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# Effects of stratospheric ozone depletion, solar UV radiation, and climate change on biogeochemical cycling: interactions and feedbacks

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Climate change modulates the effects of solar UV radiation on biogeochemical cycles in terrestrial and aquatic ecosystems, particularly for carbon cycling, resulting in UV-mediated positive or negative feedbacks on climate. Possible positive feedbacks discussed in this assessment include: (i) enhanced UV-induced mineralisation of above ground litter due to aridification; (ii) enhanced UV-induced mineralisation of photoreactive dissolved organic matter (DOM) in aquatic ecosystems due to changes in continental runoff and ice melting; (iii) reduced efficiency of the biological pump due to UV-induced bleaching of coloured dissolved organic matter (CDOM) in stratified aquatic ecosystems, where CDOM protects phytoplankton from the damaging solar UV-B radiation. Mineralisation of organic matter results in the production and release of $CO_2$, whereas the biological pump is the main biological process for $CO_2$ removal by aquatic ecosystems. This paper also assesses the interactive effects of solar UV radiation and climate change on the biogeochemical cycling of aerosols and trace gases other than $CO_2$, as well as of chemical and biological contaminants. Interacting effects of solar UV radiation and climate change on biogeochemical cycles are particularly pronounced at terrestrial-aquatic interfaces.

## Introduction

The Montreal protocol has been successful in phasing out ozone-depleting CFCs and, as a consequence, stratospheric ozone concentrations are recovering at low and mid-latitudes[1,2] (see Bais *et al.*[3]). However, springtime ozone depletion is expected to continue at polar latitudes for many decades,[4,5] largely due to climate change. A major consequence of stratospheric ozone change is altered intensity of solar UV-B radiation which in turn affects the biogeochemical cycling of carbon and other chemical elements. Terrestrial and aquatic biogeochemical cycles are discussed here in the context of their possible interactions with UV radiation and climate change (Fig. 1).

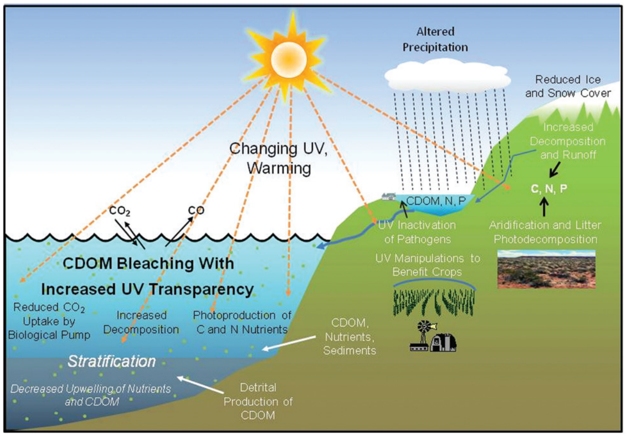

**Fig. 1** Conceptual model of aquatic and terrestrial processes that are possibly influenced by interactions between UV radiation and climate change. Recent findings on these interactions are discussed in more detail in this assessment. Reprinted from Williamson *et al.*,[250] with permission from Macmillan Publishers Ltd: Nature Climate Change, copyright 2014.

The intensity of solar UV radiation reaching the Earth's surface is also controlled by climate-related variables such as cloud cover and aerosols. In addition, the penetration of UV-B radiation into water bodies largely depends on the concentration and the optical properties of chromophoric dissolved

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organic matter (referred to as coloured dissolved organic matter, CDOM, hereafter). Climate-change related effects on terrestrial and aquatic ecosystems, *e.g.* desertification, ocean acidification and stratification, as well as land use change interact in various ways with solar UV radiation, resulting in UV-mediated feedbacks on climate. Feedbacks, combined effects and interactions of solar UV radiation and climate change on biogeochemical cycles are discussed and assessed, and gaps in knowledge identified.

## Interactive effects of stratospheric ozone depletion and climate change on terrestrial and aquatic ecosystems

We include a section that summarises some important issues of climate change, since climate change modulates the effects of solar UV radiation of biogeochemical cycles. Climate change also affects the stratospheric ozone concentration and thus the intensity of solar UV radiation reaching the Earth's surface.

### Climate change and polar stratospheric ozone depletion

Some chemistry-climate models and observations predict that an ozone 'hole' may still be present in the Antarctic spring in 2100.[4] A large loss of stratospheric ozone, comparable to that in the Antarctic ozone 'hole', was also observed over the Arctic in spring 2011[5] due, in part, to the extremely cold stratospheric Arctic winter 2010/2011.[6] In spring 2011 increased levels of solar UV radiation were observed at Arctic and sub-Arctic ground stations.[7] The Arctic stratosphere is particularly affected by radiative cooling due to Arctic amplification (enhanced warming in high northern latitudes relative to the northern hemisphere).[8] There are several reasons for the fast response of the Arctic to global warming, including increased advection of water from the Atlantic to the Arctic,[9,10] and reduced albedo due to sea ice melting and vegetation shifts.[11] Hence, increasing attention is being paid to Arctic tipping points.[12] The term "tipping point" is used for systems (*e.g.* Arctic ecosystems), where a small change in forcing could potentially cause a large change in future ecosystems.

Further detail on climate change and polar stratospheric ozone depletion is given in Bais *et al.*[3]

### Ice melting: effects on local climates

Global warming has dramatically enhanced melting of glaciers, ice caps, and sea ice in both hemispheres, with the largest present rates of melting in the Northern Hemisphere.[13–15] The Arctic sea ice, whose extent usually reaches a minimum each year in September, is particularly affected[13,15] (Fig. 2) (also see Fig. 1 in Häder *et al.*[16]). Melting of Greenland and Antarctic sea ice is mainly due to warmer ocean temperatures.[17] Increasing meltwater ponds on the surface of polar ice reduce albedo and allow more solar radiation, both UV and photosynthetically active radiation (PAR), to enter the water column through the ice[18] (see Bais *et al.*[3]). Screen and Simmonds (2010)[8] suggest that positive ice-temperature feedbacks occur in the Arctic due to increases in atmospheric water vapour content that enhances warming in the lower part of the atmosphere, especially in high northern latitudes. Sea ice melting at high latitudes could also be due to the transformation of solar UV-B radiation into heat by planktonic microorganisms in a cyclic reaction consisting of photooxidation of water at 300 nm that yields $H_2O_2$ with subsequent decomposition of $H_2O_2$ by catalase.[19]

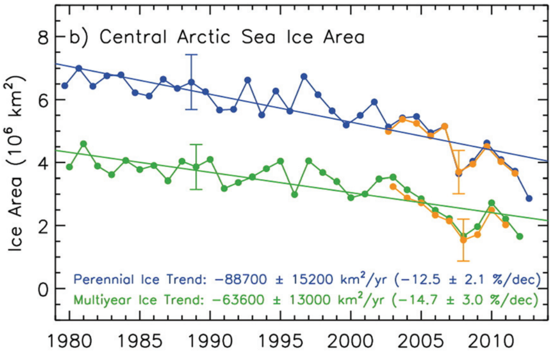

**Fig. 2** Arctic sea ice loss from 1979 to 2012 as derived from satellite passive microwave data. The yellow lines (after 2002) are from AMSR-E data. (Panel (b) of Fig. 4.4 in Chapter 4 "Observations: Cryosphere" of the IPCC Report 2013, Working Group I: Climate Change 2013: the Physical Science Basis).[13]

The decline in Arctic sea ice affects local climates, particularly in North America, Europe, and East Asia with large impacts on biogeochemical cycles. For example, changes in rates of primary production and respiration in terrestrial and aquatic ecosystems may occur as a consequence of droughts and enhanced runoff of terrestrially derived organic carbon, respectively (see below). These effects on local climates can be summarised as follows: the melting of Arctic sea ice results in increased air temperatures due to evaporation and condensation of surface water, changes in the turbulent heat fluxes and, as a consequence, in increased geopotential height over the Arctic.[20] As a result, the jet stream is transformed into Rossby waves that are characterised by cold air moving to the north and warm air moving to the south.[21,22] The higher the amplitude of Rossby waves, the slower they move from west to east, resulting in more frequent episodes of blocking of weather patterns and therefore in longer lasting extreme weather events such as droughts, flooding, cold spells, and heat.[21–25]

Further impacts of land and sea ice melting are sea level rise,[13] increases in freshwater input and hence changes in ocean circulation, reduced surface albedo[26] (see Bais *et al.*[3]), and enhanced exposure of organisms in aquatic ecosystems and on land surfaces such as tundra to solar UV radiation (this assessment and Häder *et al.*[16]). Over the period 1901–2010, global mean sea level rose by 0.19 (0.17 to 0.21) m and the IPCC WGI Report 2013 (summary for policymakers)[13] states with *high confidence* that the "rate of sea level rise since the mid-19th century has been larger than the mean rate during the previous two millennia".

### Interacting effects of stratospheric ozone depletion and climate change on ecosystems

The interplay between stratospheric ozone depletion and climate change affects atmospheric circulation, the speed and direction of winds, and, as a consequence, ocean mixing. There is a global trend of increasing values of surface and higher level wind speed, linked, in part, to stratospheric ozone depletion.[27–29] Causes of this phenomenon have been reported more than ten years ago in a key paper by Gillet and Thompson (2003).[30] Based on both observations and modeling results, these investigators found falling geopotential heights at constant pressure (500 hPa) at high southern latitudes from 1979–2000 due to Antarctic stratospheric ozone depletion and thus decreasing temperatures. Concomitantly, 500 hPa heights were rising in the middle southern latitudes, due to increasing greenhouse gas concentrations and thus increasing temperatures. This interplay between Antarctic stratospheric ozone depletion and climate change results in an upward trend of the Southern Annular Mode (SAM).[28,31,32] Positive SAM indices result in mean high values of the westerly polar vortexes and a poleward shift of the westerly wind belts at the Earth's surface.[27,33] As a consequence, net uptake of carbon dioxide in the Southern Ocean, believed to be a major sink for atmospheric $CO_2$,[34,35] may be reduced by enhanced wind-driven upwelling of carbon-rich deepwater.[36,37] Paleo-oceanographic studies suggest that a Southern Ocean $CO_2$ ventilation event might have caused glacial-interglacial changes in the atmospheric $CO_2$ concentration.[38–41] Changes in atmospheric and ocean circulation due to the combined effects of Antarctic stratospheric ozone depletion and climate change alter Southern Hemisphere weather. These alterations potentially include increased incidence of extreme events, floods, droughts, and wildfires.[42]

### Ocean warming, stratification, acidification, and deoxygenation

Global warming results in increased sea-surface temperatures (SST) and, in turn, in thermal stratification. Another effect of increasing SST is ocean deoxygenation as a consequence of reduced oxygen solubility. Furthermore, increasing $CO_2$ concentrations result in ocean acidification.[34] Ocean acidification lowers the saturation state of calcite and aragonite (Fig. 3) and thus the ability of calcifiers such as coccolithophores and corals to produce and maintain their shells of calcite and aragonite.[34,43]

Framework building corals are also sensitive to ocean warming because of the breakdown of the symbiosis with symbiotic algae (zooxanthellae), resulting in coral bleaching.[34,44–47] Algae that no longer live in symbiosis with corals are less protected from solar UV-B radiation. Furthermore, iron stress of zooxanthellae has been shown to reduce their photosynthetic efficiency and to alter the pigment composition at elevated temperatures.[48] The combined effects of increasing SST, ocean acidification and stratification, and solar UV radiation on marine ecosystems are likely to reduce the rate of primary production by phytoplankton (see below). Based on a Biogeochemical Elemental Cycling model, Laufkoetter *et al.* (2013)[49] reported a decrease in global net primary production of phytoplankton with increasing SST from 1960–2006. An excellent review article on these topics has been published by Gruber (2011).[34]

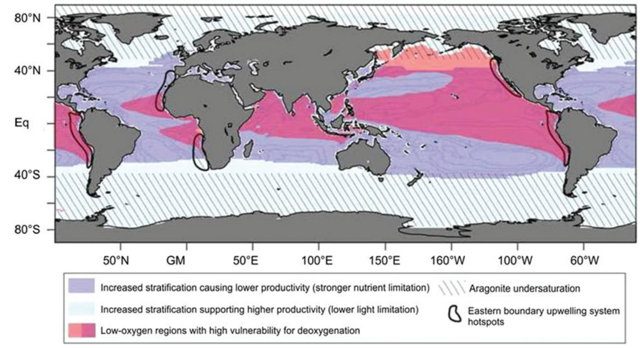

**Fig. 3** Global map showing oceanic regions of particular vulnerability to climate-change effects (see legend above). Reprinted from Gruber, 2011[34] with permission from The Royal Society: Philosophical Transactions A, copyright 2011.

### Changes in hydroclimatic conditions and continental runoff

The interplay between global warming and stratospheric ozone depletion affects precipitation patterns in space and time and enhances the intensity of precipitation extremes.[33,50–53] Cooling of the Antarctic stratosphere due to ozone depletion causes circulation cells to shift polewards, resulting in wetter conditions in the southern subtropics in the austral summer and drier conditions around 40° S.[33,51] On the other hand, strong El Niño/Southern Oscillation (ENSO) events, potentially due to global warming, cause the South Pacific convergence zone to shift towards the Equator with concomitant changes in hydroclimatic conditions resulting in more frequent weather events such as droughts, floods, and tropical cyclones.[54] In the Northern Hemisphere, the intensity of heavy precipitation events has increased over much of the land area due to warming.[52,55,56] Changes in hydroclimatic conditions may result in an enhanced input of terrestrial organic matter into aquatic systems[57–60] with consequences for the rate of UV-induced mineralisation of organic carbon (see below).

Changes in continental runoff of CDOM have consequences for the transmission of solar UV radiation into water bodies and thus for the protection of phytoplankton against the damaging UV-B radiation (see below). Remote sensing studies have provided new information on the extent of CDOM runoff and its impact on the penetration depth of UV radiation in the biologically-rich waters and coral reefs of South Florida (Fig. 4; Barnes *et al.* 2014[61]).

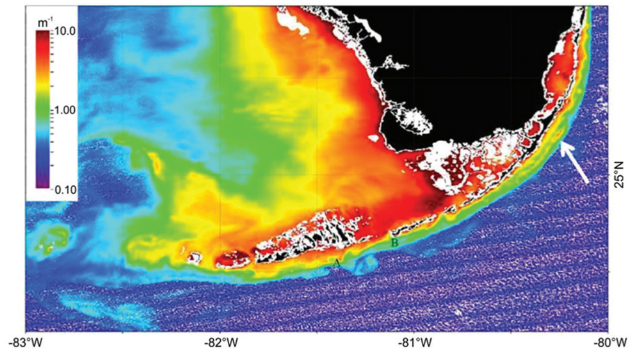

**Fig. 4** Image showing UV attenuation caused by runoff of colored dissolved organic matter in coastal regions of South Florida. Results were derived from satellite measurements (MODIS/A) on 9 January 2009 using a model described by Barnes *et al.*[61] Land is masked in black. White indicates coastline, clouds or algorithm failure. Figure modified from Barnes *et al.*[61].

## Vegetation shifts, droughts, fires, and tipping points

Climate related changes in the spatial distribution and regional intensities of precipitation and temperatures extremes, among other variables, drive vegetation shifts, droughts and the occurrence and extent of fires. This results in changes in the biogeochemical cycles that are initiated by UV interactions with the terrestrial biosphere and fire-scarred continental surfaces. Solar UV radiation also impacts the oxidative state of the atmosphere, in both the gas and aerosol phases, further influencing greenhouse gases concentrations and budgets.[62] This section seeks to provide heuristic linkages between climate related drivers such as wild fires, droughts and how UV fluxes, and changes and trends in UV fluxes, interact may push terrestrial ecosystems up to and over tipping points in ecosystem health.

Intensification of agriculture and the evolution of natural landscapes and ecosystems to managed ecosystems have increased rapidly over the past 50 years.[11,63,64] Changes in plant species also occur in regions that are undergoing large climate-related ecosystem shifts.[65] Climate-related changes in some of the Earth's largest terrestrial ecosystems are being detected.[66,67] Droughts, for example, are reducing terrestrial primary production and are increasing in many regions of the Earth.[68–71] UV radiation interacts extensively with the biogeochemical cycles that are shifting with changing land surface characteristics. The interactions of vegetation with the changing UV fluxes result in altered trace gas emission to the atmosphere including volatile organic carbon compounds (VOCs) (see below and Bornman *et al.*[72]). These UV-induced trace gas emissions include both direct emission of VOCs from plants, thought to be weakly sensitive to changes in UV radiation, and UV interactions with burned and/or modified litter. It is, however, difficult to separate changes in ecosystems due to ecosystem maturation and those due to climate change.[73]

As ozone, aerosols and trace gases change and evolve in the atmosphere, the UV radiation at the surface changes, as well as the characteristics of the surface itself.[74] UV radiation-mediated release of trace gases and aerosols from the terrestrial biosphere then changes as a result of the altered make-up of the land surface. Fires have emerged as an important component of such land surface change.[75,76] Not only do fires input massive amounts of chemicals and aerosols to the atmosphere, altering atmospheric UV radiation and chemistry, but they also leave charred substrate behind. Charcoal can persist for long periods in terrestrial systems. As a result, increasing amounts of black carbon, an important constituent of charred substrate, are entering rivers and flowing into lakes and the ocean where photochemical transformations are important sinks.[77–80] The intent of this section is to highlight and draw attention to the often ignored interactions between UV radiation, atmospheric chemistry and surface land characteristics that are dependent on the extant ecosystems. The way in which these interacting systems are changing at the same time, often at different rates, is also addressed.

Terrestrial biosphere tipping points occur due to the complex interactions between UV radiation, drought-induced aerosol distributions, anthropogenic pollution and column ozone depletion over specific areas.[7,81] UV radiation changes could represent the final source of variability that pushes/pulls the terrestrial biosphere over tipping points with large impacts on global biogeochemical cycles. Even with the general success of the Montreal protocol, there are still large areas with high UV radiation reaching the Earth's surface due to column ozone depletion.[7] Tipping points in biogeochemical cycles may be traversed by strong gradients in surface UV radiation. Biogeochemical cycles are occurring over large regions of similar ecosystem make-up and experience large differences in UV flux due to atmospheric chemistry and physical climate variables such as clouds. As in the purely physical climate system, extreme events often have a greater impact on biogeochemical cycles than a change in the mean state.[82,83] There are direct feedbacks where the processes of afforestation lead to changes in the general circulation of the atmosphere resulting in changes in precipitation.[84] Extreme events, physical climate system shifts, fires and droughts all may contribute to UV initiation of tipping points in both terrestrial and aquatic biogeochemical cycles. For example, extensive increases in melting snow and ice cover lead to increases in the exposure of aquatic ecosystems to UV and PAR,[18] which have the potential to create tipping points – shifts in photosynthetic *vs.* heterotrophic organisms where community as well as ecosystem structure and function are fundamentally altered.[85]

As ecosystems change due to climate change, fire and droughts, the chemicals released (*i.e.* hydrocarbon, $CO_2$, $CH_4$, aerosols) alter atmospheric chemistry. These biogeochemical changes have, in turn, implications for the residence times of greenhouse gases that are modulated by UV photochemistry. These interactions and biogeochemical cycling aspects of the Earth system often fall outside of traditional boundaries of scientific specialization and are only now becoming more fully appreciated.

## Interactive effects of solar UV radiation and climate change on the carbon cycle

### Carbon exchange between ocean and atmosphere

Air-sea $CO_2$ fluxes vary locally and seasonally and depend on the partial pressure of $CO_2$ and, in turn, on ocean temperature, mixing, and biology.[86,87] The main biological process that controls the uptake of $CO_2$ by the ocean is the so-called biological pump ($CO_2$ binding in photosynthesis by phytoplankton and export of dead particulate organic matter to the ocean sediment) (Fig. 5).

Rates of primary production depend on various factors including light and nutrient availability, temperature, and the species composition of phytoplankton. Also phytoplankton performance is important for efficient $CO_2$ uptake and may be negatively affected by solar UV-B radiation.[88,89] Evidence has continued to mount that the concentration of CDOM controls the penetration of UV and short-wavelength visible radiation into lakes and the coastal ocean.[61,88–91] CDOM effectively protects aquatic ecosystems from harmful UV-B radiation while permitting PAR to be transmitted into the water column. The degradation of CDOM by photochemical and biological processes leads to a loss of colour and reduced UV absorbance, both in the UV-B and UV-A regions.[92–98] As a consequence of CDOM photobleaching, the penetration depths of solar UV radiation into water bodies increase, thereby increasing the exposure of phytoplankton to damaging solar UV-B radiation (see also Häder *et al.*[16]). CDOM photobleaching is particularly evident in thermally stratified waters bodies.[95,98,99] Stratification results in a shallower mixing depth, which in addition leads to a greater exposure of phytoplankton to UV-B radiation.[100] Enhanced stratification, due to increasing sea surface temperatures, occurs mainly in low latitude marine environments where it also hinders the transport of nutrients to the euphotic zone from deeper water layers and hence negatively affects primary production.[49,101] Stratification has also been observed in ice-free Arctic marine regions due to increased meltwater input.[102] Cai *et al.*[102] predict that an ice-free Arctic Ocean will not become a larger $CO_2$ sink due, in part, to an inefficient biological pump as a consequence of negative effects of solar UV radiation on phytoplankton.

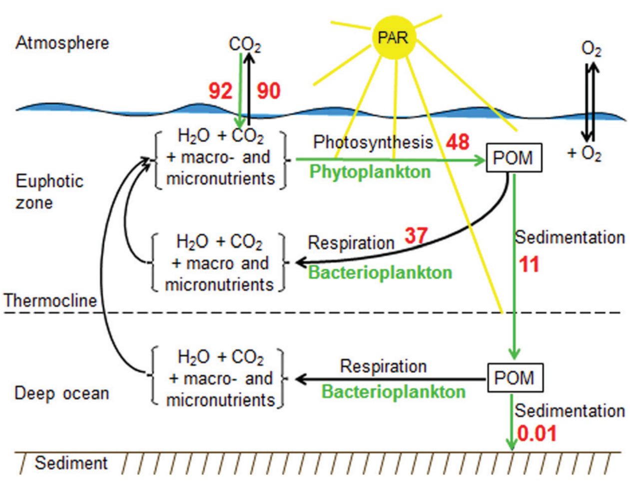

**Fig. 5** Schematic representation of the biological pump, indicated by the green arrows. The efficiency of the biological pump depends on the rates of both photosynthesis (primary production) with photosynthetic active radiation (PAR) and the formation and sedimentation of particulate organic matter (POM). Numbers in red are from Houghton[251] and correspond to approximate global mean fluxes in Pg C year$^{-1}$.

CDOM in aquatic systems originates from several sources. In the coastal ocean, continental runoff of CDOM plays an important role (see also above).[90,91,96,103–105] In the open ocean and large lakes, CDOM is a by-product of biological degradation of dead phytoplankton.[90,97,106] Thus, a reduced concentration of phytoplankton will drive decreased CDOM production, further increasing transmission of UV radiation into the ocean. The observed reductions in chlorophyll concentration that have been attributed to increasing sea surface temperatures[101] are probably caused by a combination of increased exposure to UV radiation and reduced nutrient upwelling.[107]

An important part of the biological pump is the export production, *i.e.* the formation and sedimentation of particulate organic matter (POM) stemming from dead phytoplankton and zooplankton material. The export production has decreased by 8% from 1960–2006 globally with strong spatial variability, based on model calculations.[49] One reason for this decline may be a global decrease in the biomass of small phytoplankton and diatoms in the period 1960–2006 (8.5% and 3%, respectively[49]). Ocean acidification may further reduce the biomass of coccolithophores, small calcifying phytoplankton, and hence the production of $CaCO_3$ "ballast" that enhances sinking rates of carbonate-rich POM.[34,49,108,109] Overall, the interaction of solar UV radiation with climate-change effects such as ocean stratification is likely to decrease the efficiency of the biological pump and to cause UV-mediated, positive feedbacks on atmospheric $CO_2$ (see also below).

### Carbon exchange between terrestrial ecosystems and atmosphere

The uptake of $CO_2$ by terrestrial ecosystems *via* photosynthesis of plants and the release of $CO_2$ to the atmosphere *via* decomposition of senescent plant material (litter) are affected both positively and negatively by solar UV radiation and climate change.[89,110] Climate change, and in particular the intensity and frequency of droughts in terrestrial ecosystems could negatively impact primary production by plants and crops and thus $CO_2$ uptake by terrestrial ecosystems.[13,68,71] At the same time, changes in climate that decrease cloudiness and increase UV radiation at the terrestrial surface may increase losses of carbon from terrestrial ecosystems due to increased photochemical degradation of plant material.[111]

A part of the $CO_2$ fixed by plants may be sequestered in forests or long-lived plant soil components such as woody tissue or peat in soil organic matter, thus increasing its residence time in organic pools. Plant litter on the soil surface is, however, subject to rapid degradation, which results in emissions of $CO_2$ and other greenhouse gases to the atmosphere.[89,112–114] The release of $CO_2$ from terrestrial ecosystems by microbial degradation of soil organic matter is strongly affected by temperature and moisture.[115–117] In addition, there is increasing evidence of abiotic decomposition of above ground litter due to UV radiation, particularly in arid and semiarid regions with low soil biotic activity.[111,112,114,116–124] Rates of plant litter photodegradation due to exposure to UV radiation depend on various factors, including: (i) plant cover,[111] (Fig. 6), (ii) the intensity of solar UV radiation (altitude, latitude), (iii) exposure of litter mass to solar radiation due to differences in litter area to mass ratio, and (iv) chemical composition of plant litter[118,122] (Fig. 7) (see also Bornman *et al.*[72]).

Recent information regarding the role of litter chemistry in determining the rate of UV-induced litter degradation has identified the importance of lignin in the process of photodegradation. Several studies have shown a decrease in litter lignin content with exposure to solar or UV-B radiation[125,126] and that lignin content of litter is *positively* correlated with higher rates of mass loss (Fig. 7, Austin and Ballaré[118]). The latter can be explained in terms of a higher percentage of aromatic components in lignin and thus a higher rate of light absorption in the UV and visible range.[118,120,121,127] Although abiotic photodegradation increases with the lignin content, the rate of microbial degradation tends to decrease with increasing lignin content, due to the bio-recalcitrant nature of lignin[118] (Fig. 7). Finally, there is some evidence that exposure of plant litter to solar UV-radiation can increase the bioavailability of some compounds to soil microorganisms,[112,119–121] although the mechanistic basis of this stimulation has not been established.

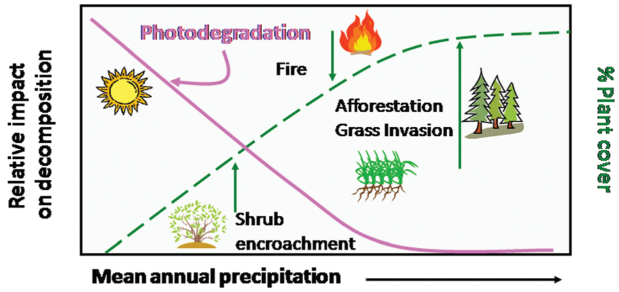

Fig. 6 Hypothesized effect of plant cover on photodegradation in terrestrial ecosystems. Plant cover is a key factor which will affect the degree of exposure to UV radiation and impacts of photodegradation as a vector of carbon loss in arid and semiarid ecosystems. As precipitation increases, primary production and resulting plant cover increase, thereby reducing the relative importance of photodegradation in mesic and humid ecosystems. Global changes such as shrub encroachment, increased fire frequency, invasion of non-native annual species and afforestation will all affect plant cover and consequently the relative impact of photodegradation on decomposition in these ecosystems. Red line shows the importance of photodegradation as rainfall increases, the dashed line is changes in plant cover. Green arrows indicate the direction of change in plant cover with global change. Figure modified from Austin (2011).[111]

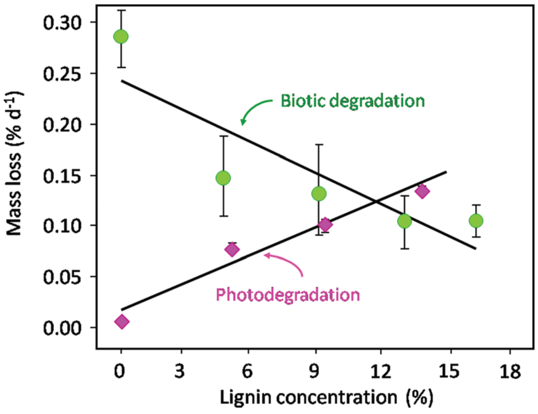

Fig. 7 Effects of lignin concentration on biotic decomposition and photodegradation. While biotic degradation of plant litter is inhibited by high lignin concentrations, lignin serves as a light absorbing compound facilitating photodegradation and carbon release from decomposing plant litter. Green circles indicate material of varying lignin concentrations which was decomposed in shaded conditions in contact with soil (biotic decomposition) while red diamonds indicate identical material of varying lignin concentrations that was isolated from the soil surface and exposed to full solar radiation. Figure modified from Austin and Ballaré (2010).[118]

The direct and indirect effects of UV radiation on decomposition of plant litter is likely to become a much more significant global pathway for terrestrial organic matter decomposition in the future. Aridification due to land use and/or climate change could amplify photodegradative losses from senescent plant litter, with large potential impacts on the carbon balance of terrestrial ecosystems. Particular attention needs to be paid to Arctic terrestrial ecosystems. The Arctic region is experiencing rapid warming and its land area, including the tundra, has large stores of carbon that are likely to be rapidly converted to GHGs with warming. For example, losses from plant litter may be enhanced due to the thawing of permafrost[119] and Arctic tundra wildfires,[128] (see also above). All of these global changes have potential to affect plant cover (Fig. 6, Austin[111]), and hence increase the importance of photodegradation in these modified ecosystems.

## The terrestrial-aquatic interface

Terrestrial and aquatic ecosystems are largely linked *via* the biogeochemical cycling of carbon. Runoff and leaching of plant litter is a major source of CDOM in aquatic environments, especially in freshwaters. In coastal marine environments, a large fraction of organic carbon originates from terrestrial ecosystems that is transported to coastal oceans (i) *via* rivers,[59,129–133] and (ii) fluxes from wetlands, particularly from mangrove swamps[134] (Fig. 4). Terrestrial organic matter (tDOM), in particular its CDOM fraction, more strongly attenuates solar UV radiation than organic matter produced within lakes and the sea due to its relatively high aromatic content,[89,94,96,103,105,135,136] where the optical properties of terrigenous CDOM arise primarily from partially oxidised lignins originating from vascular plant sources[137] (see also above). UV-induced photodegradation occurs more readily with terrestrially derived CDOM than with microbial CDOM[89,94,136,138,139] where microbial CDOM is derived from autochthonous organic sources in the ocean and lakes such as dead phytoplankton cells. In the Arctic Ocean, continental runoff is a major source of terrigenous organic material and nutrients, thereby influencing water column stratification, gas exchange, light attenuation, surface heating, biological productivity, and carbon sequestration. A remote sensing study of the pan-Arctic distribution of tDOM and continental runoff in the surface Arctic Ocean indicated a correspondence between climate-driven changes in river discharge and tDOM inventories in the Kara Sea.[103]

The major carbon substances resulting from UV-induced photodegradation of CDOM are inorganic species: dissolved inorganic carbon (DIC) and to a lesser extent carbon monoxide (CO)[96,105,140] (see Fig. 8). Photochemical DIC formation may strongly impact carbon cycling in seawater and other natural waters. For example, the annual photodegradation of CDOM exceeded the annual terrestrial input of photoreactive CDOM to the Baltic Sea, indicating that photochemical transformation is a major sink for terrestrial CDOM in such coastal systems.[141] Other mechanistic studies of the efficiencies of CDOM photodegradation have shown that DIC photoproduction rates are up to 30 times greater than CO photoproduction[96,105,140] (Fig. 8). Although not precise, these estimates suggest that $CO_2$ photoproduction rates are comparable to other oceanic $CO_2$ production terms, *e.g.* microbial respiration.

Not only the UV-induced but also the microbial degradation of DOM (respiration, see Fig. 5) results in production of $CO_2$. The rate of this process is largely controlled by the availability of DOM to heterotrophic bacteria, which in turn depends on the chemical composition of DOM.[59,127,142,143] UV-induced transformations generally decrease the bioavailability of microbial CDOM and enhance the bioavailability of terrigenous CDOM.[89,127,142] Such a UV-induced enhancement also has been observed in the case of terrestrial plant litter where the term “photochemical priming” has been used to describe this enhancement (see Bornman *et al.*[72]).

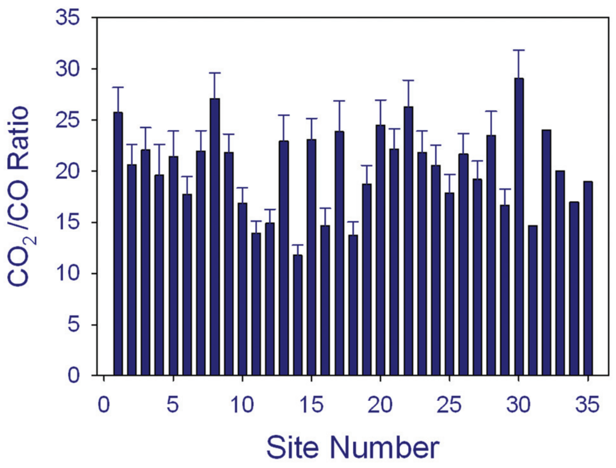

**Fig. 8** Measured ratios of sunlight-induced $CO_2$/CO photoproduction in oceanic water samples collected from a variety of locations and times. The average ratio is close to 20 in marine systems but somewhat lower in freshwaters.[96,105,140]

Climate change can influence the UV-induced degradation of CDOM through effects on its sources. For examples, melting of glaciers, ice sheets, and thawing permafrost heightens the input of microbial DOM into aquatic systems[144–146] and this source of CDOM generally becomes less biodegradable when transformed by solar UV radiation. Furthermore, both changes in continental hydrology and land use change may increase fluxes of tDOM from land to ocean[59,60,147–149] thereby enhancing UV-induced $CO_2$ production *via* mineralisation of tDOM.[132] According to Regnier *et al.* (2013),[148] the carbon flux to inland waters from soils has risen by 1.0 Pg C per year since preindustrial times. Also land use changes can affect sources of CDOM. For example, disturbance of peatlands has resulted in a 32% increase in fluvial organic flux from south-east Asia[147] and this source of tDOM likely is photodegradable. Arctic aquatic ecosystems are particularly affected by increased input of DOM due to changes in rainfall, melting of ice, snow, and the permafrost. Depending on its source, DOM in Arctic aquatic ecosystems is subject to UV-induced or microbial mineralisation, where photochemical priming plays an important role.[150]

## Links between carbon and nutrient cycles

In aquatic ecosystems, $CO_2$ fixation in photosynthesis by phytoplankton (primary production) plays a key role in linking the carbon and nutrient cycles. The rate of primary production depends, in part, on the concentration and bioavailability of macro- and micronutrients present in the euphotic zone. Many nutrients are transported into the euphotic zone from deeper water layers.[151] However, ocean stratification due to increasing sea-surface temperatures (SST) hinders the upwelling of nutrients and, as a consequence, negatively affects primary production and hence the biological pump[49,101,107](see above). Micronutrients (essential trace metals including Fe, Cu, Zn, Mn, Co, and Cd) may co-limit phytoplankton growth and primary production in marine environments.[48,152–154] The biological availability of essential trace metals depends on their chemical speciation. In general, only dissolved and weakly-bound or unchelated metals are available to phytoplankton.[155–157] For this reason, oxidation and mainly reduction processes (redox reactions) induced by solar UV radiation play an important role in the formation of bio-available metal species.[158] Increased vertical mixing of water bodies reduces rates of UV-induced redox cycling of essential metals. For example, sea-ice loss in the western Antarctic Peninsula is hypothesised to reduce iron bioavailability because of greater vertical mixing in winters with little sea ice.[159]

Iron plays a key role as a micronutrient and co-limits phytoplankton growth particularly in the so-called high-nutrient-low chlorophyll (HNLC) oceanic regions.[152,153] In oxygenated marine environments, Fe(III) is largely present in the form of solid Fe(III) phases, with low solubility. In the Southern Ocean, for example, dissolved iron concentrations range between 0.4 and 1.5 nmol $L^{-1}$.[160] However, these solid iron phases can undergo UV-induced dissolution yielding dissolved iron species[161,162] and this photochemical process has been shown to occur at pH-values of marine waters.[161] Ocean acidification (see above) can result in reduced availability of essential trace metals such as Fe, Zn, and Cd to phytoplankton, either *via* changes in the chemical speciation of metals or by decreasing the effectiveness of the enzymatic reduction of metals.[157,163] For example, the uptake rate of iron bound to the siderophore desferrioxamine B by a model diatom was by a factor of ~2 lower in seawater samples with pH 7.8 as compared to samples with pH 8.7.[163] Ocean acidification also slows down nitrogen uptake by phytoplankton under low iron conditions by lowering the efficiency of $N_2$ fixation.[164]

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

Terrestrial and aquatic environments are important atmospheric sources and sinks of trace gases and aerosols. Recent research on the air–sea exchange of trace gases has provided further evidence that these sources are strongly influenced by interactions between solar UV radiation and climate change.

### Methane

Methane is an important greenhouse gas that is stored in various reservoirs in the terrestrial, aquatic and atmospheric systems. UV radiation is involved in the release and exchange of $CH_4$ between these reservoirs as well as atmospheric chemical processes in the troposphere and stratosphere.[165–167] Temperature, water vapour, stratospheric ozone, biomass burning, and lightning $NO_x$ are the dominant sources of inter-annual changes in methane lifetime.[166] UV radiation plays a critical role in determining the effectiveness of each of these sources in inter-annual changes in methane lifetime which is ~9 year.[168] The linkages and inferences of this section revolve around the UV-mediated atmospheric chemistry, ozone, OH *etc.* that drive atmospheric methane concentrations, and how $CH_4$ release and uptake from land, aquatic and atmospheric reservoirs is influenced by UV radiation and biogeochemical cycles in general.

New satellite and airborne data assimilation techniques allow high-resolution, global estimates of the sources and sinks of atmospheric methane.[169] These emerging technologies allow quantification and evaluation of the wild-fire production of atmospheric methane, an increasing source due to the climate related increased occurrence of wildfires.[170,171] UV radiation plays a critical role in the atmospheric chemistry of methane as well as modulating its production in soils and other components of the terrestrial biosphere,[172,173] although Morsky *et al.*[174] found its role in methane production in a sub-arctic fen was more modest. The release of methane to the atmosphere from land surfaces is dependent upon climate change in the terrestrial biosphere as well as heat and UV supply to specific methane reservoirs such as permafrost regions.

Methane fluxes from the Arctic Ocean are strong and occur mainly in areas of open water between sea-ice (leads) and fractional sea-ice up to 82° N.[175] Additional sources from submarine permafrost regions have also been reported.[176] Such oceanic regions are likely to become increasing sources of atmospheric methane in the future due to climate-related changes in sea-ice cover. Warming has also been shown to affect the emission of methane in Western Siberian lakes with implications for atmospheric chemistry and UV interactions.[177] We posit that as climate changes, ocean sea-ice coverage changes and often decreases, resulting in new and increased distributions of air-sea methane flux. The resultant methane releases will change and will be occurring simultaneously with the evolving atmospheric UV radiation budget.

### Carbon monoxide

Carbon monoxide (CO) is widely produced through interactions of solar UV radiation with organic substances in aquatic and terrestrial systems. The average ratio of measured $CO_2$/CO fluxes from various marine environments is close to 20 (Fig. 8). CO participates in chemical reactions that change air quality and it is one of the most important sinks for atmospheric hydroxyl radicals ($^{\bullet}$OH). Due to its significant effects on $^{\bullet}$OH, CO also indirectly influences the concentrations of methane, halocarbons and other gases in the troposphere (see above). Recent research has provided further evidence that UV-induced processes as well as abiotic thermal processes involving tDOM in aquatic systems and plant litter on land are significant sources of CO to the atmosphere.[96,105,122,140,178–182] tDOM generally is a more efficient source of CO (higher apparent quantum yields) than microbial CDOM derived from marine sources such as algal detritus. For example, CO photoproduction efficiencies in the Tyne estuary were highest for high CDOM riverine samples and almost an order of magnitude lower for low CDOM coastal seawater samples.[180] One exception to this general observation is the unusually high efficiency of CO photoproduction from CDOM within floating Sargassum colonies.[96] There are also significant CO microbial sinks in aquatic and terrestrial systems and the competition between these sources and sinks often results in diurnal fluctuations in the net exchange of CO between biosphere and atmosphere.[181–183]

An extensive study of the sea to air exchange of $CO_2$ in the sub-arctic estuarine water body, the Canadian St. Lawrence estuary system, showed that the rates of photoproduction and microbial consumption of CO are approximately balanced.[182]

Other findings are that the photochemical efficiency for CO production from DOM in aquatic systems decreases with increasing salinity across the freshwater-marine mixing zone.[140,173,179,184]

Studies of terrestrial plants have provided additional evidence that exposure to UV radiation leads to production of CO from dead plant matter (litter) and that production rates depend on the litter traits.[123] Studies of the effects of changing wavelength on CO photoproduction from litter are uncommon but one study showed that UV radiation induces CO production from *Sequoia dendrongiganteum* litter. CO emissions were strongly reduced in the absence of oxygen as compared to air.[185] Other studies have shown that living plant leaves also photoproduce CO,[186] although the production efficiency generally is much lower than for senescent or dead vegetation.

### Nitrogen compounds

Among nitrogen-containing gases, nitrogen oxides ($NO_x = NO + NO_2$) play an important role in atmospheric chemistry, and many nitrogen gases have important interactions with UV radiation. In the troposphere, $NO_x$ enhances the formation of $O_3$ *via* UV-induced reactions (see Madronich *et al.*[187]). In the stratosphere, the opposite is the case, where $NO_x$ destroys $O_3$ by the following reaction: $NO + O_3 \rightarrow NO_2 + O_2$, where $NO_2$ acts as a catalyst in stratospheric $O_3$ destruction.[188] Furthermore, the reaction of $NO_2$ with ClO yields $ClONO_2$, a reservoir of reactive chlorine that continues to play an important role in polar stratospheric ozone depletion in the Arctic and Antarctic spring. Given these important interactions, changes in the atmospheric concentrations of nitrogen oxides due to climate change or other human activity may indirectly affect ozone recovery and the amount of UV radiation reaching the Earth's surface.

Anthropogenic $NO_x$ emission from combustion of fossil fuel, is an important source of $NO_x$ to the atmosphere. Additionally, nitric oxide (NO) from natural sources is produced mainly by anaerobic bacteria that reduce nitrate ($NO_3^-$) to nitrogen gas $N_2$;[189] NO is also a by-product of the oxidation of ammonium ($NH_4^+$) to nitrate by ammonia-oxidising soil bacteria.[189,190] Nitrous acid (HONO) emissions from ammonia-oxidising bacteria are comparable with emissions of NO.[190,191] Since soil emissions of both NO and HONO depend on the soil water content,[190] increasing soil dryness, due to climate change, may increase the emission of NO and HONO from soils. UV-induced photolysis of HONO is a major source of the hydroxyl radical ($HO^•$) (up to ~30% of production in the lower atmosphere[191]). In addition to soil emissions of $NO_x$ from biotic processes, UV-induced photolysis of $NO_3^-$ (photodenitrification) is an important source of $NO_x$ to the atmosphere.[192,193] This abiotic process has been shown recently to occur on the surface of nitrate-containing snow in the Arctic,[192] and in sea salt particles containing $Cl^-$ and $Br^-$.[193]

Another key nitrogen-containing gas is nitrous oxide ($N_2O$), an important greenhouse and stratospheric ozone depleting gas. The surface emission of $N_2O$ approximately balances the stratospheric $N_2O$ loss[188] *via* formation of the ozone destroying NO [$N_2O + O^* \rightarrow 2NO$, where $O^*$ is produced *via* photolysis of ozone: $O_3 + h\nu \rightarrow O^* + O_2$]. In terrestrial ecosystems, $N_2O$ is formed by denitrifying soil bacteria that reduce $NO_3^-$ to $N_2$.[189] $N_2O$ formation in soils depends on soil water content (SWC) and temperature and occurs at higher SWC than soil emission of HONO and NO.[190,194] Van Groenigen *et al.*[195] predict that rising levels of $CO_2$ will result in increased emissions of $N_2O$ from upland soil due to reduced plant respiration and thus higher SWC. In addition, more frequent precipitation events, due to climate change, that increase SWC could thus enhance the $N_2O$ flux from soils.[194]

In aquatic ecosystems, ammonia is produced by the UV-induced degradation of DOM[184] and $N_2O$ by both denitrifying bacteria and ammonia oxidising archaea.[196] $N_2O$ formation is particularly efficient in suboxic and hypoxic oceanic regions (~10% of the ocean volume).[197,198] The area of such regions is likely to expand (Fig. 3) due to the following factors: (i) eutrophication of coastal waters, (ii) decreasing $O_2$ solubility with warmer water temperatures, and (iii) shifts in respiration towards the upper oceanic water column because of reduced sinking velocity of particles in the ocean[108,197,199] (see also above). Furthermore, it has been shown that during storms, $N_2O$ rich subsurface water is mixed upwards[198] suggesting that more frequent storm events, due to climate change, may result in increased emission of $N_2O$ from marine environments. In addition, sea-ice retreat has been suggested to decrease the residence time of $N_2O$ in the surface water of the Arctic Ocean and thus could enhance the sea-air flux of $N_2O$.[200,201] Geoengineering *via* fertilisation of marine regions with iron could enhance marine $N_2O$ production,[202] (see also Bais *et al.*[3]).

### Halogen compounds

Biogenic processes in terrestrial and aquatic ecosystems are important sources of halocarbons other than CFC (*e.g.* the methyl halides $CH_3Br$, $CH_3Cl$, and $CH_3I$) to the atmosphere.[203–207] In aquatic ecosystems, phytoplankton is involved in the formation of these halocarbons, particularly pico-sized phytoplankton,[206] and to a lesser extent bacteria belonging to *Erythrobacter* or *Pseudomonas*.[204] The rate of halocarbon production in aquatic ecosystems also depends on the chemical composition of dissolved organic matter (DOM), with tDOM playing an important role in the formation of halocarbons such as bromoform ($CHBr_3$) and dibromomethane ($CH_2Br_2$).[207] Hence increased fluxes of tDOM from land to ocean, due to climate change, may enhance the formation of halocarbons, particularly in eutrophic coastal waters. In addition to the biotic production of halocarbons, abiotic UV-induced processes could also be involved in the formation of $CH_2ClI$, and $CH_2I_2$ in seawater.[206]

In the atmosphere, halocarbons are transformed into reactive halogen species (RHS, *e.g.* the radicals $Br^•$ and $BrO^•$), where the hydroxyl radical ($HO^•$, formed in reactions induced by solar UV radiation) acts as the oxidant.[191,208] In the troposphere, RHS react with ozone[209,210] and other gases, *e.g.* gaseous elemental mercury ($Hg^0$)[211] (see also below).

Halocarbons can reach the lowermost stratosphere and undergo UV radiation-induced transformations yielding RHS, particularly $BrO^•$, that participate in stratospheric ozone depletion.[208,212] Models suggest that the loading of the stratosphere with reactive bromine species will increase in the future due to climate change[213] and thus the destruction of ozone in the stratosphere by RHS represents a positive feedback on solar UV radiation. This feedback could be enhanced by climate-change related processes, particularly by increased input of tDOM into coastal zones[207] and by increases in ocean mixing and thus transport of $CH_3Br$ to the lower stratosphere.[208]

### Aerosols

Atmospheric aerosols play an important role in the biogeochemistry of greenhouse gases, atmospheric circulation trends due to changes in climate and atmospheric chemistry.[214] The surfaces of atmospheric aerosol particles provide reactive multi-phase regions for chemical transformations in the atmosphere. Surfaces, as well as the liquid phase portions inside the aerosols, interact with UV radiation to process chemicals critical to climate and atmospheric chemistry in general. Aerosol distributions and trends in distributions due to climate change alter UV fluxes to Earth's surface. This is due to direct blocking of UV radiation by aerosols in the atmosphere and the fact that the distributions and the radiative and chemical make–up of the aerosols are evolving as climate changes.

Aerosols affect circulation directly *via* interactions with radiation with attendant thermal gradient impacts.[215,216] This means that strong feedbacks exist between aerosol distributions, UV radiation, and the circulation that influence precipitation and atmospheric transport.[217] Changes in the distribution of atmospheric aerosols are occurring at the same time as shifts in terrestrial and aquatic and marine ecosystems.[218] UV radiation is involved in and affected by biogeochemical feedbacks that result from chemical exchanges at the Earth surface, physical circulation changes and human-induced modification of the environment. UV interactions with the liquid phase of marine aerosol particles result in trace gas production, which alter the oxidation state of the atmosphere. Fe compounds have recently been implicated in these aerosol multiphase interactions.[219] Aerosols not only scatter and absorb atmospheric UV radiation they influence and change atmospheric gas and liquid phase chemistry.

Urbanisation and managed agriculture have resulted in changing patterns of atmospheric dust distributions and deposition.[220] These dust aerosols, which affect the transparency of the troposphere, have a concurrent impact on UV flux to aquatic and terrestrial ecosystems. Non-Asian sources are a significant source of dust to the North Pacific[221] and will likely result in significant changes in the supply of nutrients, as organically bound Fe and P is transported atmospherically from continental regions to ocean ecosystems.[147,218,222] Information from studies of the impacts of volcanic supplies of aerosols are being used to predict the impact of future aerosol distributions on the carbon cycle.[223]

There is an emerging realisation that liquid phase UV-driven aerosol chemistry can influence biogeochemical cycling of atmospheric greenhouse gases.[224] This means that not only do atmospheric aerosols modulate surface UV fluxes *via* their distribution in the atmospheric column, but also the multiphase chemical processes that occur on/in aerosols affect the oxidative state of the atmosphere. An example of this multiphase chemistry is the Fe chemistry in aerosols that influences atmospheric radicals, oxidative state and lifetimes of greenhouse gases.[219] These newly identified biogeochemical cycles assist in understanding some of the interactions between UV radiation, aerosol chemistry and atmospheric greenhouse gas distributions.

## Combined effects of solar UV radiation and climate change on chemical and biological contaminants

### Organics

Global climate change and interactions with solar ultraviolet radiation will potentially influence chemical fate and bioaccumulation in terrestrial and aquatic environments.[225,226] Reviews and modeling studies have particularly focused on the Arctic and persistent organic pollutants (POPs)[227–229] and predict the following effects: (1) Increased ambient temperatures could lead to increased emissions of chemicals through passive volatilisation from materials and stockpiles; (2) Increased emissions of POPs are predicted as a result of changing land-use patterns and changes in global agricultural practices, such as pesticide formulations and application rates; (3) Changes in energy use will affect use and release of chemicals; (4) Increases in the frequency of forest fires will increase the emissions of polycyclic aromatic hydrocarbons and other combustion by-products such as charcoal and black carbon.

Although POPs are chemicals such as chlorinated compounds that are resistant to biodegradation and/or to photodegradation through direct absorption of sunlight, these chemicals can be transformed by indirect photoreactions that involve natural substances such as tDOM (or related natural organic substances that were isolated from soils or natural waters), peroxides, nitrate or certain trace metals. Most of the recent examples of indirect photoreactions involve participation of tDOM.[228,230–233] Chemicals having a wide variety of structural features participate in these indirect photoreactions including chlorinated contaminants,[228,233] antibiotics,[232] beta-blockers,[231] and other drugs.[230]

One manner through which environmental variables influenced by global climate change could affect contaminant toxicity involves direct effects of the variable on chemical characteristics. The toxicity of polycyclic aromatic hydrocarbons (PAHs), for example, can be photoactivated by solar UV radiation.[226] The intensity and wavelength distribution of UV radiation, key factors in determining PAH phototoxicity, are likely to be affected by variables altered by climate change. For example, these variables could include decreases in pH that can increase water clarity, thereby increasing exposure of aquatic animals to UV radiation, and increased inputs of CDOM or particulate carbon to aquatic systems, which would effectively reduce UV penetration. Hence, specific influences of climate change on UV intensity in aquatic systems are likely to be site- and situation-specific.

Although increased UV-B radiation can negatively affect the growth and viability of many organisms in aquatic food webs, sensitivity to UV radiation has the beneficial effect of disinfecting pathogens.[141,234–236] This process is facilitated by climate and UV-induced changes that alter exposure of surface-dwelling organisms through increased water transparency and stratification, and reduced ice and snow cover. For example, human pathogenic viruses, which are frequently found in rivers, lakes and drinking water, are sensitive to solar UV radiation[236] and disinfection by solar UV irradiation (SODIS) is becoming a widely-used tool for purification of drinking water in developing countries.[235] The observed increases in CDOM in aquatic environments can have opposing effects on pathogen levels. On the one hand, the increases in CDOM reduce UV exposure and thus disinfection by direct photoinactivation of parasites and pathogens. On the other hand, photoinactivation of pathogens can be enhanced through photosensitisation by CDOM.[236]

**Inorganics: mercury**

Mercury (Hg) is one of the inorganic priority pollutants and its biological availability and thus toxicity is strongly affected by solar UV radiation and climate change. Mercury is not an essential metal and is toxic at very low concentrations. Most mercury released to the atmosphere is in the form of gaseous elemental mercury ($Hg^0$), which can be transported over long distances and is deposited mainly in the oxidised form as divalent mercury ($Hg^{II}$).[237] In the oxidation process, the radicals $BrO^{\bullet}$ and $Br^{\bullet}$, that are formed in UV-induced reactions, play a key role.[211] In addition, UV-induced re-reduction of $Hg^{II}$ occurs in the troposphere, however, at a lower rate than $Hg^0$ oxidation.[237] Following deposition to terrestrial and aquatic ecosystems, $Hg^{II}$ undergoes methylation yielding methylmercury (MeHg), the toxic form of mercury. In sunlit surface waters MeHg may undergo UV-induced decomposition, a process that is enhanced by DOM.[60]

Climate change may amplify effects of solar UV radiation on the biogeochemical cycling of mercury. For example, ocean warming increases the sea-air flux of $Hg^0$.[238] As a consequence, the rate of oxidation of $Hg^0$ to $Hg^{II}$ (*via* UV-induced formation of reactive radicals, see above) can be expected to increase since the oxidation rate depends on the concentration of both reactive radicals and $Hg^0$. Hence it is likely that the combined effects of ocean warming and solar UV radiation on the biogeochemical cycling of mercury result in increased formation of the toxic form of mercury.

**Nanomaterials**

In addition to organic contaminants and mercury, new chemicals are coming into global markets that require initial assessment. Inorganic and organic engineered nanomaterials (ENMs) and their composites with polymers and coatings (see also Andrady *et al.*[239]) are being introduced into the environment through widespread use in consumer products. Concerns about their health and safety have stimulated research on their persistence and toxicity. UV-induced photoreactions are important environmental processes for ENMs such as nanosilver, nano-titanium dioxide, fullerenes, carbon nanotubes and graphene oxide. These photoreactions are sensitised by tDOM in some cases. For example, nanosilver can be readily formed by the tDOM-induced photoreduction of ionic silver,[240,241] a sunlight-induced process that helps reverse toxicity associated with oxidation of nanosilver. UV-induced processes initiate the environmental release of ENMs from polymer nanocomposites by photodegradation of the polymer matrix.[242]

## Gaps in knowledge

Our understanding of the interacting effects of solar UV radiation and climate change on the biogeochemical cycling of carbon, nitrogen and halogen compounds, essential and toxic metals, and on the fate of organic pollutants has increased in the four years since our last assessment. However, there remain important gaps in knowledge. For example, climate models generally do not include effects of solar UV radiation on biogeochemical cycles. To do this would be important for predicting trends in the net $CO_2$ sink strength of terrestrial and aquatic ecosystems.

Terrestrial and aquatic ecosystems are currently net $CO_2$ sinks on a global average, where the $CO_2$ uptake corresponds to *ca.* 30% and 25%, respectively, of anthropogenic $CO_2$ emission.[243,244] However, the $CO_2$ sink strength of terrestrial and aquatic ecosystems may decrease due to climate change[49,245,246] and interactions between solar UV radiation and climate change could accelerate this decline. Based on a biogeochemical elemental cycling model (without taking into account effects of solar UV radiation), Laufkoetter *et al.*[49] simulated a decrease in phytoplankton net primary production by 6.5% within 50 years (1960–2006) on a global average, due to various climate-change related factors, including ocean stratification. A decrease in net primary production by phytoplankton is likely to reduce the efficiency of the biological pump and thus the $CO_2$ sink strength of aquatic ecosystems. Even without a decrease in the global $CO_2$ sink strength of terrestrial and aquatic ecosystems, their capacity to take up $CO_2$ does not keep pace with increasing atmospheric $CO_2$ concentrations.[243,247,248]

As discussed earlier, an important effect of solar UV-radiation in aquatic ecosystems is photobleaching of CDOM, resulting in increased transmission of the damaging solar UV-B radiation into water bodies with negative effects on photosynthetic organisms (organisms such as phytoplankton that transform $CO_2$ into organic matter). The enhancement of UV-induced bleaching of CDOM due to stratification of water bodies therefore represents a UV-mediated, positive feedback on climate. In terrestrial ecosystems a positive feedback on climate is increased UV-induced decomposition and mineralisation of above ground litter (under release of $CO_2$) due to aridification and decreased plant cover from human activity.

Important greenhouse gases other than $CO_2$ are nitrous oxide ($N_2O$) and methane ($CH_4$). Climate change, *via* changing precipitation and temperature distributions and extreme events, can have large impacts on the emission of these gases. For example, $N_2O$ and $CH_4$ emissions from plants may be increased through temperature effects, indirectly due to rising $CO_2$ levels. UV-induced inhibition of microbial processes in aquatic systems can also influence trace gas exchange such as CO and $N_2O$ to air. Interactions in atmospheric chemistry also exist *via* UV-induced reactions involving $N_2O$ resulting in the formation of ozone destroying compounds.

Halocarbons such as methyl bromide ($CH_3Br$), which are emitted by phytoplankton, are other gases that undergo UV-induced transformations to highly reactive species and thus also have the potential to cause stratospheric ozone depletion. Changes in oceanic phytoplankton distributions and community structure due to climate change is expected to alter rates of emission of these trace gases. Highly reactive species formed in UV-induced transformations of halocarbons also react with tropospheric pollutants, *e.g.* gaseous elemental mercury yielding the precursor of the bioavailable and thus toxic form of mercury. While there exists a large body of literature on the effects of climate change or of solar UV radiation on the fate of mercury, the interactive effects of climate change and solar UV radiation on the biogeochemical cycling of mercury have, to our knowledge, not yet been extensively studied.

Levels of organic pollutants and pathogens in aquatic environments are affected by interactions with changing climate and solar UV radiation. For example, UV radiation can inactivate pathogenic viruses by direct pathways and also by indirect pathways that involve sensitisation by CDOM. CDOM, a climate-sensitive component of most aquatic environments, can also modulate pathogen levels by screening out the UV component of sunlight.

The combined effects of solar UV radiation and climate change on biogeochemical cycles are likely to be particularly pronounced in the Arctic due to Arctic amplification that also hinders the recovery of the stratospheric ozone concentration in Arctic spring. As a consequence of Arctic stratospheric ozone depletion, increased levels of solar UV radiation reach Arctic terrestrial and aquatic ecosystems. Negative effects of solar UV-B radiation on phytoplankton and thus on the biological pump are expected in ice-free Arctic marine regions, particularly in combination with stratification due to increasing melt-water input. Based on a radiation transfer model, Fountoulakis *et al.* (2014)[249] predict that up to 10 times higher levels of solar UV irradiance will enter large parts of the Arctic Ocean by 2100, compared to the 1950s, mainly due to Arctic sea-ice melting. Furthermore, increased emissions of $CO_2$ *via* mineralisation of organic matter due to thawing permafrost and Arctic tundra wildfires as well as decreased albedo due to vegetation shifts,[11] have large effects on carbon cycling in the Arctic[150] and together can act as a positive feedback on global warming. Therefore, more attention needs to be paid to Arctic tipping points.

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