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[Environmental effects of ozone depletion and its interactions with climate change: 2010 assessment](#)

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Effects of solar UV radiation and climate change on biogeochemical cycling: interactions and feedbacks

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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 1, which is based on results presented in this and previous UNEP reports.^{1,2} 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.

It is clear that many factors will lead to changes in solar UV radiation reaching Earth's surface.³ To briefly summarize, after a period of several decades when depletion of stratospheric ozone

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Table 1 Summary of selected direct and indirect effects of solar UV radiation on biogeochemical cycles, based on this and previous reports.^{1,2} Several of these direct and indirect effects may operate concurrently on the biogeochemical system

Element	Environmental compartment	Impact on biogeochemical cycling
Carbon	Terrestrial ecosystems	<ol style="list-style-type: none"> 1. Impact on plant growth, morphology and photosynthesis, and interactions between species, and community composition 2. Enhances emissions of CH₄ and CO 3. Impacts on litter composition and decomposition and organic matter decomposition
	Aquatic ecosystems	<ol style="list-style-type: none"> 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 CO₂ and CO production and microbial lability of DOM 3. Impact on spectral properties of water column
	Atmosphere	<ol style="list-style-type: none"> 1. Impact on ecosystem-atmosphere exchange of trace C gases, <i>e.g.</i> CO₂, CO, CH₄ 2. Effects on atmospheric chemistry, <i>e.g.</i> on reactions involving OH and ozone
Nitrogen	Terrestrial Ecosystems	<ol style="list-style-type: none"> 1. Effects on nitrogen fixation 2. Impacts on nitrification, N₂O 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, CH₄/CO sinks
	Aquatic ecosystems	<ol style="list-style-type: none"> 1. Impact on ammonification of dissolved organic N 2. Effects on nitrogen fixation 3. Increased hypoxia with increased nitrous oxide emissions from ocean 4. Effects on CDOM production and UV attenuation
	Atmosphere	<ol style="list-style-type: none"> 1. Impact on ecosystem-atmosphere exchange of trace N gases. 2. Effects on atmospheric chemistry, <i>e.g.</i> on reactions involving OH and ozone.
Sulfur	Terrestrial Ecosystems	<ol style="list-style-type: none"> 1. Uptake and release of DMS and COS by vegetation.

Table 1 (Contd.)

Element	Environmental compartment	Impact on biogeochemical cycling
	Aquatic ecosystems	<ol style="list-style-type: none"> 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	<ol style="list-style-type: none"> 1. Impact on ecosystem-atmosphere exchange of S gases, <i>e.g.</i> DMS, COS 2. Impact on conversion of DMS and other S compounds to aerosols/cloud condensation nuclei
Phosphorus and metals	Terrestrial ecosystems	<ol style="list-style-type: none"> 1. Perturbation of P cycling in plant rhizosphere 2. Degradation of organic matter and with resulting impacts on soil fertility.
	Aquatic ecosystems	<ol style="list-style-type: none"> 1. Effects on biological availability of metal nutrients, <i>e.g.</i> Fe, Cu, Mn, and metal pollutants, <i>e.g.</i> Hg 2. Formation of ROS by Fe reactions
	Atmosphere	<ol style="list-style-type: none"> 1. Indirect impacts on ecosystem-atmosphere exchange of trace gases <i>via</i> changes in nutrient availability
Oxygen	Terrestrial Ecosystems	<ol style="list-style-type: none"> 1. Effects on O₂ uptake during litter decomposition
	Aquatic ecosystems	<ol style="list-style-type: none"> 1. Effects on O₂ production by photosynthesis of and O₂ consumption by DOC oxidation 2. Effects on formation and degradation of H₂O₂ and other ROS, <i>e.g.</i> HO₂ and OH
	Atmosphere	<ol style="list-style-type: none"> 1. Effects on ecosystem-atmosphere exchange and chemical oxidation processes
Halogens	Terrestrial ecosystems	<ol style="list-style-type: none"> 1. Production of organohalogens
	Aquatic ecosystems	<ol style="list-style-type: none"> 1. Effects on biogenic production and consumption of organohalogens
	Atmosphere	<ol style="list-style-type: none"> 1. Decomposition of methyl halides, sea salt derived particles and CFC substitutes

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.³ 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 mean³), 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 paper 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.^{4,5} 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.² 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).⁶ The increasing concentration of CO₂ in the atmosphere is a major driver for human-induced climate change, with the most recent IPCC report⁶ estimating its RF as 1.66 ± 0.17 W m⁻², far higher than any other factor (Table 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 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 2). There is increasing evidence that aerosols and clouds

Table 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.⁶ Note that the inherent time scales of the different links vary significantly

Element of change	IPCC ⁶ estimate of radiative forcing/W m ⁻²	Links with stratospheric ozone change and changing UV radiation
Carbon dioxide (CO ₂)	+1.66 ± 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 ± 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 ¹⁶⁰
Montreal Protocol gases	+0.32 ± 0.03	Now declining due to implementation of the Montreal Protocol; see McKenzie <i>et al.</i> ³ Naturally-produced halogen compounds from terrestrial and aquatic ecosystems may be affected by climate change
Nitrous oxide (N ₂ O)	+0.16 ± 0.02	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 McKenzie <i>et al.</i> ³
Total aerosols	-0.5 ± 0.4	Affected indirectly by changing UV radiation through effects on volatile organic compounds (VOCs), dimethylsulfide (DMS) and other trace gases; see McKenzie <i>et al.</i> ³
Clouds	-0.7	Affected indirectly by changing UV radiation through effects on volatile organic compounds (VOCs), dimethylsulfide (DMS) and other trace gases; see McKenzie <i>et al.</i> ³

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.³ However, the effects of such changes in UV radiation on the components of biogeochemical cycling remain poorly understood.

Solar UV radiation may also affect the nitrogen and sulfur cycles that can directly affect climate through changes in concentrations of atmospheric trace gases such as nitrous oxide, NO_x (NO plus NO₂) and dimethylsulfide (DMS). NO_x and DMS influence atmospheric chemistry and cloud formation, and hence radiative forcing (see Table 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.³ Nitrous oxide is not only an important greenhouse gas but it also plays a dominant role in chemical reactions that deplete stratospheric ozone.⁷ 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 paper 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.^{6,8-10} Ecosystems are net CO₂ sinks on a global average but some regions are net CO₂ sinks and others net sources.¹¹⁻¹³ A recent analysis indicates that the airborne fraction has likely increased from 40% to 45% during the past 50 years¹⁰ due to reductions in terrestrial and oceanic sinks caused by climate change, stratospheric ozone depletion and other environmental changes.¹⁴⁻¹⁸ Decreasing sink strengths of terrestrial and aquatic ecosystems cause positive feedbacks that amplify the growth of atmospheric CO₂ and accelerate future climate warming.^{15,19-22} For example, fire was found to be a primary disturbance that changes terrestrial ecosystems from carbon sinks to sources.²³

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.^{2,24} 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 ozone³ 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^{2,4,25-27} 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 albedo³ 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.²⁸ The effects of these future changes in climate on the vegetation cover of specific regions remain somewhat controversial. However, for most low to mid-latitude systems, the most likely changes in plant communities, such as decline in woodland or reduced vegetation cover (Fig. 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,²⁹ felling of woodland,³⁰ and shrub invasion in arid systems.³¹ 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.³² 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. 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,^{15,23,33-37} 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

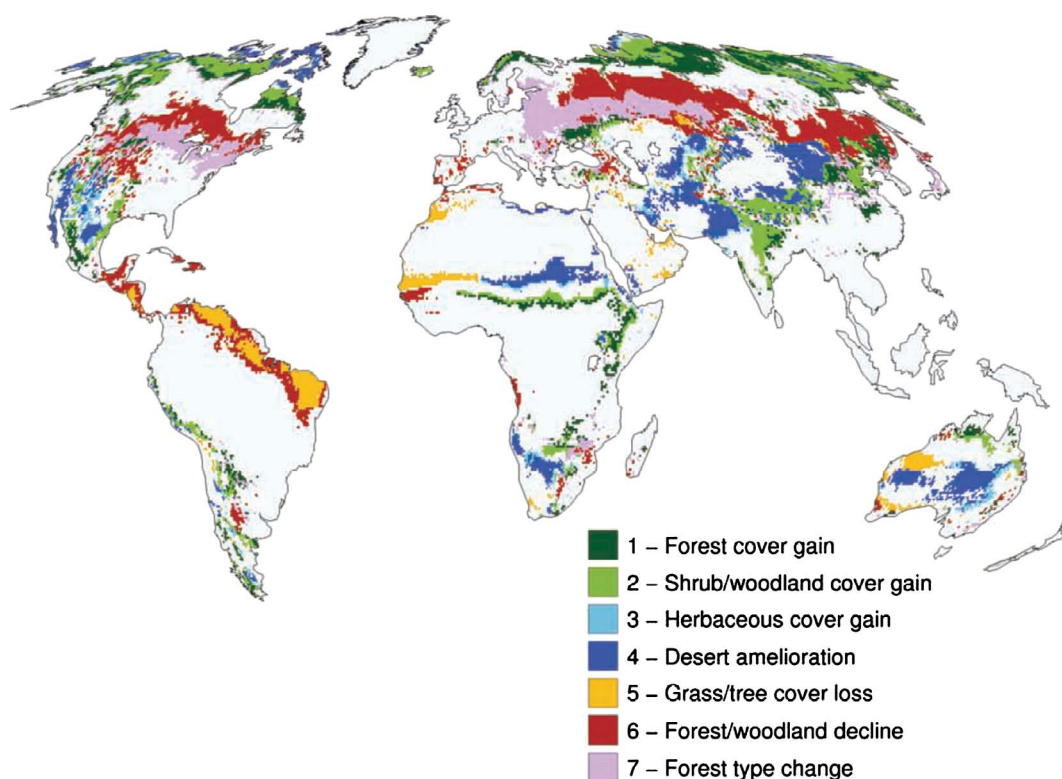


Fig. 1 Projected appreciable changes in terrestrial ecosystems by 2100 relative to 2000 as simulated by the Dynamic Global Vegetation/Lund-Potsdam-Jena Model (DGVM LPJ) for two Special Report Emission Scenarios forcing two climate models: (a) Hadley Centre Coupled Model - Version 3 (HadCM3 A2), (b) 5th 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 (Fig. 4.3 of Fischlin *et al.*²⁸).

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.³

In summary, at low to 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.⁴ 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.³⁸ The effects of exposure to UV radiation on primary producers in lakes and the ocean interact with climate-induced damage of primary producers^{16,39-45} 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).^{2,41,45,46}

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. 2). However, CDOM is subject to photobleaching,⁴⁵⁻⁶³ a process that occurs particularly efficiently in stratified systems.^{2,45,47,48,51,63} The increase in CDOM concentrations with increasing latitude (Fig. 3) is consistent with decreased rates of photobleaching as surface UV irradiance decreases.^{47,63} 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.⁶³ 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.⁶³

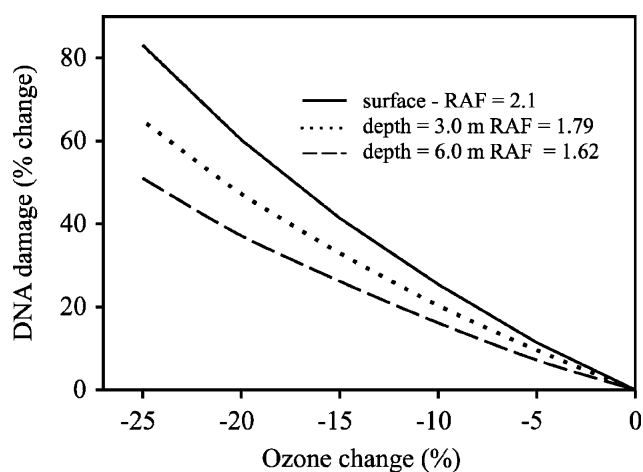


Fig. 2 Computed dependence of DNA damage and the associated radiation amplification factors on depletion of total ozone at different depths at Looe Key Reef in Florida, USA.⁴⁵ The action spectrum of Setlow²³⁷ was used in the computation of DNA damage. Dose and radiation amplification factor (RAF) are defined in McKenzie *et al.*³ 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.*⁴⁵ Copyright (2008) by the American Society of Limnology and Oceanography, Inc., reproduced with permission.]

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.¹¹ 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.⁶⁴ Vertical stratification of the ocean, which is accompanied by increases in sea surface temperature (SST), results in decreased net primary productivity (Fig. 4).⁶⁴ The vertical stratification of marine systems is caused by various factors including SST.⁶⁵⁻⁶⁷ For example, the seasonal stratification in a small marine basin is primarily determined by temperature,⁶⁷ 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

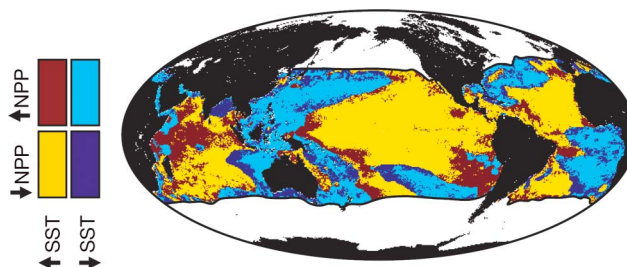


Fig. 4 Relationships between changes in sea surface temperatures (SST) and net primary productivity (NPP) in the ocean for the warming period from 1999 to 2004. Yellow: increase in SST, decrease in NPP. Light blue: decrease in SST, increase in NPP. Dark blue: decreases in SST and NPP. Dark red: increases in SST and NPP. [Adapted from Fig. 3(c) in Behrenfeld *et al.*, 2006;⁶⁴ copyright 2010 by Nature Publishing Group, license no. 2531680927098, reproduced with permission.]

Furthermore, ocean stratification has been reported to increase with climate-related increasing strength of El Niño-Southern Ocean Oscillation (ENSO) cycles.⁶⁴ 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.⁶⁶ Increased stratification and sea surface temperatures likely will move poleward in the temperate regions

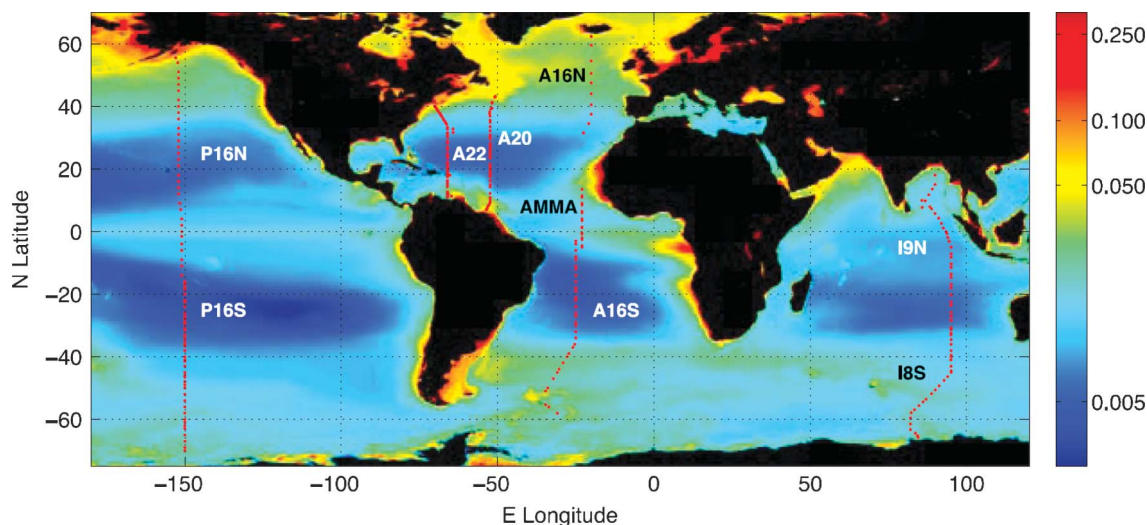


Fig. 3 Distribution of CDOM absorption coefficients at 443 nm from satellite ocean colour observations derived from Global System for Mobile Communications (GSM) satellite retrieval of merged SeaWiFS and MODIS Aquadata.^{47,63} Field observations collected on meridional transects showed that UV absorption 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.*⁶³]

during the upcoming century, with resulting decreases in marine productivity and oxygen concentrations^{11,64,68} and concurrent adverse effects on life in the ocean.⁶⁸ 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 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.^{5,45,46,69}

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.¹

The detrimental effects of UV-B exposure on marine organisms might be partially offset by CO₂ fertilization effects³⁷ and ocean warming,⁷⁰ although increasing CO₂ concentration has been shown to enhance the sensitivity of some algal species to UV-B radiation.^{39,44} 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^{6,71,72} and to a smaller extent by atmospheric deposition of acidity⁷¹ and increased vertical stratification⁶⁸) also attenuates oceanic CO₂ uptake by reducing the ability of calcifying marine organisms, including corals, to produce calcareous skeletal structures.^{68,73–78} 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,^{78–81} and the adverse effects of solar UV radiation on corals are related to their increased susceptibility to UV damage with warming.⁸² These changes combine to decrease the CO₂ buffer capacity of marine systems.^{18,72,74,83–85} 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.⁸⁶ 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.³⁸

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.^{11,16,21,87,88} 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).^{16,87} As a consequence, enhanced wind-driven ventilation of carbon-rich deepwater occurs in this region

resulting in a reduced atmosphere-ocean gradient of CO₂.^{11,16,87} In addition to this effect, inhibition of photosynthesis caused by enhanced solar UV-B radiation associated with stratospheric ozone depletion³ also contributes to reduced CO₂ uptake in this region.⁴⁰ 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.^{11,16,87}

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 extremes,⁸⁹ as well as land-use changes,¹⁰ are likely to increase the input of organic carbon into streams, rivers and lakes (Fig. 5).^{90–96} 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 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.^{96–99} 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). 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.

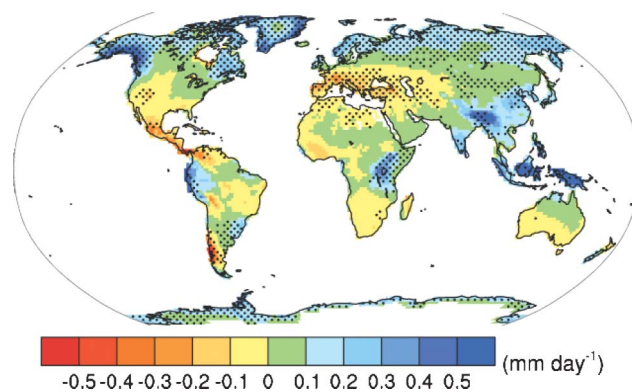


Fig. 5 Multi-model mean changes in runoff (mm per day) for the IPCC Special Report Emission Scenarios A1B (balanced) for the period 2080 to 2099 relative to 1980 to 1999 (see <http://www.ipcc.ch/pdf/special-reports/spm/sres-en.pdf>). Changes are annual means for this scenario. Runoff changes are shown at land points with valid data from at least 10 models [Fig. 10.12(c) in Meehl *et al.*²³⁸].

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.^{49,55–57,59,100–106} Photochemically reactive DOM is subject to UV-induced transformations^{58,61,92,102,107} that enhance DOM bioavailability to heterotrophic bacteria^{58,61,92,96,102} and, in turn, microbial respiration with production of CO₂ and consumption of O₂.^{61,99} Mineralization of DOM also occurs as a purely abiotic, UV-induced process.^{55,56,59,107–111} Photoreactions driven by solar UV

radiation also release DOM from sediments.^{112,113} The rate of UV-induced DOM transformations and mineralization is likely to increase as a consequence of enhanced stratification and acidification of aquatic systems.^{2,45,48,51,107}

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.¹¹⁴ 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.¹¹⁵

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.² 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),^{2,116,117} 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,¹¹⁸ and more generally from nitrogenous air pollutants. However, interactions between these changing nitrogen inputs and changing solar UV radiation remain poorly understood.⁴

A substantial part of the ocean (67%–75%) has been estimated to be limited by nitrogen,¹¹⁹ particularly by nitrate (NO₃⁻).¹¹⁴ 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.^{67,68,120} As a result, the ability of phytoplankton to take up N₂ may become increasingly important.^{121,122} Nitrogen fixation in the ocean is inhibited by exposure to UV radiation through damage to N₂-fixing organisms.⁴¹ 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.^{118,119}

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.¹¹⁵ Precipitation^{123–125} and deposition of continental dust³⁸ 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.¹²⁶ 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^{127,128} and of dissolved Fe(III) species.^{125,129–131} 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.⁷² 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.⁵ 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^{132,133} or no N immobilization in semi-arid ecosystems independent of direct UV effects.^{134,135} 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.¹³⁶

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.^{2,137} 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. 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.³² 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^{2,25} 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.⁴ Fires, leaching and runoff are other important pathways for nutrient loss from terrestrial ecosystems that are affected by climate change.²³

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 sulfur compounds (Tables 1–2). 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 (CH_4) produces the second highest radiative forcing after CO_2 (Table 2).⁶ As with CO_2 , the atmospheric concentration of methane in recent decades has been the highest ever¹³⁸ and these increases can be attributed to a number of human activities.⁶ However, unlike the continuing, well-defined and well-understood increase in CO_2 , 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.^{139–141} 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.¹⁴²

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.¹⁴³ However, the observation of Keppler and colleagues¹⁴² 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,^{144–150} partly because not all studies have been able to detect aerobic methane production under laboratory conditions.^{124,151} However, there is now good evidence that this is a photochemical process brought about by previously undefined chemical reactions occurring in plant cell walls.^{150,152,153} 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.^{154–156} Calculations to scale-up from 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,¹⁴² the current balance of evidence suggests a rather minor contribution compared with other sources.^{148,157,158} 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. 6).¹⁵⁸ This conclusion was based on modeled estimates that used an action spectrum for photoproduction of methane from pectin,¹⁵⁹ a common component of plant leaves. We agree with the recent review¹⁵⁷ 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.

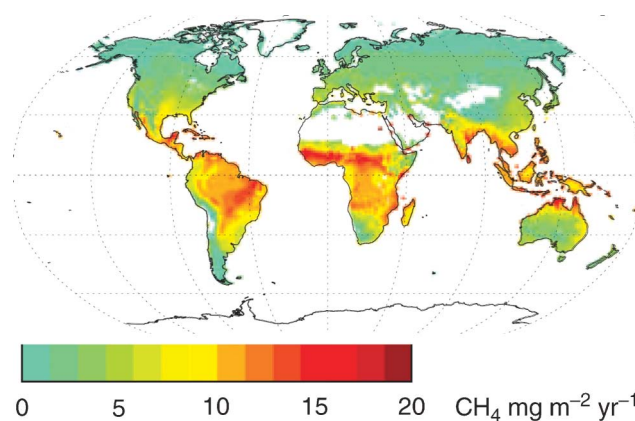


Fig. 6 Estimated total annual aerobic methane production induced by solar UV irradiation of plant foliage (adopted from Bloom *et al.*¹⁵⁸). The action spectrum for methane production used for this modelling simulation was obtained from McLeod *et al.*¹⁵⁹ The global distribution for methane production 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. [Copyright 2010 by John Wiley and Sons, Inc.; license no. 2523120844682, reproduced with permission.]

Carbon monoxide

The carbon monoxide (CO) concentration in the troposphere has important effects on atmospheric composition through its effects on hydroxyl radical ($\cdot\text{OH}$) concentration.¹⁶⁰ CO makes a small direct contribution to radiative forcing (Table 2) but calculations taking into account its interactions with aerosols result in substantial increases in its estimated role in radiative forcing.¹⁶¹ Natural sources have been estimated to account for up to half of global CO emissions,⁶ and of these, wildfires, especially their smoldering phase, are an important source that is increasing with climate change. Carbon monoxide is one of the main trace gases that is 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.³ A number of recent

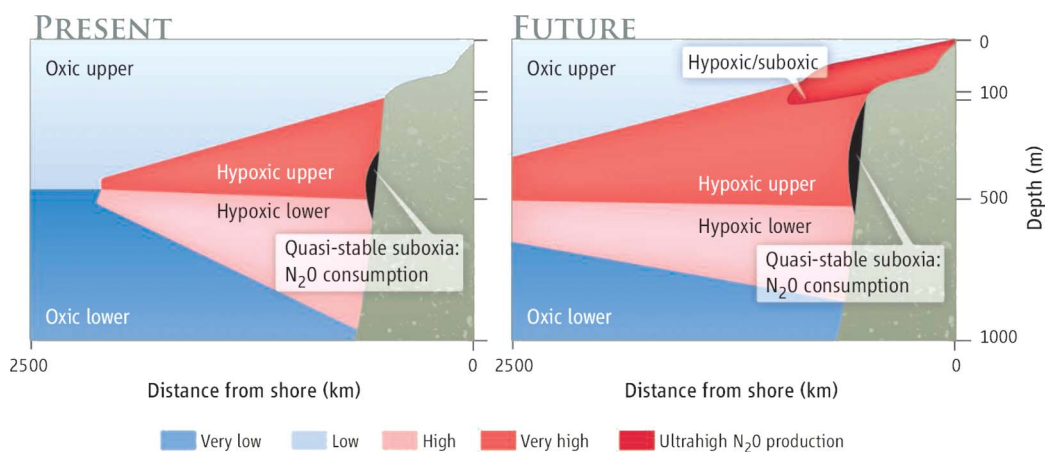


Fig. 7 Conceptualization of future changes in hypoxic regions of the ocean that may lead to enhanced nitrous oxide emissions to the atmosphere, especially from coastal regions. Climate changes are forecasted to increase hypoxia in the upper layers of the coastal ocean. The resulting oxygen-depleted waters have favourable conditions for high production of nitrous oxide. From L. A. Codispoti, Interesting times for marine N_2O , *Science*, 2010, **327**, 1339–1340.¹⁷⁴ Reproduced with permission from AAAS.

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 .^{110,162} Several recent studies have indicated that CO photoproduction in the ocean is approximately balanced by microbial consumption,^{111,163–166} although microbial uptake is somewhat less important in northern waters¹⁶⁶ and can be photoinhibited during daytime.¹⁶⁷ 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.²

Nitrogen compounds

Ecosystem-atmosphere exchange of reactive nitrogen (ammonium and nitrogen oxide gases) is influenced by UV-B radiation and climate change.^{2,24,168} A number of human activities introduce reactive nitrogen into ecosystems¹¹⁸ and direct uptake by terrestrial vegetation is one important sink for these compounds.¹⁶⁹ 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.¹⁷⁰ 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.¹⁷¹

Nitrous oxide (N_2O) is an important greenhouse and ozone-depleting gas (Table 2) and its atmospheric concentration is rising. The bulk of emissions come from natural sources and the remainder from human activities, especially agricultural practices.¹⁷² Nitrous oxide and other greenhouse gases could be an unintended by-product of the agricultural production of biofuels.^{154,173} 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.¹¹⁹ 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. 7).¹⁷⁴ 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.⁷ 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),¹⁷⁵ while temperate woodland ecosystems are a net source of CH_3Br .¹⁷⁶ The Arctic tundra is a regional sink for both CH_3Br and CH_3Cl .¹⁷⁷ Coastal vegetation may be net sources of methyl halides,^{178–181} or net sinks.^{182,183} Even within individual ecosystems, methyl halide fluxes vary depending, for example, on weather, the extent of flooding, and the removal of vegetation.^{178–180,182,183} Soil fungi have been confirmed as potential sources of methyl halides.¹⁸⁴ Climate change may affect halocarbon budgets from terrestrial systems through warming and decreasing soil moisture.^{177,185} 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.^{186–189}

Marine ecosystems, particularly tropical oceanic regions, are also important sources of halogen compounds, above all bromoform (CHBr_3), that are released from phytoplankton.^{190–193} 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,¹⁹¹ 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 change¹⁹⁴ and possibly to UV-induced photoreactions involving chloride and CDOM.¹⁹⁵ Increased stratification may reduce outgassing of bromoform by limiting mixing between the surface and the subsurface layer where maximum concentrations are located.¹⁹⁶ 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 DMS¹⁹⁰ 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.^{161,197} 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 alter 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.³

Changes in UV radiation may affect phytoplankton emissions of sulfur compounds and hydrocarbons that form aerosols that, in turn, affect clouds over the ocean. DMS is the major source of volatile sulfur to the marine atmosphere. UV-B radiation plays a major role in the cycling of DMS and related compounds both in polar¹⁹⁸ and temperate oceans.¹⁹⁹ 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.²⁰⁰ Melting sea ice can release substantial quantities of DMS, leading to elevated concentration of DMS in seawater,²⁰¹ 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.^{202,203} On the other hand, UV exposure can reduce nitrogen limitation in surface waters,^{137,204} and this process may decrease algal DMS production. Furthermore, photolysis of DMS is an important sink of DMS in the upper ocean.^{2,205}

Volatile organic compounds (VOCs) produced by terrestrial plants can contribute to aerosol production.^{206,207} The effects of UV-B radiation on these emissions appear to vary between different types of plant VOC,^{208–210} 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.²¹¹

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.¹⁶⁰ In addition, the future projected changes in solar UV radiation³ 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.²¹² 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.²¹³ BrO and Br produced by UV-induced chemistry (see above under 'Halogen compounds') rapidly remove GEM from the atmosphere by oxidizing it.²¹⁴ Mercury isotopic composition in the Arctic is strongly influenced by sunlight-induced photoreactions of mercury in the snow.²¹⁵ In aquatic systems the oxidation of dissolved gaseous mercury (DGM) to divalent mercury (Hg(II)) is induced by solar UV radiation.^{216–220} 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.^{221,222} Fish and other seafood are important sources of mercury in the human diet.²²³ Overall, rates of bioaccumulation and transfer through the aquatic food web are susceptible to ecological, biogeochemical and climatic influences.²²⁴ 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 Cu^{2+} .²²⁵ 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.^{225–227} 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.²²⁸ The environmental fate of these organic pollutants depends on many factors,²²⁸ and will be subject to the effects of various elements

Table 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 McKenzie *et al.*³ 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 than 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 and in more detail in the text of the paper

Change	Expected direction(s) of change, 2010–2100	Effect of change on UV radiation reaching surface	Relative magnitude of effect on UV irradiance	Area affected	Relative magnitude of effect of interaction on global biogeochemical cycling
Terrestrial					
Stratospheric ozone	Increase ²³⁵	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) ²³⁵	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 ²³⁵	Increase	Small to medium	Regional	Small
Latitudinal change in location of ecosystems in response to climate change	Shift poleward ²⁸	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 cover due to climate change	Increase or decrease ²⁸	Decrease or increase	Little effect of increased cover, but decreases will increase penetration to the surface	Global, but marked regional variation.	Net effect remains hard to determine due to geographical variation in changes
Changes to ice and snow cover due to climate change	Decrease ²³⁶	Decreased albedo leading to decreased UV exposure to above-ground organisms	Large	Local to poles	Large
Oceans and lakes					
Stratospheric ozone	Increase ²³⁵	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 (including tropics) ²³⁵	Decrease overall, but marked variation, including increases in some places (including tropics)	Large	Global, but with marked regional variation	Increased primary productivity at the poles, especially in Southern Hemisphere
Atmospheric aerosols	Increase/decrease ²³⁵	Decrease/increase	Small	Regional-global	Small

Table 3 (Contd.)

Change	Expected direction(s) of change, 2010–2100	Effect of change on UV radiation reaching surface	Relative magnitude of effect on UV irradiance	Area affected	Relative magnitude of effect of interaction on global biogeochemical cycling
Oceans and lakes					
Input of coloured dissolved organic matter	Increased ^{90–96}	Decreased	Largest effect in circumpolar N. Hemisphere	Local (coastal)	Increased conversion of terrestrial organic carbon to CO ₂
Stratification	Increases ^{64–66}	Increases	Large in tropics, growing in mid-latitudes	Affects both ocean and freshwater lakes	Significant decrease in productivity in the mid-latitudes
Changes to ice cover due to climate change	Decrease ²³⁶	Increase	Large	Local to poles	Large
Water availability and quality	Increasing at high latitudes; decreasing at low latitudes; changed availability from alpine snowmelt	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 <i>via</i> pollutant photodegradation; increased long range transport of pollutants

of climate change.²²⁹ UV radiation also affects the environmental chemistry of organic pollutants such as pesticides, accelerating the rate of degradation in water, ice and snow,^{230–232} both through direct and indirect photodegradation mediated by reactive oxygen species.²³³ 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 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.^{11,15,16,19–21,37,87,234} 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>).²⁸

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