation of ozone depleting substances (ODSs) in the stratosphere as measured by **effective stratospheric chlorine** amounts.

Figure 13a: The measurement of past and predicted future concentrations of halocarbons in the stratosphere (Reproduction of Fig. 5.1 in the Scientific Assessment of Ozone Depletion: 2010 http://us-cdn.creamermedia.co.za/assets/articles/attachments/29653_898_executivesummary_emb.pdf).

b. UV Radiation changes

The Montreal Protocol had a huge influence on UV B radiation.

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 196 countries of the world. 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 2010 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 ozone depleting substances have been decreasing for over ten years, and are expected to continue to decrease in the future (Figure 13a).

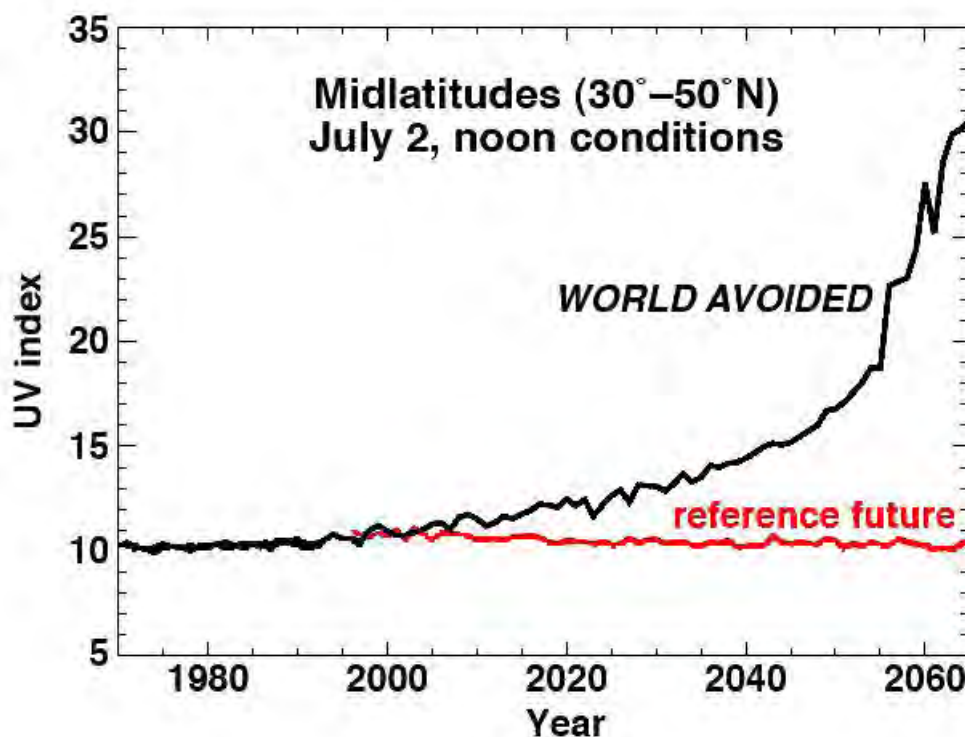


Figure 13b: Prediction of the UV Index indicating what could have happened in the absence of a Montreal Protocol from Figure 5.11 Scientific Assessment of Ozone Depletion: 2010.

http://us-cdn.creamermedia.co.za/assets/articles/attachments/29653_898_executivesummary_emb.pdf

c. Effect 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” during the time it took 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. 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 developed-country emissions of greenhouse gases.

Figure 13c shows the GWP-weighted emissions of CFC, HCFC, HFC, and CO₂ for the period 1960 – 2050 and the corresponding emissions for CFCs from 1987-2020 following a scenario in which there is no Montreal Protocol regulation. The CFC curves include all principal ODSs in the Montreal Protocol except HCFCs. The emissions of individual compounds are multiplied by their respective Global Warming Potentials (GWPs) to obtain aggregate emissions expressed as equivalent GtCO₂ yr⁻¹ (as used in the 2007 IPCC report). The colour-shaded regions show ranges of emissions of CFCs, HCFCs, HFCs, and CO₂ as indicated in the panel legends. The high and low labels identify the upper and lower limits in the global baseline scenarios. Shown for reference are emissions for the range of one of the scenarios (SRES CO₂) from the IPCC 2007 report and the 450- and 550-ppm CO₂ stabilization scenarios. The reduction of CFCs has been very beneficial in mitigating climate change due to increasing CO₂, but if the projected growth rate of the HFC replacement chemicals continues, the rate of warming due to their increase could approach that due to increasing CO₂.

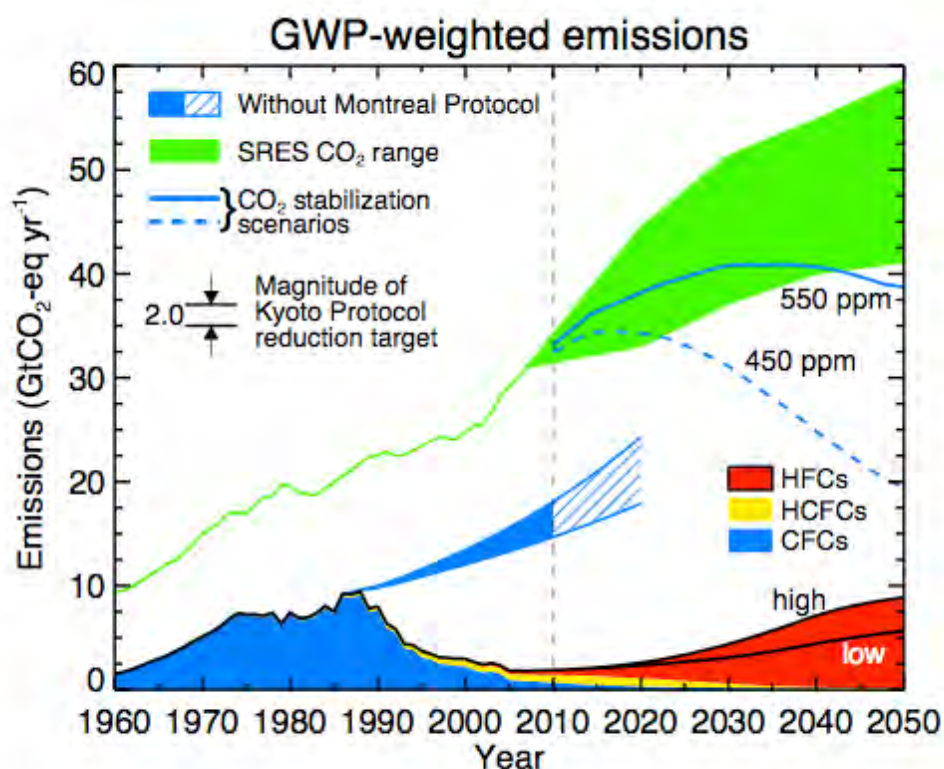


Figure 13c: Effect of the Montreal Protocol on the climate change (Figure provided by Dr Mack McFarland from Velders, et al., *Proc. Nat. Acad. Sci. USA.*, 2009, **106**, 10949-10954). Background: CO₂ -equivalence is the contribution to climate forcing from different greenhouse-gas emissions. It can be compared by scaling the emissions with the associated global warming potentials (GWPs) to form „CO₂ -equivalent“ emissions. Typically, the 100-yr GWP is used. HFC emissions in 2050 will largely offset the climate benefits already achieved by the Montreal Protocol in terms of annual emissions reductions. HFC emissions are projected to reach 5.5–8.8 GtCO₂-eq yr⁻¹ in 2050. In comparison, ODS emissions peaked at 9.4 GtCO₂-eq yr⁻¹ in 1988 and could have reached 15–18 GtCO₂-eq yr⁻¹ in 2010 in the absence of Montreal Protocol regulations.

Q14. 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.niwasience.co.nz
WOUDC	http://www.woudc.org
Environment Canada	http://www.ec.gc.ca

