

Interactive effects of ozone depletion and climate change on biogeochemical cycles †

Richard G. Zepp,^a Terry V. Callaghan^{b,c} and David J. Erickson III^d

^a United States Environmental Protection Agency, 960 College Station Road, Athens, Georgia 30605-2700, USA

^b Abisko Scientific Research Station, S-98107 Abisko, Sweden

^c Sheffield Centre for Arctic Ecology, Department of Animal and Plant Sciences, University of Sheffield, Tpton Experimental Gardens, 26 Tptonville Road, Sheffield, UK S10 5BR

^d Computational Climate Dynamics Group, Computer Science and Mathematics Division, Oak Ridge National Laboratory, P.O. Box 2008, MS 6367 Oak Ridge, TN 37831-6367, USA

First published as an Advance Article

The effects of ozone depletion on global biogeochemical cycles, *via* increased UV-B radiation at the Earth's surface, have continued to be documented over the past 4 years. In this report we also document various effects of UV-B that interact with global climate change because the detailed interactions between ozone depletion and climate change are central to the prediction and evaluation of future Earth environmental conditions.

There is increasing evidence that elevated UV-B has significant effects on the terrestrial biosphere with important implications for the cycling of carbon, nitrogen and other elements. Increased UV has been shown to induce carbon monoxide production from dead plant matter in terrestrial ecosystems, nitrogen oxide production from Arctic and Antarctic snowpacks, and halogenated substances from several terrestrial ecosystems. New studies on UV effects on the decomposition of dead leaf material confirm that these effects are complex and species-specific. Decomposition can be retarded, accelerated or remain unchanged. It has been difficult to relate effects of UV on decomposition rates to leaf litter chemistry, as this is very variable. However, new evidence shows UV effects on some fungi, bacterial communities and soil fauna that could play roles in decomposition and nutrient cycling. An important new result is that not only is nitrogen cycling in soils perturbed significantly by increased UV-B, but that these effects persist for over a decade. As nitrogen cycling is temperature dependent, this finding clearly links the impacts of ozone depletion to the ability of plants to use nitrogen in a warming global environment. There are many other potential interactions between UV and climate change impacts on terrestrial biogeochemical cycles that remain to be quantified.

There is also new evidence that UV-B strongly influences aquatic carbon, nitrogen, sulfur, and metals cycling that affect a wide range of life processes. UV-B accelerates the decomposition of colored dissolved organic matter (CDOM) entering the sea *via* terrestrial runoff, thus having important effects on oceanic carbon cycle dynamics. Since UV-B influences the distribution of CDOM, there is an impact of UV-B on estimates of oceanic productivity based on remote sensing of ocean color. Thus, oceanic productivity estimates based on remote sensing require estimates of CDOM distributions. Recent research shows that UV-B transforms dissolved organic matter to dissolved inorganic carbon and nitrogen, including carbon dioxide and ammonium and to organic substances that are either more or less readily available to micro-organisms. The extent of these transformations is correlated with loss of UV absorbance by the organic matter. Changes in aquatic primary productivity and decomposition due to climate-related changes in circulation and nutrient supply, which occur concurrently with increased UV-B exposure, have synergistic influences on the penetration of light into aquatic ecosystems. New research has confirmed that UV affects the biological availability of iron, copper and other trace metals in aquatic environments thus potentially affecting the growth of phytoplankton and other microorganisms that are involved in carbon and nitrogen cycling. There are several instances where UV-B modifies the air–sea exchange of trace gases that in turn alter atmospheric chemistry, including the carbon cycle.

Introduction

Former UNEP reports have assessed the impacts of UV-B on biogeochemical cycling in terrestrial and aquatic ecosystems.^{1,2} The term “biogeochemical cycles” is used here to refer to the complex interaction of biological, chemical, and physical processes that control the exchange and recycling of matter and energy at and near the Earth's surface. Research on biogeochemical cycles focuses on the transport and transformation of substances in the natural environment. Here, we report on new

findings that highlight the importance of UV-B impacts on biogeochemistry or modify our earlier understanding. UV effects on biogeochemical cycling also have the potential to interact with effects on carbon and nutrient cycling mediated through current climate changes and predicted changes in climate (IPCC)³. We present evidence here for such interactive effects as well as the basis for expecting potentially important effects that have not yet been demonstrated.

Terrestrial ecosystems

Changes in solar UV radiation can affect terrestrial biogeochemistry in at least two important interconnected ways. Firstly, the effects can involve the cycling of carbon including

† This article is published as part of the United Nations Environmental Programme: Environmental effects of ozone depletion and its interactions with climate change: 2002 assessment.

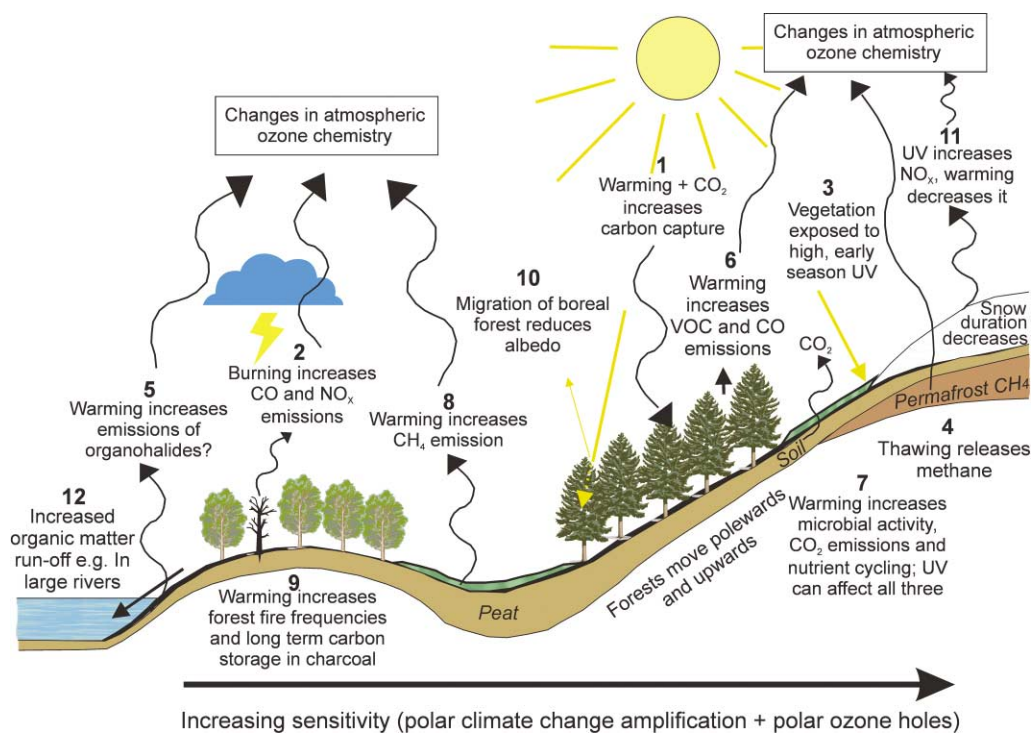


Fig. 1 Conceptual model illustrating the potential effects of enhanced UV radiation and climate change on biogeochemical cycles in terrestrial ecosystems. The evidence and bases for numbered hypotheses and processes relating to specific effects are discussed in the text. Key: CO = carbon monoxide, NO_x = oxides of nitrogen, CH₄ = methane, CO₂ = carbon dioxide, VOC = volatile organic compounds.

its capture (photosynthesis), storage (biomass and soil organic matter content) and release (plant and soil organism respiration). Secondly, UV exposure can affect the cycling of mineral nutrients such as nitrogen, upon which plant production and ecosystem productivity are dependent (Fig. 1).

A review of UV effects on biogeochemical cycles⁴ published since the last UNEP report¹, demonstrated the complexity of UV impacts on decomposition processes which are species and system-specific, and suggested that, overall, the effects were small and transient. However, there have been new studies, some of which show particular effects of UV-B on carbon and nitrogen cycling that are likely to be important in the long term. The implications of this recent research are presented here.

UV effects on terrestrial biogeochemistry

Carbon cycling. The capture of atmospheric carbon dioxide by green plants in photosynthesis and its storage in plant tissues (phytomass) is the fundamental process that supports life in the biosphere. The accumulation of dead organic matter in soils also stores carbon, making it less available as a greenhouse gas in the atmosphere. In contrast, the microbial respiration of organisms that decompose dead organic matter in the soil, together with the respiration of other organisms in the biosphere, return carbon to the atmosphere where it adds to existing greenhouse gases. Sometimes the gases released, such as methane and carbon monoxide, are chemically active and could alter atmospheric chemistry.

A quantitative review by Searles *et al.*⁵ of experiments seeking to identify the effect of UV on plants showed that shoot biomass and leaf area were decreased modestly by UV-B enhancement. However, shoot biomass was reduced only under very high levels of UV-B. Increased UV-B radiation was suggested to have little direct impact on carbon capture and storage in phytomass. Specific systems might, however, deviate from this general trend. Shoot density (number per m²) and height of a bog moss (*Sphagnum fuscum*) in a subarctic mire were reduced, although productivity was not affected over a two year period, probably due to high variability in the biomass

data.⁶ However, changes in the number of shoots could have long-term implications for biomass.

Microbial decomposition controls carbon and nutrient storage in soils, release to the atmosphere and availability to plants. Decomposition is controlled by numerous physical and biological parameters. Among the most important are temperature, soil moisture and the chemistry of the dead organic matter substrate. UV-B affects the chemistry of living leaves and these changes are often inherited by litter (dead organic material that falls to the ground).¹ Paul *et al.*⁴ showed that the chemistry of leaf litter as influenced by UV-B is chemical and species specific. Carbohydrates, cellulose, nitrogen, tannins and lignin vary greatly in both magnitude and direction in response to UV-B treatments. UV-B usually decreased the concentration of nitrogen in litter, although the effect is variable and often insignificant.⁴ As nitrogen content of litter is usually positively correlated with decomposition rate, increased UV would be expected to reduce decomposition rates in those litters where nitrogen concentrations are decreased. This expectation is supported by general increases in the carbon : nitrogen and carbon : lignin ratios under elevated UV-B as these parameters are generally good predictors of decomposition rate. In addition, increases in soluble phenolics in Scots pine seedlings under ambient UV, compared with exclusion treatments (where UV is filtered out),⁷ suggest another mechanism for expected decreased decomposition rates under higher UV-B levels in some species.

The soil flora and fauna also determine the rate of decomposition and the transformations and cycling of carbon and mineral nutrients. Early results showing that UV-B radiation can directly affect fungal and faunal communities associated with plant litter have been confirmed by recent studies. These show species-specific responses of soil fungi,⁸ litter and leaf surface fungi⁹ and fungi that are symbionts with oak. Overall, leaf surface fungi and the oak symbiont were more tolerant of elevated UV-B than soil and litter fungi. UV-B can also affect soil microfauna: amoebae were more numerous at near-ambient than in attenuated UV-B levels in UV filtration experiments on a southern Argentinian heathland.^{5,10} Soil microorganisms can also be affected indirectly.¹¹ After 5 years exposure of a

subarctic heath to enhanced UV-B radiation, alone and in combination with elevated CO₂, there were striking changes in microbial carbon and bacterial community structure. Microbial carbon was decreased by 50% in the UV-B treatment. The use of various carbon sources exposed to soil microorganisms suggested either a lower or less active population of bacteria in the enhanced UV treatments. Also, sole carbon source utilization tests, in which a range of individual carbon sources are made available as bacterial substrates, showed that UV-B caused a change in the soil microbial community structure, resulting almost certainly from a change in the dominant bacterial species.

Recently, a coordinated series of field experiments decomposed standard birch leaf litter under ambient and elevated UV-B at sites ranging from 38°N in Greece to 78°N on Arctic Svalbard¹². Transient changes in the fungal community decomposing the litter were found at a subarctic site¹² and were similar to those recorded by Newsham *et al.*¹³ on oak litter. Significant reductions in the mass loss of litter decomposing under enhanced UV-B occurred at two of the four sites.

UV-B can accelerate litter decomposition by photochemical processes. Although Moody *et al.*⁹ showed no photodegradation of leaf litter by weight loss, other results have demonstrated that senescent and dead leaves from temperate deciduous plants and tropical grasses produce CO on exposure to solar UV radiation.¹⁴ A recent study in Brazil provided additional evidence that CO is photoproduced from litter. Highest fluxes were late in the dry season, especially following burning of the Cerrado.¹⁵ A recent estimate indicated that about 60 teragrams (1 teragram equals 10¹² g) of CO may be produced annually from this process on a global basis.¹⁶ This is similar to earlier estimates and is sufficiently large that it should not be neglected when considering the global CO budget, particularly as CO reacts in the troposphere to influence ozone, other oxidants and aerosols.

Nitrogen oxides can also be produced from photodegradation processes in polar snowpacks in Greenland¹⁷, Michigan¹⁸ and the Antarctic.¹⁹ The process could result in destruction of tropospheric ozone in the snow pack but the extent and speed of ozone destruction probably also involve a catalytic destruction by bromide.¹⁷ Experiments²⁰ and field observations¹⁹ have shown that UV-B radiation induces the photochemical transformations of a variety of organic and inorganic substances containing nitrogen.

The release or storage of carbon and mineral nutrients depends on the final outcome of the indirect and direct effects of UV-B on decomposition.²¹ New studies, since those reported by Zepp *et al.*¹ and Paul *et al.*,⁴ confirm that UV-B effects are species and system-specific, with both increases²¹⁻²⁴, decreases^{8,12} (two of four sites) and no change in decomposition rates recorded¹² (two of four sites)²⁴ or inferred from lack of UV-B effects on leaf litter chemistry.²⁵ UV-B modifications of dead plant material of pine not only vary from species to species, but also from seed source to seed source.²⁴ Overall, studies that show effects of enhanced UV-B on decomposition suggest that these effects are small and confined to initial stages of decomposition according to Moody *et al.*¹² Even so, small effects over large areas are likely to be important. Recent findings that UV-B affects microbial immobilization of nitrogen and the structures of microbial communities after 5 years¹¹, and that UV-B effects on oak litter decomposition rate are maintained after four years²³, emphasize that our understanding is limited by the low number of long-term UV-B field experiments.

Nutrient cycling. In most natural and semi-natural terrestrial ecosystems, the availability of nitrogen in soil strongly constrains plant growth and productivity. In unmanaged and, to a lesser extent, managed ecosystems, the input of nitrogen to ecosystems by the fixation of atmospheric nitrogen is important.

This process commonly occurs by the activity of cyanobacteria that are free living or grow in symbiotic relationships with plants such as algae and lichens, and symbiotic rhizobia that are symbionts of higher plants. It has been known for some time that UV-B radiation reduces the fixation of nitrogen by cyanobacteria in rice paddy fields and other aquatic environments,²⁶ and the activity of N-fixing rhizobia bacteria.²⁷ Recently, work in the Arctic where nitrogen availability to plants is particularly limiting, has shown that UV-B radiation can constrain potential N₂ fixation there. Nitrogen fixation potential by cyanobacteria associated with one moss exposed to enhanced UV-B in the Northern Arctic was reduced by 50% compared with natural conditions, whereas that associated with a subarctic moss was not affected.²⁸ In addition, there was a 50% reduction in nitrogen fixation potential of a lichen exposed to enhanced UV-B in the Subarctic.²⁸

UV-B induces changes in the assimilation and allocation of mineral nutrients and other chemicals within the tissues of some plant species.²⁹ Changes in tissue chemistry that are inherited by litter affect decomposition²⁴ and nutrient cycling. However, not all species show changes in tissue chemistry when exposed to UV-B. Little impact of UV-B was expected on decomposition and nutrient cycling in mid-latitude dune grasslands³⁰ and oak woodlands²⁵ based on UV supplementation experiments that showed insignificant changes in plant tissue chemistry. Despite lack of change in tissue chemistry, however, decomposition was accelerated in the oak system.^{22,23} In contrast to studies showing no change, nitrogen concentrations in dead plant matter from several European heathlands, when decomposing under enhanced UV-B, were decreased.⁴ Although the fate of this nitrogen (*i.e.* subsequent uptake by plants, microbial immobilization or leaching) was not investigated, a recent long-term study showed that enhanced UV-B resulted in a significant immobilization of nitrogen in microbial biomass in a subarctic heath soil.¹¹ Microbial N increased over 100% in UV-B exposed field plots compared to control plots and microbial biomass C : N ratio decreased by 320%. These effects could possibly be the result of UV-B impacts on exudation of microbial resources from roots of plants irradiated with enhanced UV-B as suggested by Klironomos and Allen³¹. Many plants increase their ability to take up nutrients by having a symbiotic relationship with a fungus (a mycorrhiza) that provides an efficient nutrient foraging and capture system for the plant. However, exposure to enhanced UV-B can reduce this potential by up to 20%.²⁷ The processes of microbial immobilization of nitrogen and reduced mycorrhizal infection are expected to further limit nutrient availability and plant productivity.

Interactions between climate change and UV-B impacts on terrestrial biogeochemical cycling

Models of future climate change predict significant changes in variables that are important to terrestrial ecosystems such as temperature, precipitation, radiation reaching the Earth's surface and increases in atmospheric CO₂ concentration. There are several areas where interactions between climate change and UV-B that are non-additive and complex in nature can lead to non-linear changes in the behavior of biogeochemical cycles. UV exposure may induce changes in biological systems that moderate or enhance species responses to changes in climate and their roles in element cycling. Also, changes in climate, such as earlier snow melt in spring, might increase the exposure of species and biogeochemical processes to potential damage from UV-B.

Carbon fluxes and pools in phytomass. Changes in climate and/or climate variability have already had significant effects on carbon dynamics in terrestrial ecosystems^{32,33}, in that "greenness" of vegetation, length of the growing season and

biomass have increased in middle and northern latitudes of the Northern hemisphere. Such changes could potentially interact with UV-B effects. If moisture remains unaffected, climatic warming and increased atmospheric concentrations of CO₂ will increase carbon pools in phytomass, particularly in northern forests and tundra, due to increased growth of existing vegetation (Fig. 1, pathway 1) and displacement of this existing vegetation by more productive vegetation (Fig. 1).^{34–37} Increased biomass production has already occurred in northern areas due to recent warming.³² However, UV-B has the potential to reduce biomass in some ecosystems and should to some extent modify the increase in carbon in phytomass due to warming.

Climate change induces disturbance of vegetation, which is important because it increases forest fires (Fig. 1, pathway 2), forest pest outbreaks, over-grazing, drought, and thawing permafrost. For example, defoliation of forests due to increased insect pest outbreaks resulting from greater pest survival in milder winters^{38,39} could interact with UV-mediated changes in food quality that increase^{40–42} or decrease grazing⁵ leading to changes in carbon and nitrogen pools over large areas. Earlier snow melt has been exposing plants in the Northern Hemisphere to higher UV levels in Spring³³ (Fig. 1, pathway 3), and thawing permafrost and methane-containing clathrates have the potential to release large quantities of CH₄ (Fig. 1, pathway 8).⁴³

Plants of some ecosystems, particularly those of salt marshes, but also peatlands and forest floor vegetation, are important in enhancing fluxes of halogenated hydrocarbons from the biosphere to the atmosphere (Fig. 1, pathway 5).⁴⁴ This is important in contributing to the global pool of these chemically reactive substances.^{45,46} Some plant species are particularly efficient at transporting halomethanes into the atmosphere. As this is an active physiological process, emissions should increase in response to warming. The emissions of halogenated compounds from coastal salt marshes also are likely to be affected by sea level rise associated with global warming. Any impact of elevated UV-B on plant species that emit halocarbons would modify expected responses due to global warming. Warming also induces significant changes in the production and emission of VOCs that are derived from terrestrial vegetation, resulting in an alteration in the tropospheric production of ozone and a resulting perturbation of the oxidative capacity of the troposphere^{47,48} (Fig. 1, pathway 6).

Changes in the production of CO by UV-induced oxidation of plant matter could be affected by climate change in several ways. Climate-sensitive parameters such as humidity and temperature have important effects on the efficiency of CO photo-production (Fig. 1, pathway 6).^{14–16} The efficiency increases as temperature and humidity increase. Also, CO production efficiencies increase sharply as plants start to senesce and die and so increased drought frequency associated with climate change in some regions could increase UV-induced CO emissions.¹⁴

Carbon pools and fluxes in soils. If moisture remains unaffected, climatic warming will lead to decreased carbon pools in soils, particularly in northern forests and tundra where global warming is amplified, and in peatlands and wetlands where carbon storage is most pronounced.^{49–51} The mechanism involved increased rates of microbial decomposition and an increased flux of carbon as CO₂ from dryer areas (Fig. 1, pathway 7) and CO₂ and CH₄ from wetter areas (Fig. 1, pathway 8). Methane is an important greenhouse gas and a major source of hydrogen for the production of water vapor *via* reaction with hydroxyl radicals in the stratosphere. Thus, increased CH₄ may enhance ozone depletion on polar stratospheric clouds (PSCs). In contrast, higher UV-B should increase carbon storage in soils in which nutrients are particularly limiting to plant growth by changing litter quality and influencing decomposer organisms (Fig. 1, pathway 7), although in some ecosystems, higher UV-B may reduce carbon storage in soil or remain

neutral. Paul *et al.*⁴ suggest that any changes in carbon storage will be small and they imply that small changes will be insignificant. However, even small changes in carbon storage in peatlands, northern boreal forests and tundra, where most of the earth's organic carbon is stored,⁵² could be at least regionally important. In wetland ecosystems, *e.g.* rice paddies, the magnitude of emissions of CH₄ to the atmosphere depends on the particular plant species present.⁵³ Global methane emissions are likely to increase by 45% for a global 2 °C average warming (Fig. 1, pathway 8).⁵⁴ Any negative impact of UV on the activity of those plants that efficiently transport CH₄ to the atmosphere could be important in reducing the impact of warming on CH₄ emissions as shown by Niemi *et al.*⁵⁵ In drier ecosystems, such as arid lands, with high UV-B, storage of soil carbon during warming will be reduced by increased UV-B and warming together, because of photodegradation of litter and reduced litter production through increased water stress. On the other hand, warming will result in increased carbon storage due to reduced microbial activity limited by water. The balances between these complex interactions are unknown.

Increased atmospheric CO₂^{56,57} and UV-B radiation both result in a change in litter chemistry that would suggest additive or even synergistic decreases in decomposition and increased carbon storage in soils (but see Norby and Cotrufo⁵⁸ for a cautionary viewpoint). Experimentally increased UV-B and CO₂ together are likely to increase microbial immobilisation of nitrogen that is, in turn, expected to reduce nitrogen availability for plant production.¹¹

Fire reduces short-term carbon storage but enhances the storage of a fraction for millennia by producing charcoal (Fig. 1, pathway 9), a persistent form of carbon⁵⁹, but it also results in loss of nitrogen to the atmosphere⁶⁰, reducing productivity over the long term in nitrogen-limited ecosystems. Fires also increase the UV-mediated release of CO from vegetation and litter¹⁵. Fire frequency is increasing in some areas such as the boreal forests of North America and is expected to increase further as a result of global warming: this could affect atmospheric ozone chemistry.^{47,48} Moreover, since many forest fires occur in the mid- to high-northern latitudes, these burned regions are particularly subject to ozone depletion and increases in UV.

Effects of warming through impacts on surface energy and water balances. Increased atmospheric CO₂ concentrations result in less water use by plants which leads to less evaporative cooling and thus warming of the earth's surface in daytime.⁶¹ Increased UV-B might also restrict water loss by plants through stomata (small pores in leaves)⁶² and together with increased CO₂, there is potential to increase surface temperature additively. In addition, models of feedbacks from vegetation to the climate system calculate that decreases in albedo (reflectivity) associated with the displacement of tundra by evergreen forest will dominate over the negative feedback of increased carbon sequestration (Fig. 1, pathway 10).^{35,36} If UV-B affects the optical properties of leaves, there could be an effect on albedo (reflectivity).

Nitrogen cycling. Climatic warming, assuming a constant moisture content, will stimulate nitrogen cycling rates in soils as a result of increased microbial decomposition of litter⁵¹ and possibly increased activity of free-living and symbiotic nitrogen fixers. UV-B can reduce or increase nitrogen cycling rates through its effects on litter decomposition (overall the effect is to reduce nitrogen cycling) and it can also reduce nitrogen fixation by cyanobacteria directly. Again, the balance between the processes is unknown but warming effects are likely to dominate over UV effects (Fig. 1, pathway 7). The results of changes in nitrogen cycling are two-fold. Firstly, there will be changes in the amount of N₂O, which participates in chemical reactions

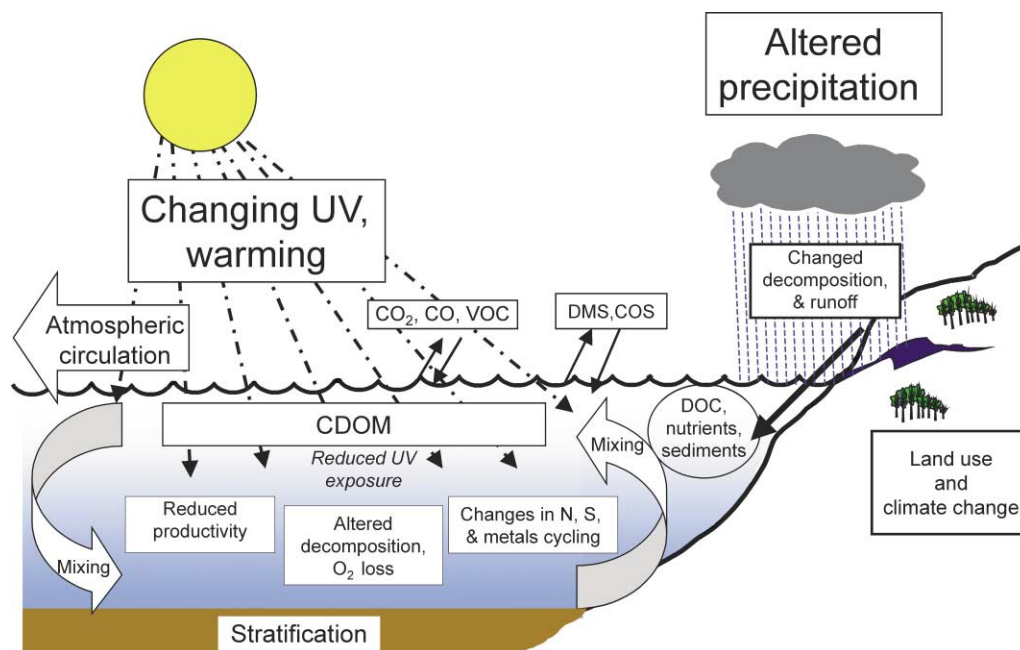


Fig. 2 Aquatic biogeochemical cycles affected by UV radiation and their interaction with other co-occurring environmental changes such as global warming and land use change. Key: DMS dimethyl sulfide; CDOM colored dissolved organic matter, the primary UV absorbing substance in aquatic environments; DOC dissolved organic carbon (see text for explanation).

that affect stratospheric O_3 , emitted from soil to atmosphere. Secondly, plant productivity will increase in response to increased temperature caused by greenhouse warming and to enhanced nitrogen availability in most mesic to dry terrestrial ecosystems. Also, NO_x production by snowpacks will be reduced because of reduced snow duration (Fig. 1, pathway 11).³

Aquatic ecosystems

Changes in UV can have significant effects on aquatic carbon cycling, nutrient cycling, and water-air trace gas exchange. In this section we discuss results on UV-aquatic biogeochemistry interactions that were obtained since our last report¹, taking into account the fact that co-occurring climate change can influence the UV effects (Fig. 2). UV effects on aquatic ecosystems are further treated in Häder *et al.*,²⁶ and Kerr *et al.*⁶³ provide additional updates on recent measurements of UV radiation in aquatic systems.

UV effects on aquatic biogeochemistry

Carbon cycling. Phytoplankton communities are primarily responsible for the production of biomass in large lakes and the ocean. Direct DNA damage caused by UV-B has been observed in Antarctic marine phytoplankton and bacterioplankton during mid-summer, especially under stratified conditions related to melting shelf ice.⁶⁴ A recent study has shown that the UV sensitivity of mid-latitude estuarine phytoplankton photosynthesis is remarkably similar to that previously observed for Antarctic phytoplankton.⁶⁵ These results provide further evidence that UV reduces phytoplankton productivity globally in the ocean, although the UV sensitivity of open ocean phytoplankton is still poorly defined. On the other hand, UV photoinhibition of productivity may be partially offset by other indirect effects of UV on iron in the ocean. Photoreactions of complexed iron enhance its biological availability,⁶⁶ a process that may stimulate productivity in parts of the sea that are iron limited, such as the Southern Ocean.⁶⁷ Atmospheric iron deposition correlates closely with observed productivity in parts of the sea.⁶⁸ Thus, the net impact of increased UV on phytoplankton productivity is unclear at this point. However, a recent study based on remote sensing indicates that global oceanic chlorophyll has decreased globally between the early 1980's and

the late 1990's.⁶⁹ The overall decrease was attributed to changes in upper ocean mixing, mixed layer depth, sea surface temperature and nutrient supply caused by climate change.⁶⁹ Based on other research that is discussed below, the decreases could have been partly attributable to increases in UV exposure in the upper ocean caused by ozone depletion and by climate-induced changes in mixing, stratification and UV penetration.

As discussed in this volume²⁶ and in the UNEP 1998 report^{1,70}, other indirect effects involving trophic level interactions may also affect ecosystem productivity. For example, recent research indicates that the vertical migration of zooplankton is sensitive to UV radiation.^{71,72} This finding has important implications for the flux of carbon through the microbial food web, which involves transfer of biomass from the primary producers to metazoa and bacteria. Thus, the net impact on carbon capture is clearly not a linear function of UV exposure.

UV effects on decomposition of aquatic organic matter are caused by inhibition of microbial activity, by direct photodegradation of colored dissolved organic matter (CDOM) and particulate organic carbon (POC) to CO_2 and other gases, and by UV-induced photodegradation of CDOM to readily decomposable compounds that are referred to here as biologically-labile photoproducts (BLPs). Bacterial activity is inhibited by UV-B radiation and direct DNA damage has been demonstrated in field studies.^{64,73,74} The greatest damage to bacterioplankton is observed in the upper layer of poorly mixed, stratified waters. However, observations showed that the reduction in microbial activity is attenuated with increased winds and surface layer mixing and the activity is rapidly restored in the dark *via* repair and regrowth.^{73,74} A modeling study concluded that changes in UV radiation caused by ozone depletion could have a more serious net impact on bacterial activity than UV increases attributable to decreased CDOM concentrations.⁷⁵ Viruses can influence microbial diversity and activity, including decomposition, and viral activity is sensitive to UV-B exposure.⁷⁶

In freshwaters and the coastal ocean, a large part of the CDOM is "terrestrially-derived", *i.e.* it is derived from the decomposition of terrestrial plant matter that is transported from the land (Fig. 1, pathway 2). Microorganisms do not readily decompose terrestrially-derived CDOM, but its transformation can be accelerated when it is exposed to solar ultraviolet

radiation. Recent research has provided additional evidence that the two major decomposition processes induced by solar UV are direct photoproduction of both dissolved inorganic carbon (DIC)⁷⁷⁻⁷⁹ and labile organic substances that are readily assimilated by microorganisms.⁸⁰⁻⁸⁷ UV exposure also enhances the decomposition of particulate organic carbon in freshwaters.⁸⁸ Other recent results seem to indicate that the net effect of UV exposure on algal- or some plant-derived DOC is a reduction in biological lability.^{83,89-92} Exposure to solar UV radiation also causes changes in CDOM isotopic content,^{93,94} that are useful in understanding the fate and transport of carbon and oxygen in the environment.^{77,95}

The direct photodegradation processes involve, in part, reactive oxygen species (ROS) such as hydrogen peroxide, superoxide ions and hydroxyl radicals, as well as short-lived reductants such as hydrated electrons that are produced on absorption of UV radiation.⁹⁶⁻¹⁰³ Complex interactions of the ROS with iron and copper complexes that are present in surface waters and in precipitation^{103,104} help control the nature and extent of carbon cycling in aquatic environments.^{77,100,105}

Marine scientists have long debated the fate of terrestrially-derived organic matter on entry to the ocean. Experimental studies indicate that the DOC in the open ocean is primarily of marine origin, although some terrestrial character would have been expected.^{87,93,106} Recent experimental and modeling research indicates that UV-stimulated decomposition can potentially consume all of the input of CDOM from land.^{95,107} Most of this decomposition potentially occurs in coastal areas of the Northern hemisphere, with substantial contributions from high-latitude coastal regions.

Recent studies of a wide range of freshwater and marine environments have shown that CDOM, and, to a lesser extent in the open ocean, organic colloids, play an important role in the attenuation of solar UV and blue radiation.¹⁰⁸⁻¹¹¹ CDOM effectively protects aquatic ecosystems from harmful UV-B radiation while permitting beneficial photorepairing (UV-A) and photosynthetically active radiation to be much more efficiently transmitted into the water. Changes in CDOM concentrations occur seasonally in freshwaters^{112,113} and the ocean^{108,111} and they also likely are linked to climate change, acid deposition¹¹⁴ and land use changes. The UV absorbance and fluorescence of CDOM decreases with exposure to solar UV radiation and recent research has demonstrated that this "photobleaching" process is induced most efficiently by UV-B radiation.¹¹⁵⁻¹¹⁷ A combination of photochemical and microbial processes is responsible for the photobleaching^{77,85,99,107,115,117} and the efficiency is affected by factors such as oxygen concentration^{77,95} and temperature.⁹³ Although one study in U.S. freshwaters has indicated that photobleaching rates are related to acid-neutralizing capacity¹¹⁸, other investigations in Chilean, Argentinian and Antarctic freshwaters indicate that alkalinity has no detectable effect (H. Zagarese, personal communication, 2002). The UV-induced changes in CDOM concentrations can influence remote sensing of oceanic productivity, which is based on observations of ocean color. New results indicate that CDOM makes a major contribution to remotely-sensed ocean color.¹⁰⁸

Nutrient cycling. UV radiation can affect nitrogen cycling in various ways: through effects on nitrogen-related enzymatic activity by microorganisms such as photoinhibition of nitrogen-fixing microorganisms²⁶ and, indirectly, through effects on the biological availability of essential trace elements, such as iron, that stimulate the growth of nitrogen fixers; and through enhanced decomposition of persistent dissolved organic nitrogen to biologically labile nitrogenous photo-products. Nitrogen is a limiting nutrient in remote parts of the open ocean and thus impacts of UV radiation on important nitrogen fixing cyanobacteria such as *Trichodesmium*¹¹⁹ or the newly discovered N-fixing marine nanoplankton¹²⁰ potentially

could be ecologically significant. Iron plays a role in stimulating the growth of *Trichodesmium*.¹²¹ It has been proposed that the iron deposited in the sea *via* long range transport of terrestrial dust⁶⁸ can stimulate rapid growth of this organism and that related increases in biologically-available nitrogen can trigger growth in toxic organisms such as *Gymnodinium breve*.¹²² UV-induced photoreactions of iron are known to affect its biological availability in the sea.⁶⁶

Biologically labile nitrogen compounds such as nitrate, ammonium and amino acids are rapidly recycled by the biota in aquatic systems, while N-containing substances whose structures are too complex or randomized to be readily assimilated accumulate in the water column. In aquatic environments with limited N-fixation or low external inputs of labile N, the labile compounds drop to almost unmeasurable levels in the photic zone where productivity occurs, while the persistent dissolved organic nitrogen (DON) accumulates. Interactions of UV radiation and DON provide a pathway for the conversion of persistent DON to compounds that are more easily assimilated by aquatic microorganisms. Recent results suggest that photochemically-produced labile nitrogen compounds can be an important source of biologically available nitrogen in coastal regions.¹²³⁻¹²⁵

Phosphorus cycling can potentially also be affected by exposure to UV. The changes in microbial consortia that are discussed in the carbon cycling section likely influence phosphorus cycling as well. In addition, recent research has provided additional evidence that UV photolysis of phosphate-humic substance complexes can enhance phosphorus cycling in aquatic environments.^{126,127}

UV-B and trace gas exchange. The aquatic environment is an important atmospheric source and sink of trace carbon, sulfur and other gases. Recent research on the air-sea exchange of trace gases has provided evidence that the sources and sinks of certain carbon and sulfur gases are strongly influenced by solar UV radiation.¹²⁸

New research has appeared on the effects of UV radiation on the emissions of volatile organic compounds (VOC) and carbon monoxide from aquatic environments. These gases participate in chemical reactions that change air quality in the atmosphere. Isoprene emissions correlate with chlorophyll concentrations, indicating that phytoplankton or reactive DOM released by phytoplankton is the source^{128,129} and thus that phytoplankton inhibition by UV likely alters isoprene emissions. The sea is thought to be a net source of CO, but this source has been subject to a wide range of estimates. A recent study estimated a much lower CO photoproduction in the ocean than previously reported and that most of this CO production was consumed by microorganisms rather than escaping to the atmosphere.¹³⁰ CO is photoproduced most efficiently by UV-B radiation and the efficiencies for CO photoproduction from terrestrially-derived CDOM are much larger than those observed with open ocean CDOM. This difference in efficiencies, which largely accounts for the lower estimated CO photoproduction in the open ocean, suggests that the photoreactivity of open-ocean CDOM derived from algae may be quite different from that of terrestrially-derived CDOM.

Atmospheric sulfur plays an important role in the radiative balance of the atmosphere. Anthropogenic sources are dominant in highly industrialized regions and are reasonably well defined. Natural sources and sinks of sulfur gases are much less well defined than anthropogenic sources, but have received greater scrutiny in recent years due to their potential involvement in the regulation of climate in remote parts of the ocean. The major source of natural sulfur gases is the sea. Of particular interest are the sulfur gases, dimethylsulfide (DMS) and carbonyl sulfide (COS). Both of these compounds are formed predominantly in aerobic marine environments, *i.e.* the

upper layers of the ocean, and their sources and sinks are affected by solar UV radiation.

DMS, the predominant volatile sulfur compound in the open ocean, is believed to be involved in the formation of marine aerosols. Thus, DMS emissions may lead to modification of the reflectivity of marine clouds and have a cooling influence on the atmosphere. One might expect that, since DMS is closely related to primary productivity of certain phytoplankton species and that phytoplankton photosynthesis is inhibited by UV, DMS concentrations may decrease as surface UV increases. This has indeed been found to be the case in Antarctica under the ozone hole.¹²⁸ On the other hand, a recent report provided evidence that DMS and dimethylsulfoniopropionate (DMSP), the oceanic precursor of DMS, has an antioxidant function in marine algae¹³¹. Thus, exposure of certain algae to UV, an important driver of cellular oxidant production, presumably would stimulate DMS production. The highest concentrations of DMS occur in the Southern Ocean during early to mid-spring as the sea ice melts¹³², a time in which that region also experiences high UV exposure due to ozone depletion. This indicates that the Southern Ocean may be a region of intense interactions between sulfur biogeochemistry and ozone depletion. Other recent research on the sensitivity of zooplankton to UV radiation^{71,72} suggests a potentially significant role of UV-zooplankton interactions in DMS production, whereby DMS emissions increase when the phytoplankton are stressed by zooplankton grazing. Recently it was also shown that changes in physical quantities such as mixed layer depth also influence DMS sea-to-air fluxes *via* UV-related biogeochemical interactions.¹³³ Photooxidation of DMS in the upper ocean is another significant sink that is induced by solar UV radiation.^{134–136}

COS is the most concentrated sulfur gas in the troposphere and it is believed to play a role in the maintenance of the stratospheric sulfate layer, although this role may be more limited than was originally believed.^{1,128} COS is primarily produced in surface seawater by the UV-related degradation of dissolved organic matter and it is degraded mainly by hydrolysis. In a modeling effort to describe global air-sea fluxes of COS based on known information about its sources and sinks, it was estimated that the open ocean was a net source of COS.¹³⁷

Interactions between climate change and UV-B impacts on biogeochemical cycles in freshwater, estuarine and coastal systems

UV penetration and global warming. Aquatic biogeochemical cycles can be affected in several ways through effects of various global environmental changes on UV exposure. Climate and land use change affect the movement of UV-attenuating dissolved and particulate substances from land into water (Fig. 1, pathway 12, Fig. 2). Such substances, particularly CDOM, control the penetration of UV-B into many aquatic environments.^{26,112,113,138–140} Microorganisms that are often exposed to UV-B radiation can develop cellular UV-protective substances such as mycosporine-like amino acids that absorb in the UV region.²⁶ Such organisms or detritus derived from them can contribute significantly to UV attenuation in ecosystems that have low concentrations of DOC.¹⁴¹ Observed seasonal changes have provided evidence for the important influence of climatic change on UV penetration into freshwaters^{112,113,138,142,143} and the ocean.^{110,111} Droughts, for example, reduce terrestrial inputs of CDOM and sediments into aquatic environments.^{138,142} In contrast, increased precipitation may reduce UV penetration by enhancing runoff (see Fig. 1, pathway 12 and Fig. 2). Shifts in soil moisture content and related changes in oxygen content affect the microbial production of soil humic substances and thus can alter inputs of this important source of CDOM in freshwaters. Moreover, global warming, through changes in atmospheric circulation, precipitation patterns,

temperature, and length of warm season, can affect stratification and vertical mixing dynamics in freshwaters and the sea.¹⁴⁴ Stratification can result in increased UV penetration and exposure in the upper water column, a phenomenon that is driven in part by UV-induced decomposition of UV-absorbing substances in the surface water.^{109–111,139,143} Changes in vertical mixing dynamics also can affect phytoplankton photosynthesis.¹⁴⁵ Reductions in oceanic primary productivity over the past decade have been attributed to climate change effects on the upper ocean⁶⁹ and this effect may be caused in part by increased UV penetration. The interactions of bacteria, organic matter, temperature and UV changes are complex and it is impossible at this point to predict how climate warming might affect UV penetration into aquatic environments. However, recent observations have shown that the warm upper layers of freshwaters and the ocean that develop under stratified conditions are generally much more UV transparent than deeper, cooler waters.^{109–111,113,139,143}

The past effects of climate change on UV exposure have had an impact on freshwater sedimentary records in a remarkable way. Careful analysis of fossil diatom assemblages in Canadian subarctic lake sediments has provided clear evidence of the impacts of climate change on UV penetration in Canadian lakes during the Holocene.^{146,147}

Carbon and nitrogen cycling. The possible effects of climatic warming on carbon capture and decomposition have been recently discussed in several reviews of freshwater^{138,148,149} and oceanic ecosystems.¹⁴⁴ Increasing temperatures tend to increase the rates of biological production and decomposition, but other factors such as reductions in nutrient concentrations in freshwaters related to altered hydrology could limit the increases. In the case of the oceans, the expected increase in the efficiency of phytoplankton photosynthesis and biological carbonate production due to warming may be counteracted by the effects of increased stratification that will likely lead to reduced CO₂ uptake.^{69,144} Stratification can affect CO₂ air-sea exchange by reducing uptake caused by the “solubility pump,” *i.e.* the transport of carbon from the upper ocean to the deep ocean, and it also may result in decreased photosynthesis and changed microbial decomposition caused by reduced nutrient upwelling⁶⁹ and increased exposure of microorganisms to UV-B. Vertical transport is the primary determinant of what chemical constituents and organisms are brought into the UV-illuminated layer and how long they stay there and stratification greatly slows vertical transport. Transport can be important when certain biogeochemical processes are slow compared to movement into and back out of the photic zone, *e.g.* for processes in which the overall impact depends on the sequence and timing of UV exposure. An example of processes likely to be affected by climate-related changes is decomposition by bacteria that are susceptible to strong UV damage but have weak repair capability.

Other UV interactions with co-occurring environmental changes can include: (1) pH related changes on productivity caused by increases in atmospheric CO₂ or acid deposition^{114,138} (2) increased UV phototoxicity caused by pollution of aquatic environments by substances such as polycyclic aromatic hydrocarbons (PAH) derived from the usage of fossil fuels,^{150,151} (3) large-scale changes in organic carbon movement from land to the sea caused by climate change, such as the increased Arctic inputs of CDOM to the coastal ocean that will affect UV induced carbon cycling in this region¹⁵² and climate-related and UV-induced changes on the decomposition of the CDOM in the Arctic Ocean.^{95,107,152}

Sulfur cycling. Any UV-B related changes at the surface of the ocean that result in the alteration in DMS flux to the atmosphere and the subsequent formation of particles will also alter the atmospheric radiation budget for the affected region.

UV effects on vertical migration of zooplankton can reduce the amount and timing of grazing induced release of DMS from marine phytoplankton. Recent results indicate that DMS emissions are possibly enhanced by an interaction between upper ocean stratification and UV inhibition of bacterioplankton that degrade DMS before it can escape the sea into the atmosphere.¹³³ DMS concentrations in the upper ocean also are affected by UV-related photooxidation.¹³⁴ The net effect is a feedback whereby climate warming and changing UV influence DMS release to the atmosphere. DMS conversion to particles in the atmosphere then results in a net change in radiative forcing. Carbonyl sulfide (COS) is formed by UV-induced photoreactions of dissolved organic sulfur in the upper ocean. Changes in climate-related vertical mixing dynamics and upper ocean temperature can greatly alter COS sea to air flux.¹³⁷ Model projections indicate that climate warming (mainly by decreasing COS solubility) and increased CO₂ levels (with resulting decreased pH and reduced hydrolysis of COS) should result in increased COS emissions from the open ocean.

Metal, oxygen and halogen cycling. Metals, especially iron and copper, play an important role in the upper ocean and freshwater biogeochemistry both by participating in UV-induced processes that produce and consume peroxides and other oxidants that participate in biogeochemical processes and also as essential trace elements for plankton. Inputs of metals and peroxides to aquatic systems change with changing precipitation patterns.^{103,104,153} UV-induced photoreactions of organic complexes of metals increase their biological availability.^{66,154} Changes in the biotic sources of such complexes as well as pH changes related to climate change would likely affect metal-UV biogeochemistry.

Oxygen cycling is also induced by UV interactions with dissolved organic matter. UV absorption by CDOM results in oxygen consumption^{77,83,95} and the production of reactive oxygen species (ROS) such as hydrogen peroxide, superoxide ions, singlet molecular oxygen, and hydroxyl radicals. ROS derived from the interactions of UV and DOM can participate in a variety of reactions with metals that help determine the oxidative capacity of the surface waters and the cycling of metals. Increased global temperatures are likely to change the rates and mechanisms of these reactions but the net effects are poorly defined.

The interactions of global warming and UV in halogen cycling are complex. The oceans are a net sink for organic halides¹⁵⁵ and, because hydrolytic loss of the halides is more sensitive to temperature change than biological production, global warming is likely to increase this sink. Increased UV may reduce production of the organic halides by inhibiting algal synthesis of these compounds or it may stimulate production by partly abiotic pathways, e.g. by UV-induced photoreactions that produce methyl iodide in the upper ocean¹⁵⁶ and or by enhancing formation of brominated methane derivatives such as bromoform *via* reactions of hydrogen peroxide with bromoperoxidases.^{157,158}

Acknowledgements

We wish to thank D. Gwynn Jones, T. Christensen, W. Helbling, H. Zagarese and P. Neale for helpful input and to A. Kristofersson for help with Fig. 1. We are grateful to N. Blough, W. Miller, D. Koopmans, D. Bronk and O. Zafiriou for making as yet unpublished material available. The UK Department for Environment, Food and Rural Affairs kindly supported the participation of T.V.C. This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use by the U.S. EPA.

References

- 1 R. G. Zepp, T. V. Callaghan and D. J. Erickson, III, Effects of enhanced solar ultraviolet radiation on biogeochemical cycles, *J. Photochem. Photobiol. B*, 1998, **46**, 69–82.
- 2 R. G. Zepp, T. V. Callaghan and D. J. Erickson, III, Effects of increased solar ultraviolet radiation on biogeochemical cycles, *Ambio*, 1995, **24**, 181–187.
- 3 IPCC, *IPCC guidelines for national greenhouse gas inventories*, OECD, Paris, France, 1997.
- 4 N. D. Paul, T. V. Callaghan, S. Moody, D. Gwynn-Jones, U. Johanson and C. Gehrke, in *Stratospheric ozone depletion: the effects of enhanced UV-B radiation on terrestrial ecosystems*, ed. J. Rozema, Backhuys Press, Leiden, 1999, pp. 117–134.
- 5 C. L. Ballaré, M. C. Rousseaux, P. S. Searles, J. G. Zaller, C. V. Giordano, T. M. Robson, M. M. Caldwell, O. E. Sala and A. L. Scopel, Impacts of solar ultraviolet-B radiation on terrestrial ecosystems of Tierra del Fuego (Southern Argentina). An overview of recent progress, *J. Photochem. Photobiol. B*, 2001, **62**, 67–77.
- 6 C. Gehrke, Effects of enhanced UV-B radiation on production-related properties of a *Sphagnum fuscum* dominated subarctic bog, *Funct. Ecol.*, 1998, **12**, 940–947.
- 7 M. Turunen, W. Heller, S. Stich, H. Sandermann, M.-L. Sutinen and Y. Norokorpi, The effects of UV exclusion on the soluble phenolics of young Scots pine seedlings in the subarctic., *Environ. Poll.*, 1999, **106**, 219–228.
- 8 K. J. Duguay and J. N. Klironomos, Direct and indirect effects of enhanced UV-B radiation on the decomposition and competitive abilities of saprobic fungi, *Appl. Soil. Ecol.*, 2000, **14**, 157–164.
- 9 S. A. Moody, K. K. Newsham, P. G. Ayres and N. D. Paul, Variation in the responses of litter and phylloplane fungi to UV-B radiation (290–315 nm), *Mycol. Res.*, 1999, **103**, 1469–1477.
- 10 P. S. Searles, S. D. Flint, S. B. Diaz, M. C. Rousseaux, C. L. Ballaré and M. M. Caldwell, Solar ultraviolet-B radiation influence on *Sphagnum* bog and *Carex* fen ecosystems: first field season findings in Tierra del Fuego, Argentina, *Global Change Biology*, 1999, **5**, 225–234.
- 11 D. Johnson, C. D. Campbell, D. Gwynn-Jones, J. A. Lee and T. V. Callaghan, Arctic soil microorganisms respond more to long-term ozone depletion than to atmospheric CO₂, *Nature*, 2002, **416**, 82–83.
- 12 S. Moody, N. D. Paul, L. O. Björn, T. V. Callaghan, J. A. Lee, Y. Manetas, J. Rozema, D. Gwynn-Jones, U. Johanson, A. Kyriassis and A. Oudejans, The direct effects of UVB radiation on *Betula pubescens* litter decomposing at four European field sites., *Plant Ecol.*, 2001, **154**, 29–36.
- 13 K. K. Newsham, A. R. McLeod, J. D. Roberts, P. D. Greenslade and B. A. Emmet, Direct effects of elevated UV-B radiation on the decomposition of *Quercus robur* leaf litter, *Oikos*, 1997, **79**, 592–602.
- 14 D. W. Schade, R. M. Hoffman and P. J. Crutzen, CO emissions from degrading plant matter: measurements (I), *Tellus*, 1999, **51B**, 889–908.
- 15 K. Kisselle, R. Zepp, R. Burke, A. Pinto, M. Bustamante, S. Opsahl, R. Varella and L. Viana, Seasonal soil fluxes of carbon monoxide in burned and unburned Brazilian savannas, *J. Geophys. Res. D*, 2002, in press.
- 16 D. W. Schade and P. J. Crutzen, CO emissions from degrading plant matter: estimate of a global source strength (II), *Tellus*, 1999, **51B**, 909–918.
- 17 M. C. Peterson and R. E. Honrath, Observations of rapid photochemical destruction of ozone in snowpack interstitial air, *Geophys. Res. Lett.*, 2001, **28**, 511–514.
- 18 R. E. Honrath, M. C. Peterson, M. P. Dziobak, J. E. Dibb, M. A. Arsenault and S. A. Green, Release of NO_x from sunlight-irradiated midlatitude snow, *Geophys. Res. Lett.*, 2000, **27**, 2237–2240.
- 19 A. E. Jones, R. Weller, P. S. Anderson, H. W. Jacobi, E. W. Wolff, O. Schrems and H. Miller, Measurements of NO_x emissions from the Antarctic snowpack, *Geophys. Res. Lett.*, 2001, **28**, 1499–1502.
- 20 Y. Dubowski and M. R. Hoffmann, Photochemical transformations in ice: implications for the fate of chemical species, *Geophys. Res. Lett.*, 2000, **27**, 3321–3324.
- 21 J. Rozema, B. Kooi, R. Broekman and L. Kuijper, in *Stratospheric ozone depletion: the effects of enhanced UV-B radiation on terrestrial ecosystems*, ed. J. Rozema, Backhuys Press, Amsterdam, 1999, pp. 135–156.
- 22 K. K. Newsham, P. D. Greenslade, V. H. Kennedy and A. R. McLeod, Elevated UV-B radiation incident on *Quercus robur* leaf canopies enhances decomposition of resulting leaf litter in soil, *Global Change Biology*, 1999, **5**, 403–409.
- 23 K. K. Newsham, J. M. Anderson, T. H. Sparks, P. Splatt, C. Woods and A. R. McLeod, UV-B effect on *Quercus robur* leaf litter

- decomposition persists over four years, *Global Change Biology*, 2001, **7**, 479–483.
- 24 W. J. Cybulski, W. T. Peterjohn and J. H. Sullivan, The influence of elevated ultraviolet-B radiation (UV-B) on tissue quality and decomposition of loblolly pine (*Pinus taeda* L.) needles, *Environ. Exp. Bot.*, 2000, **44**, 231–241.
- 25 K. K. Newsham, P. Platt, P. A. Coward, P. D. Greenslade, A. R. McLeod and J. M. Anderson, Negligible influence of elevated UV-B radiation on leaf litter quality of *Quercus robur*, *Soil Biol. Biochem.*, 2001, **33**, 659–665.
- 26 D.-P. Häder, H. D. Kumar, R. C. Smith and R. C. Worrest, Aquatic ecosystems: effects of increased solar ultraviolet radiation and interactions with other climatic change factors., *Photochem. Photobiol. Sci.*, 2003, in press.
- 27 J. W. M. Van de Staaij, J. Rozema and R. Aerts in *Stratospheric ozone depletion: the effects of enhanced UV-B radiation on terrestrial ecosystems*, ed. J. Rozema, Backhuys Press, Amsterdam, 1999, pp. 159–171.
- 28 B. Sølheim, U. Johanson, T. V. Callaghan, J. A. Lee, D. Gwynn Jones and L. O. Björn, The nitrogen fixation potential of arctic cryptogam species is influenced by enhanced UV-B radiation, *Oecologia*, 2002, **133**, 90–93.
- 29 M. M. Caldwell, C. L. Ballaré, J. F. Bornman, S. D. Flint, L. O. Björn, A. H. Teramura, G. Kulandavailu and M. Tevini, Terrestrial ecosystems, increased solar ultraviolet radiation and interactions with other climatic change factors, *Photochem. Photobiol. Sci.*, 2003, in press.
- 30 H. A. Verhoef, J. M. H. Verspagen and H. R. Zoomer, Direct and indirect effects of ultraviolet-B radiation on soil biota, decomposition and nutrient fluxes in dune grassland soil systems, *Biol. Fert. Soils*, 2000, **31**, 366–371.
- 31 J. N. Klironomos and M. F. Allen, UV-B mediated changes on below-ground communities associated with the roots of *Acer saccharum*., *Funct. Ecol.*, 1995, **9**, 923–930.
- 32 R. B. Myneni, J. Dong, C. J. Tucker, R. K. Kaufmann, P. E. Kauppi, J. Liski, L. Zhou, V. Alexeyev and M. K. Hughes, A large carbon sink in the woody biomass of northern forests, *Proc. Nat. Acad. Sci. USA*, 2001, **98**, 14784–14789.
- 33 R. B. Myneni, C. D. Keeling, C. J. Tucker, G. Asrar and R. R. Nemani, Increased plant growth in the northern high latitudes from 1981–1991, *Nature*, 1997, **386**, 698–702.
- 34 J. M. Melillo, A. D. McGuire, D. W. Kicklighter, B. Moore, III, C. J. Vorosmarty and A. L. Schloss, Global change and terrestrial net primary production, *Nature*, 1993, **363**, 234–240.
- 35 R. A. Betts, P. M. Cox, S. E. Lee and F. I. Woodward, Contrasting physiological and structural vegetation feedbacks in climate change simulations, *Nature*, 1997, **387**, 796–799.
- 36 P. Cox, R. Betts, C. Jones, S. Spall and I. Totterdell, Acceleration of global warming due to carbon-cycle feedbacks in a coupled climate model, *Nature*, 2000, **408**, 184–187.
- 37 R. Harding, P. Kuhry, T. R. Christensen, M. T. Sykes, R. Dankers and S. van der Linden, Climate feedbacks at the tundra-taiga interface, *Ambio Special Report*, 2002, 47–55.
- 38 O. Tenow, Hazards to a mountain birch forest—Abisko in perspective. Plant ecology in the subarctic Swedish Lapland, *Ecol. Bulls.*, 1996, **45**, 104–114.
- 39 S. Neuvonen, P. Niemelä and T. Virtanen, Climate change and insect outbreaks in boreal forests: the role of winter temperatures, *Ecol. Bulls.*, 1999, **47**, 63–67.
- 40 N. Buck and T. V. Callaghan, Impacts of increased UV-B radiation on the autumn moth caterpillar *Epirrita autumnata*. In: Animal responses to global change, *Ecol. Bulls.*, 1999, **47**, 68–76.
- 41 A. Lavola, R. Julkunen-Tiitto, P. Aphalo, T. de la Rosa and T. Lehto, The effect of UV-B radiation on UV-absorbing secondary metabolites in birch seedlings grown under simulated forest soil conditions, *New Phytol.*, 1997, **137**, 617–621.
- 42 A. Lavola, R. Julkunen-Tiitto, H. Roininen and P. Aphalo, Host-plant preference of an insect herbivore mediated by UV-B and CO₂ in relation to plant secondary metabolites, *Biochem. Syst. Ecol.*, 1998, **26**.
- 43 K. A. Kvenvolden, Gas hydrate, humans, *Ann. N. Y. Acad. Sci.*, 2000, **912**, 17–22.
- 44 C. H. Dimmer, P. G. Simmonds, G. Nickless and M. R. Bassford, Biogenic fluxes of halomethanes from Irish Peatland ecosystems, *Atmos. Environ.*, 2001, **35**, 321–330.
- 45 R. C. Rhew, B. J. Miller and R. Weiss, Natural methyl bromide and methyl chloride emissions from coastal salt marshes, *Nature*, 2000, **403**, 292–295.
- 46 Y. Yokouchi, Y. Nojiri, L. A. Barrie, D. Toom-Sauntry, T. Machida, Y. Inuzuka, H. Akimoto, H.-J. Li, Y. Fujinuma and S. Aoki, A strong source of methyl chloride to the atmosphere from tropical coastal land, *Nature*, 2000, **403**, 295–298.
- 47 R. L. McKenzie, L. O. Björn, A. Bais and M. Ilyas, Changes in biologically active ultraviolet radiation reaching the Earth's surface, *Photochem. Photobiol. Sci.*, 2003, in press.
- 48 K. R. Solomon, X. Tang, S. R. Wilson, P. Zanis and A. F. Bais, Changes in tropospheric composition and air quality due to ozone depletion, *Photochem. Photobiol. Sci.*, 2003, in press.
- 49 W. C. Oechel, S. T. Hastings, G. Vourlitis, M. Jenkins, G. Riechers and N. Grulke, Recent change of Arctic tundra ecosystems from a net carbon dioxide sink to a source, *Nature*, 1993, **361**, 520–523.
- 50 W. C. Oechel, G. L. Vourlitis, S. J. Hastings and S. A. Bochkarev, Change in arctic CO₂ flux over two decades: Effects of climate change at Barrow, Alaska, *Ecol. Apps*, 1995, **5**, 846–855.
- 51 J. M. Melillo, D. W. Kicklighter, A. D. McGuire, W. T. Peterjohn and K. M. Newkirk, in *Role of nonliving organic matter in the earth's carbon cycle* eds. R. G. Zepp and C. H. Sonntag, John Wiley & Sons, New York, 1995, pp. 175–189.
- 52 A. D. McGuire and J. E. Hobbie, in *Modeling the Arctic System: A Workshop Report of the Arctic System Science Program*, The Arctic Research Consortium of the United States, Fairbanks, Alaska, 1997, pp. 53–54.
- 53 M. G. Öqvist and B. H. Svensson, Vascular plants as regulators of emissions from a subarctic mire ecosystem., *Geophys. Res. Lett.*, in press.
- 54 T. R. Christensen, A. Joabsson, L. Ström, N. Panikov, M. Mastezanov, M. Öquist, B. H. Svensson, H. Nykänen, P. Martikainen and H. Oskarsson Factors Controlling Large Scale Variations in methane Emissions from Wetlands, submitted.
- 55 R. Niemi, P. J. Martikainen, J. Silvola, A. Wulff, S. Turtola and T. Holopainen, Elevated UV-B radiation alters fluxes of methane and carbon dioxide in peatland microcosms., *Global Change Biology*, 2002, **8**, 361.
- 56 M. M. Couteaux, M. Mousseau, M. L. Celerier and P. Bottner, Increased atmospheric CO₂ and litter quality: decomposition of sweet chestnut leaf litter with animal food webs of different complexities, *Oikos*, 1991, **61**.
- 57 M. F. Cotrufo, P. Ineson and A. P. Rowland, Decomposition of tree litters grown under elevated CO₂: effect of litter quality., *Plant and Soil*, 1994, **163**, 121–130.
- 58 R. L. Norby and M. F. Cotrufo, A question of litter quality, *Nature*, 1998, **396**, 17–18.
- 59 T. A. J. Kuhlbusch and P. J. Crutzen, A global estimate of black carbon in residues of vegetation fires representing a sink of atmospheric CO₂ and a source of O₂, *Global Biogeochem. Cycles*, 1996, **9**, 491–501.
- 60 T. A. J. Kuhlbusch, J. M. Lobert, P. J. Crutzen and P. Warneck, Molecular nitrogen emissions from denitrification during biomass burning, *Nature*, 1991, **351**, 135–137.
- 61 B. A. Kimball, P. I. Pinter, R. Garcia, R. LaMorte, G. W. Wall, D. J. Hunsaker, G. Wechsung, F. Wechsung and T. Kartschall, Productivity and water use of wheat under free-air CO₂ enrichment., *Global Change Biology*, 1995, **1**, 429–442.
- 62 L. Negash and L. O. Björn, Stomatal closure by ultraviolet radiation, *Physiol. Plant.*, 1986, **66**, 360–364.
- 63 J. B. Kerr, G. Seckmeyer, A. F. Bais, G. Bernhard, M. Blumthaler, S. B. Diaz, N. Krotkov, D. Lubin, S. Madronich, R. L. McKenzie, A. A. Sabziparvar and J. Verdebout, in *Scientific Assessment of Ozone Depletion: 2002*, WMO (World Meteorological Organization), Global Ozone Research and Monitoring Project, Report No. 47, 2003, in press.
- 64 A. G. J. Buma, M. K. D. Boer and P. Boelen, Depth distributions of DNA damage in Antarctic marine phyto- and bacterioplankton exposed to summertime UV radiation., *J. Phycol.*, 2001, **37**, 200–208.
- 65 A. T. Banaszak and P. J. Neale, Ultraviolet radiation sensitivity of photosynthesis in phytoplankton from an estuarine environment, *Limnol. Oceanogr.*, 2001, **46**, 592–603.
- 66 K. Barbeau, E. L. Rue, K. W. Bruland and A. Butler, Photochemical cycling of iron in the surface ocean mediated by microbial iron(III)-binding ligands, *Nature*, 2001, **413**, 409–413.
- 67 S. W. Chisholm, Stirring times in the Southern Ocean, *Nature*, 2000, **407**, 685–687.
- 68 D. J. Erickson, III, J. L. Hernandez, P. Ginoux, W. Gregg, R. Kawa, M. Behrenfeld, W. Esaias, C. McClain and J. Christian, Atmospheric iron deposition to the surface ocean and remotely sensed color: A global satellite correlation analysis, *EOS Trans. AGU*, 2001, **81**, F57.
- 69 W. W. Gregg and M. E. Conkwright, Decadal changes in global ocean chlorophyll, *Geophys. Res. Lett.*, 2002, **29**.
- 70 D. P. Häder, H. D. Kumar, R. C. Smith and R. C. Worrest, Effects on aquatic ecosystems, *J. Photochem. Photobiol. B*, 1998, **46**, 53–68.

- 71 D. M. Leech and C. E. Williamson, In situ exposure to ultraviolet radiation alters the depth distribution of *Daphnia*, *Limnol. Oceanogr.*, 2001, **46**, 416–420.
- 72 S. C. Rhode, M. Pawlowski and R. Tollrian, The impact of ultraviolet radiation on the vertical distribution of zooplankton of the genus *Daphnia*, *Nature*, 2001, **412**, 69–72.
- 73 W. H. Jeffrey, P. Aas, M. M. Lyons, R. B. Coffin, R. J. Pledger and D. L. Mitchell, Ambient solar-radiation induced photodamage in marine bacterioplankton, *Photochem. Photobiol.*, 1996, **64**, 419–427.
- 74 W. H. Jeffrey, R. J. Pledger, P. Aas, S. Hager, R. B. Coffin, R. Vonhagen and D. L. Mitchell, Diel, depth profiles of DNA photodamage in bacterioplankton exposed to ambient solar ultraviolet radiation, *Marine Ecol. Prog. Ser.*, 1996, **137**, 283–291.
- 75 Y. Huot, W. H. Jeffrey, R. F. Davis and J. J. Cullen, Damage to DNA in bacterioplankton: A model of damage by ultraviolet radiation and its repair as influenced by vertical mixing, *Photochem. Photobiol.*, 2000, **72**, 62–74.
- 76 S. W. Wilhelm, M. G. Weinbauer, C. A. Suttle and W. H. Jeffrey, The role of sunlight in the removal and repair of viruses in the sea, *Limnol. Oceanogr.*, 1998, **43**, 586–592.
- 77 H. Gao and R. G. Zepp, Factors influencing photoreactions of dissolved organic matter in a coastal river of the southeastern United States, *Environ. Sci. Technol.*, 1998, **32**, 2940–2946.
- 78 S. C. Johannessen and W. L. Miller, Quantum yield for the photochemical production of dissolved inorganic carbon in the ocean, *Mar. Chem.*, 2001, **76**, 271–283.
- 79 A. V. Vähätalo, M. S. Salonen, P. Taalas and K. Salonen, Spectrum of the quantum yield for photochemical mineralization of dissolved organic carbon in a humic lake, *Limnol. Oceanogr.*, 2001, **45**, 664–676.
- 80 S. Bertilsson and L. J. Tranvik, Photochemically produced carboxylic acids as substrates for freshwater bacterioplankton, *Limnol. Oceanogr.*, 1998, **43**, 885–895.
- 81 S. Bertilsson and L. J. Tranvik, Photochemical transformation of dissolved organic matter in lakes, *Limnol. Oceanogr.*, 2000, **45**, 753–762.
- 82 I. Obernosterer and G. J. Herndl, Differences in the optical and biological reactivity of the humic and nonhumic dissolved organic carbon component in two contrasting coastal marine environments, *Limnol. Oceanogr.*, 2000, **45**, 1120–1129.
- 83 I. Obernosterer, B. Reitner and G. J. Herndl, Contrasting effects of solar radiation on dissolved organic matter and its bioavailability to marine bacterioplankton, *Limnol. Oceanogr.*, 1999, **44**, 1645–1654.
- 84 M. A. Moran, W. M. Sheldon and J. E. Sheldon, Biodegradation of riverine dissolved organic carbon in five estuaries of the southeastern United States, *Estuaries*, 1999, **22**, 55–64.
- 85 M. A. Moran, W. M. Sheldon and R. G. Zepp, Carbon loss and optical property changes during long-term photochemical and biological degradation of estuarine dissolved organic matter, *Limnol. Oceanogr.*, 2000, **45**, 1254–1264.
- 86 M. A. Moran and R. G. Zepp, in *Microbial Ecology Of The Oceans*, ed. D. Kirchman, Wiley, New York, 2000, pp. 201–228.
- 87 K. Mopper and D. J. Kieber, in *The effects of UV radiation in the marine environment*, eds. S. de Mora, S. Demers and M. Vernet, Cambridge University Press, 2000, pp. 101–129.
- 88 A. M. Anesio, L. J. Tranvik and W. Graneli, Production of inorganic carbon from aquatic macrophytes by solar radiation, *Ecology*, 1999, **80**, 1852–1859.
- 89 R. Benner and B. Biddanda, Photochemical transformations of surface and deep marine dissolved organic matter: Effects on bacterial growth, *Limnol. Oceanogr.*, 1998, **43**, 1373–1378.
- 90 A. M. Anesio, C. M. T. Denward, L. J. Tranvik and W. Graneli, Decreased bacterial growth on vascular plant detritus due to photochemical modification, *Aquat. Microb. Ecol.*, 1999, **17**, 159–165.
- 91 L. J. Tranvik and S. Kokalj, Decreased biodegradability of algal DOC due to interactive effects of UV radiation and humic matter, *Aquat. Microb. Ecol.*, 1998, **14**, 301–307.
- 92 S. Ziegler and R. Benner, Effects of solar radiation on dissolved organic matter in a subtropical seagrass meadow, *Limnol. Oceanogr.*, 2000, **45**, 257–266.
- 93 S. Opsahl and R. G. Zepp, Photochemically-induced alteration of stable carbon isotope ratios (^{13}C) in terrigenous dissolved organic carbon, *Geophys. Res. Lett.*, 2001, **28**, 2417–2420.
- 94 C. L. Osburn, D. P. Morris, K. A. Thorn and R. E. Moeller, Chemical and optical changes in freshwater dissolved organic matter exposed to solar radiation, *Biogeochem.*, 2001, **54**, 251–278.
- 95 S. S. Andrews, S. Caron and O. C. Zafiriou, Photochemical oxygen demand in marine waters: A major sink for colored dissolved organic matter?, *Limnol. Oceanogr.*, 2000, **45**, 267–277.
- 96 P. P. Vaughan and N. V. Blough, Photochemical formation of hydroxyl radical by constituents of natural waters, *Environ. Sci. Technol.*, 1998, **32**, 2947–2953.
- 97 B. H. Yocis, D. J. Kieber and K. Mopper, Photochemical production of hydrogen peroxide in Antarctic waters, *Deep Sea Res., Pt 1-Oceanog. Res. Pap.*, 2000, **47**, 1077–1099.
- 98 J. V. Goldstone and B. M. Voelker, Chemistry of superoxide radical in seawater: CDOM associated sink of superoxide in coastal waters, *Environ. Sci. Technol.*, 2000, **34**, 1043–1048.
- 99 J. V. Goldstone, M. J. Pullin, S. Bertilsson and B. M. Voelker, Reactions of hydroxyl radical with humic substances: Bleaching, mineralization, and production of bioavailable carbon substrates, *Environ. Sci. Technol.*, 2002, **36**, 364–372.
- 100 B. M. Voelker, D. L. Sedlak and O. C. Zafiriou, Chemistry of superoxide radicals (O_2^-) in seawater: Reactions with organic Cu complexes, *Environ. Sci. Technol.*, 2000, **34**, 1036–1042.
- 101 J. G. Qian and D. J. Kieber, Photochemical production of the hydroxyl radical in Antarctic water Deep-Sea Res. Part 1, *Oceanogr. Res. Pap.*, 2001, **48**, 741–759.
- 102 T. E. Thomas-Smith and N. V. Blough, Photoproduction of hydrated electron from constituents of natural waters, *Environ. Sci. Technol.*, 2001, **35**, 2721–2726.
- 103 R. J. Kieber, W. J. Cooper, J. D. Willey and G. B. Avery, Hydrogen peroxide at the Bermuda Atlantic Time Series Station. Part 1: Temporal variability of atmospheric hydrogen peroxide and its influence on seawater concentrations, *J. Atmos. Chem.*, 2001, **39**, 1–13.
- 104 R. J. Kieber, K. Williams, J. D. Willey, S. Skrabal and G. B. Avery, Iron speciation in coastal rainwater: concentration and deposition to seawater, *Mar. Chem.*, 2001, **73**, 83–95.
- 105 L. Emmenegger, R. Schwarzenbach, L. Sigg and B. Sulzberger, Light-induced redox cycling of iron in circumneutral lakes, *Limnol. Oceanogr.*, 2000, **46**, 49–61.
- 106 W. Ludwig, The age of river carbon, *Nature*, 2001, **409**, 466.
- 107 W. L. Miller, M. A. Moran, W. M. Sheldon, R. G. Zepp and S. Opsahl, Determination of apparent quantum yield spectra for the formation of biologically labile photoproducts, *Limnol. Oceanogr.*, 2002, **47**, 343–352.
- 108 D. A. Siegel, S. Maritorea, N. B. Nelson, D. A. Hansell and M. Lorenzi-Kayser, Global distribution and dynamics of colored dissolved and detrital organic materials, *J. Geophys. Res.*, 2002, **107**, in press.
- 109 N. B. Nelson and D. A. Siegel, in *Biogeochemistry of Marine Dissolved Organic Matter*, eds. D. A. Hansell and C. A. Carlson, Academic Press, 2002.
- 110 N. B. Nelson, D. A. Siegel and A. F. Michaels, Seasonal dynamics of colored dissolved organic matter in the Sargasso Sea (Part I), *Deep Sea Res.*, 1998, **45**, 931–957.
- 111 A. Vodacek, N. V. Blough, M. D. DeGrandpre, E. T. Peltzer and R. K. Nelson, Seasonal variation of CDOM and DOC in the Middle Atlantic Bight: terrestrial inputs and photooxidation, *Limnol. Oceanogr.*, 1997, **42**, 674–686.
- 112 C. E. Williamson, R. S. Stemberger, D. P. Morris, T. M. Frost and S. G. Paulsen, Ultraviolet radiation in North American lakes: Attenuation estimates from DOC measurements and implications for plankton communities, *Limnol. Oceanogr.*, 1996, **41**, 1024–1034.
- 113 D. P. Morris, H. Zagarese, C. E. Williamson, E. G. Balseiro, B. R. Hargreaves, B. Modenutti, R. Moeller and C. Queimalinos, The attenuation of solar UV radiation in lakes and the role of dissolved organic carbon, *Limnol. Oceanogr.*, 1995, **40**, 1381–1391.
- 114 W. F. Donahue, D. W. Schindler, S. J. Page and M. P. Stainton, Acid induced changes in DOC quality in an experimental whole-lake manipulation, *Environ. Sci. Technol.*, 1998, **32**, 2954–2960.
- 115 R. F. Whitehead, S. d. Mora, S. Demers, M. Gosselin, P. Monfort and B. Mostajir, Interactions of ultraviolet-B radiation, mixing, and biological activity on photobleaching of natural chromophoric dissolved organic matter: A mesocosm study, *Limnol. Oceanogr.*, 2000, **45**, 278–291.
- 116 C. L. Osburn, H. E. Zagarese, D. P. Morris, B. R. Hargreaves and W. E. Cravero, Calculation of spectral weighting functions for the solar photobleaching of chromophoric dissolved organic matter in temperate lakes, *Limnol. Oceanogr.*, 2001, **46**, 1455–1467.
- 117 R. Del Vecchio and N. V. Blough, Photobleaching of chromophoric dissolved organic matter in natural waters: Kinetics and modeling, *Mar. Chem.*, 2003, in press.
- 118 I. Reche, M. L. Pace and J. J. Cole, Relationship of trophic and chemical conditions to photobleaching of dissolved organic matter in lake ecosystems, *Biogeochem.*, 1999, **44**, 259–280.
- 119 J. A. Fuhrman and D. G. Capone, Nifty nanoplankton, *Nature*, 2001, 593–594.

- 120 J. P. Zehr, J. B. Waterbury, P. J. Turner, J. P. Montoya, E. Omoregie, G. F. Steward, A. Hansen and D. M. Karl, Unicellular cyanobacteria fix N₂ in the subtropical North Pacific Ocean, *Nature*, 2001, **412**, 635–638.
- 121 I. Berman-Frank, J. T. Cullen, Y. Shaked, R. M. Sherrell and P. G. Falkowski, Iron availability, cellular iron quotas, and nitrogen fixation in *Trichodesmium*, *Limnol. Oceanogr.*, 2001, **46**, 1249–1260.
- 122 J. M. Lenes, B. P. Darrow, C. Cattrall, C. A. Heil, M. Callahan, G. A. Vargo, R. H. Byrne, J. M. Prospero, D. E. Bates, K. A. Fanning and J. J. Walsh, Iron fertilization and the *Trichodesmium* response on the West Florida shelf, *Limnol. Oceanogr.*, 2001, **46**, 1261–1277.
- 123 K. L. Bushaw-Newton and M. A. Moran, Photochemical formation of biologically-available nitrogen from dissolved humic substances in coastal marine systems, *Aquat. Microb. Ecol.*, 1999, **18**, 185–292.
- 124 W. W. Wang, M. A. Tarr, T. S. Bianchi and E. Engelhaupt, Ammonium photoproduction from aquatic humic, colloidal matter, *Aquat. Geochem.*, 2000, **6**, 275–292.
- 125 D. J. Koopmans and D. A. Bronk, Photochemical production of inorganic nitrogen from dissolved organic nitrogen in waters of two estuaries and adjacent surficial groundwaters, *Aquat. Microb. Ecol.*, **26**, 295–304.
- 126 M. J. Boavida and R. G. Wetzel, Inhibition of phosphatase activity by dissolved humic substances and hydrolytic reactivation by natural ultraviolet light., *Freshwater Biol.*, 1998, **40**, 285–293.
- 127 E. M. Espeland and R. G. Wetzel, Complexation, stabilization, and UV photolysis of extracellular and surface-bound glucosidase and alkaline phosphatase: Implications for biofilm microbiota, *Microb. Ecol.*, 2001, **42**, 572–585.
- 128 D. J. Erickson, III, R. G. Zepp and E. Atlas, Ozone depletion and the air-sea exchange of greenhouse and chemically reactive trace gases, *Chemosphere-Global Change Science*, 2000, **2**, 137–149.
- 129 D. J. Erickson III, and J. L. Hernandez, in *American Geophysical Union Monograph: Gas Transfer at Water Surfaces* eds. M. A. Donelan, W. M. Drennan, E. S. Saltzman and R. Wanninkhof, 2002, pp. 312–317.
- 130 O. C. Zafriou, S. A. Andrews and W. Wang, Concordant estimates of oceanic carbon monoxide source and sink processes in the Pacific yield a balanced global “blue-water” CO budget, *Global Biogeochem. Cycles*, in press.
- 131 W. G. Sunda, D. J. Kieber, R. P. Kiene and S. A. Huntsman, An antioxidant function for DMSP and DMS in marine algae, *Nature*, 2002, **418**, 317–320.
- 132 M. A. J. Curran and G. B. Jones, Dimethyl sulfide in the Southern Ocean: Seasonality and flux, *J. Geophys. Res.*, 2000, **105**, 20–459.
- 133 R. Simó and C. Pedrós-Alió, Role of vertical mixing in controlling the oceanic production of dimethyl sulfide, *Nature*, 1999, **402**, 396–398.
- 134 D. A. Toole, D. J. Kieber, R. P. Kiene and D. A. Siegel, The quantum yield of dimethylsulfide (DMS) photooxidation in the Sargasso Sea, *EOS Trans., American Geophysical Union*, 2002, **83**.
- 135 D. Slezak, A. Brugger and G. J. Herndl, Impact of solar radiation on the biological removal of dimethylsuloniopropionate and dimethylsulfide in marine surface waters, *Aquat. Microb. Ecol.*, 2001, **25**, 87–97.
- 136 A. D. Hatton, Influence of photochemistry on the marine biogeochemical cycle of dimethylsulphide in the northern North Sea, *Deep Sea Res.*, 2002, **49**, 3039–3052.
- 137 D. Preiswerk and R. G. Najjar, A global, open-ocean model of carbonyl sulfide and its air-sea flux, *Global Biogeochem. Cycles*, 2000, **14**, 585–598.
- 138 D. W. Schindler, J. P. Curtis, B. R. Parker and M. P. Stainton, Consequences of climate warming and lake acidification for UV-B penetration in North American boreal lakes, *Nature*, 1996, **379**, 705–708.
- 139 D. A. Siegel and A. F. Michaels, Quantification of non-algal light attenuation in the Sargasso Sea: Implications for biogeochemistry and remote sensing, *Deep Sea Res.*, 1996, **43**, 321–346.
- 140 M. D. DeGrandpre, A. Vodacek, R. Nelson, E. J. Burce and N. V. Blough, Seasonal seawater optical properties of the U.S. Middle Atlantic Bight., *J. Geophys. Res.*, 1996, **101**, 22727–22736.
- 141 I. Laurion, M. Ventura, J. Catalan, R. Psenner and R. Sommaruga, Attenuation of ultraviolet radiation in mountain lakes: Factors controlling the among- and within-lake variability, *Limnol. Oceanogr.*, 2000, **45**, 1274–1288.
- 142 D. W. Schindler, Widespread effects of climatic warming on freshwater ecosystems in North America, *Hydrol. Process.*, 1997, **11**, 1043–1067.
- 143 D. P. Morris and B. R. Hargreaves, The role of photochemical degradation of dissolved organic matter in regulating UV transparency of three lakes on the Pocono Plateau, *Limnol. Oceanogr.*, 1997, **42**, 239–249.
- 144 P. Falkowski, R. J. Scholes, E. Boyle, J. Canadell, D. Canfield, J. Elser, N. Gruber, K. Hibbard, P. Högberg, S. Linder, F. T. Mackenzie, B. I. Moore, T. Pedersen, Y. Rosenthal, S. Seitzinger, V. Smetacek and W. Steffen, The global carbon cycle: A test of our knowledge of Earth as a system, *Science*, 2000, **290**, 291–296.
- 145 P. J. Neale, E. W. Helbling and H. Zagarese, in *UV effects in aquatic organisms and ecosystems* eds. E. W. Helbling and H. Zagarese, Royal Society of Chemistry, Cambridge, UK, 2002, in press.
- 146 P. R. Leavitt, R. D. Vinebrooke, D. B. Donald, J. P. Smol and D. W. Schindler, Past ultraviolet radiation environments in lakes derived from fossil pigments, *Nature*, 1997, **388**, 457–459.
- 147 R. Pienitz and W. F. Vincent, Effect of climate change relative to ozone depletion on UV exposure in subarctic lakes, *Nature*, 2000, **404**, 484–487.
- 148 M. V. Moore, M. L. Pace, J. R. Mather, P. S. Murdoch, R. W. Howarth, C. L. Folt, C. Y. Chen, H. F. Hemond, P. A. Flebbe and C. T. Driscoll, Potential effects of climate change on freshwater ecosystems of the New England/Mid-Atlantic region, *Hydrol. Process.*, 1997, **11**, 925–947.
- 149 P. J. Mulholland, G. R. Best, C. C. Coutant, G. M. Hornberger, J. L. Meyer, P. J. Robinson, J. R. Stenberg, R. E. Turner, F. Veraherrera and R. G. Wetzel, Effects of climate change on freshwater ecosystems of the Southeastern United States and the Gulf Coast of Mexico, *Hydrol. Process.*, 1997, **11**, 949–970.
- 150 G. T. Ankley, S. A. Collyard, P. D. Monson and P. A. Kosian, Influence of ultraviolet light on the toxicity of sediments contaminated with polycyclic aromatic hydrocarbons., *Environ. Toxicol. Chem.*, 1994, **13**, 1791–1796.
- 151 G. T. Ankley, R. J. Erickson, G. L. Phipps, V. R. Mattson, P. A. Kosian, B. R. Sheedy and J. S. Cox, Effects of light intensity on the phototoxicity of fluoranthene to a benthic macro-invertebrate., *Environ. Sci. Technol.*, 1995, **29**, 2828–2833.
- 152 J. A. E. Gibson, W. F. Vincent, B. Nieke and R. Pienitz, Control of biological exposure to UV radiation in the Arctic Ocean: Comparison of the roles of ozone and riverine dissolved organic matter, *Arctic*, 2000, **53**, 372–382.
- 153 R. J. Kieber, B. Peake, J. D. Willey and B. Jacobs, Iron speciation and hydrogen peroxide concentration in New Zealand rainwater., *Atmos. Environ.*, 2001, **35**, 6041–6048.
- 154 W. G. Sunda, in *Role Of Non-Living Organic Matter in the Earth's Carbon Cycle* eds. R. G. Zepp and C. Sonntag, Wiley, New York, 1994, pp. 191–207.
- 155 J. Butler, Atmospheric chemistry-Better budgets for methyl halides?, *Nature*, 2000, **403**, 260–261.
- 156 R. M. Moore and O. C. Zafriou, Photochemical production of methyl iodide in seawater, *J. Geophys. Res.*, 1994, **99D**, 16415–16420.
- 157 R. M. Moore, R. Tokarczyk, V. K. Tait M. Poulin and C. Green, in *Naturally-Produced Organohalogenes* eds. A. Grimvall and W. B. De Leer, Kluwer Academic Publishers, 1995.
- 158 R. Wever, G. M. Tromp, B. E. Krenn and A. Marjani, Vantol, Brominating activity of the seaweed *Ascophyllum nodosum*, *Environ. Sci. Technol.*, 1991, **25**, 446–449.