

# Environmental effects of ozone depletion and its interactions with climate change: Progress report, 2005

United Nations Environment Programme, Environmental Effects Assessment Panel†

Received 3rd November 2005, Accepted 8th November 2005

First published as an Advance Article on the web 29th November 2005

DOI: 10.1039/b515670j

Since the first assessments in 1989, the complexity of the linkages between ozone depletion, UV-B radiation and climate change has become more apparent. This makes it even clearer than before that we are dealing with long-term developments, which can be complicated by large year-to-year variability.

## Introduction

The Vienna Convention for the Protection of the Ozone Layer (1985) exerts its specific actions *via* the Montreal Protocol on Substances that Deplete the Ozone Layer (1987). Almost all countries are involved; only six, with limited release of ozone depleting substances, have not yet ratified the Protocol.

The Parties to the Montreal Protocol are informed by three panels of experts. One of these is the Environmental Effects Assessment Panel (EEAP), which deals with effects of ozone depletion and its interactions with climate change. The EEAP produces an extensive assessment report for the Parties to the Montreal Protocol every four years, and in the intermediate years a brief Progress Report is prepared. These assessments aim at readability for non-specialists, but are based on scientific information published in the scientific literature. The latest full report was published in *Photochem. Photobiol. Sci.*, 2003, **2**, 1–72 and the previous progress report in *Photochem. Photobiol. Sci.*, 2005, **4**, 177–184.

## Ozone and UV changes

### International measures to control ozone depleting substances are working and the beginning of ozone recovery is no longer controversial

Statistical trend analyses have demonstrated that, globally, the average column of ozone reached a minimum in the late 1990s, and since then has started to recover at mid-latitudes in both hemispheres.<sup>1</sup> The analysis included the effects of variations in atmospheric circulation patterns. The observed changes in ozone are consistent with those expected from changes in atmospheric chemistry that would result from the actions mandated by the Montreal Protocol. However, the correlations with changes in atmospheric circulation<sup>1–3</sup> may indicate an interaction between ozone depletion and climate.

### Low concentrations of springtime ozone are predicted to persist in polar regions

In Antarctica, the springtime stratospheric ozone “hole” will continue to recur for the next decades. There will continue to be a large year-to-year variability. For example, the ozone hole in 2005 was large (Fig. 1) and developed early, like the record sized hole in 2003, but was rather small in 2004. Very large year-to-year variability is expected to continue in the Arctic, depending on the minimum temperatures reached. With global climate change, temperatures in the Arctic stratosphere are expected to continue to decrease, increasing the likelihood of severe ozone depletion on the surfaces of polar stratospheric clouds. For every degree of stratospheric cooling, a reduction in ozone of 15 Dobson Units can be expected.<sup>4</sup> This sensitivity is three times larger than had been estimated previously from model calculations, making future polar ozone depletion more susceptible to climate change.

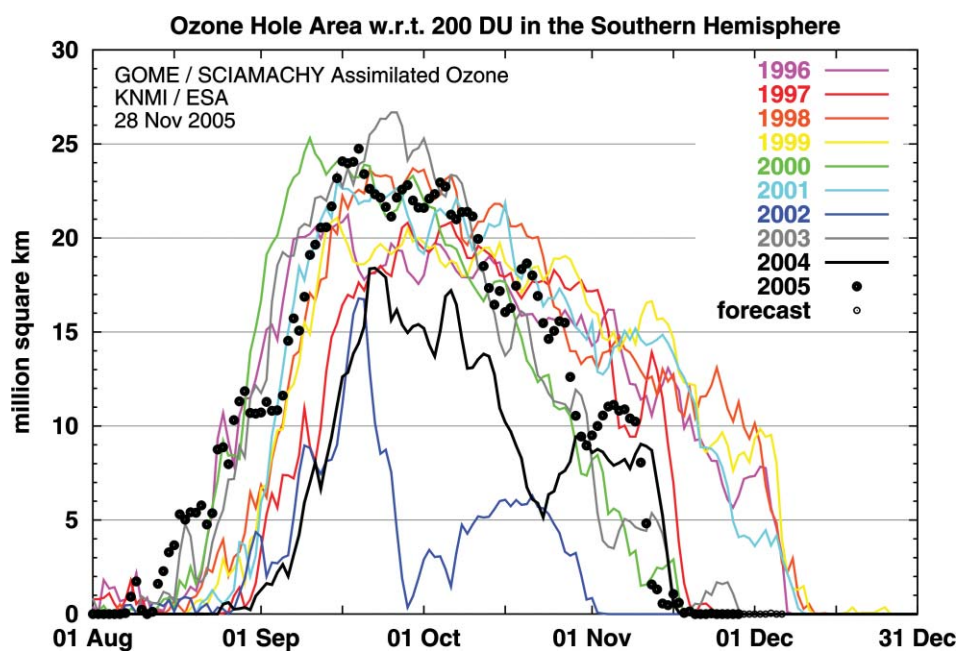
### Our understanding of interactions between ozone depletion and climate change has improved significantly

The effects of climate change on ozone depletion may be most pronounced—yet least understood—at high latitudes,<sup>5</sup> where springtime ozone losses are expected to continue up to ~2020.<sup>6</sup> The role of changes in atmospheric circulation seems increasingly important in modulating ozone variability.<sup>7–10</sup> Ozone heats the stratosphere by absorbing incoming solar energy and outgoing infrared from the surface of the earth. A significant component of the observed stratospheric cooling ( $-0.17$  °C decade<sup>-1</sup>) can be attributed to ozone depletion, rather than being solely a radiative effect of climate change.<sup>11</sup> Consequently, the future impact of climate change on the ozone layer at mid-latitudes may be diminished. Interactions with solar activity may also be more important for ozone depletion and UV increases than previously thought.<sup>12–19</sup>

### Further contributions towards understanding the effects of aerosols on UV radiation reaching the Earth's surface are now available

The UV absorbing properties of aerosols are now quantified<sup>20–24</sup> leading to improvements of satellite algorithms for more effective treatment of the interference of tropospheric aerosols in the derivation of surface UV irradiances.<sup>25,26</sup> This will enable more accurate satellite estimates of UV in the future.

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**Fig. 1** Area (millions of km<sup>2</sup>) where the total ozone column in the Southern Hemisphere is less than 220 DU (Dobson Unit, where 1 DU = 0.01 mm thickness at standard temperature and pressure). All the years from 1996 to 2005 (black dots) are shown. Graphic prepared by the KNMI, Het Koninklijk Nederlands Meteorologisch Instituut and ESA (European Space Agency) using data from GOME (Global Ozone Monitoring Experiment) a satellite based instrument and the scanning imaging absorption spectrometer for atmospheric chartography (SCIAMACHY) on board the ESA Envisat satellite.

**Reconstruction of historical UV records has improved, and the observed changes of UV radiation in recent decades are consistent with those expected from changes in ozone and atmospheric transmission**

Time series of UV irradiances, extended several decades back from the start of the ozone depletion, are now available. The longest of these goes back to the 1920s when ozone measurements first became available,<sup>27</sup> depicting fluctuations of similar magnitude to observations in the last two decades.

Measurements of UV irradiance at various locations over northern mid-latitudes show that surface UV has increased in the 1980s and 1990s as a consequence of ozone depletion and increasing atmospheric transmission.<sup>27-33</sup> The period since the “turnaround” in ozone is too short to reveal unequivocal changes in UV radiation. However, data since the late 1990s from some Southern Hemisphere sites indicate that surface UV radiation has levelled off<sup>34</sup> or may even be decreasing.<sup>35</sup>

**Attempts have been made to reconstruct historical ozone or UV-B amounts for periods prior to the modern instrumented records and prior to human impacts**

These include: (1) measurements from historical records of star spectra, back to about 1900;<sup>36-38</sup> (2) analyses of pigments in herbarium specimens,<sup>39,40</sup> over periods of up to ~100 years, and (3) analyses of pigments in lake sediments<sup>41,42</sup> and analyses of tree rings,<sup>43,44</sup> over thousands of years. Most of these attempts are still in a method development stage, but some show promise for the future.

**Methyl bromide constitutes the largest source of bromine atoms to the stratosphere and therefore plays an important role in the depletion of stratospheric ozone<sup>45</sup>**

There are still large uncertainties in the identification and quantification of significant sources and sinks of methyl bromide (and other simple organic halides).<sup>46</sup> New sources<sup>47-50</sup> for these compounds are still being discovered but uncertainties prevail. The phase-out of methyl bromide usage is important for the short-term recovery of stratospheric ozone concentrations. Our knowledge of its effects over longer periods is limited by uncertainties in the magnitudes of sources and sinks.<sup>51</sup> New information that becomes available about these will improve existing models and our understanding of its involvement in atmospheric processes.<sup>52,53</sup>

**Health**

**The incidence rates of sunlight-induced skin cancer continue to rise rapidly in light-skinned populations**

Results from the Netherlands, the UK, Australia and the USA document these trends in basal cell carcinoma (BCC), squamous cell carcinoma (SCC) and cutaneous malignant melanoma (CMM).<sup>54-57</sup> Forecast modelling of these tumours in the Netherlands predicts that their rates will double by 2015.<sup>58</sup> In Minnesota, USA, the increases in BCC and SCC were most apparent in men and women under the age of 40 years and there was a disproportionate increase in BCC in young women.<sup>55</sup> In the UK between 1975 and 2000, CMM has shown the largest increase in incidence rates compared with other major tumours, and

modelling results suggest that, even with sun avoidance and use of sunscreens, the melanoma incidence rate will not decrease for about another 30 years, by which time the rate may be twice that found currently.<sup>56</sup> Similar projections for Australia indicate that, by 2011, melanomas will represent 11% of all new cancer cases in men and will have overtaken lung cancer (10%) as the third most common cancer for men of all ages.<sup>57</sup> These findings emphasize the need for skin cancer prevention programs, particularly those aimed at young adults, in order to lessen the adverse impacts of increasing UV-B exposure.

#### **Recent animal experiments confirm that it is UV-B and not UV-A radiation that initiates melanomas**

In a study using transgenic mice that develop melanomas which closely resemble those of humans, UV-B radiation induced CMM while UV-A did not, even at doses considered biologically relevant.<sup>59</sup> These experiments suggest that reducing exposure to UV-B is important in reducing CMM incidence in human populations.

#### **Adverse solar UV effects on the eye can be enhanced by the presence of clouds**

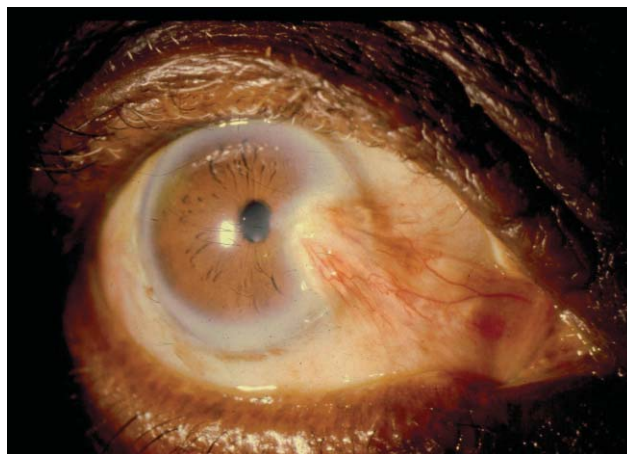
The eye is protected from most direct solar UV radiation by its anatomical location and physiological defence mechanisms (*e.g.*, squinting, pupil constriction) to bright light.<sup>60</sup> Indirect, *i.e.*, reflected and/or diffuse UV, however, plays a major role in acute solar photokeratitis and is also important in cataract formation. Under cloud cover (when light levels are lower and greater scatter occurs), the natural defence mechanisms of the eye relax, and the surface and interior of the eye receive more of the incident UV. At the same time, the effective UV-B incident on the eye can be increased under cloud cover.<sup>61,62</sup> These results confirm the need for eye protection from solar UV radiation even when it is not sunny.

#### **Recent reports confirm that sunlight-associated pterygium occurs in people of all skin colours**

On the basis of *in vitro* studies, pterygium (a common inflammatory, proliferative and invasive lesion of the human cornea that can severely impair vision; Fig. 2) appears to result from UV-B-induced intracellular damage to epithelial cells.<sup>63</sup> The accumulated exposure to sunlight<sup>64,65</sup> and a variety of genes, such as those involved in the repair of DNA damage,<sup>66-68</sup> influence the development of pterygia in human populations. All outdoor workers, regardless of skin colour, would thus benefit from eye protection.

#### **Evidence suggesting a role for sunlight-induced vitamin D production in the prevention of several cancers is accumulating**

A number of recent epidemiologic studies have concluded that self-estimated sun exposure was associated with reduced risk of some internal tumours, *e.g.*, non-Hodgkin lymphoma and prostate cancer.<sup>69-71</sup> In addition, one report found an increased 5-year survival following the diagnosis of early stage CMM with increasing solar exposure assessed not only by self-estimated solar exposure but also through the measurement of solar elastosis (one



**Fig. 2** Photograph of a pterygium.

measure of skin aging).<sup>72</sup> A common suggestion from the above studies was that the observed protective effects might be due to an increase in vitamin D which has been shown to have a role in controlling the proliferation of tumour cells. However, it should be noted that at least one report, of a prospective epidemiologic study, found no association between plasma concentrations of active vitamin D or its precursor and the incidence of prostate cancer.<sup>73</sup>

Many studies indicate that there is widespread vitamin D insufficiency and deficiency, especially in populations living at mid to high latitudes. The exposure to UV-B required to provide sufficient vitamin D to maintain optimal immune and other functions is not currently known but is likely to vary from person to person depending on skin characteristics (colour, thickness), health and nutritional status and vitamin D receptor genotype.<sup>74</sup> It has been estimated that, for healthy light-skinned individuals, the exposure required would be about 5 minutes per day 3 times a week while darker skinned individuals the exposure required would be 10 minutes per day 3 times a week.<sup>75,76</sup> Others believe that a greater solar exposure is required.<sup>77</sup> Indeed it is thought by some that where there is insufficient solar UV-B radiation due to season, latitude or lifestyle, various foods may require fortification with vitamin D.<sup>78,79</sup>

#### **For several internal cancers and particular autoimmune diseases, the benefits from increases in ambient UV-B are hard to predict**

There are inadequacies of personal UV dosimetry in human population studies and a lack of suitable animal experiments. However, although the incidence rates of skin cancers have risen in association with increased levels of sun exposure, there has not been a trend towards a decrease in internal cancers such as prostate and breast or in autoimmune diseases such as multiple sclerosis (for example the incidence of prostate cancer is increasing steadily in almost all countries<sup>80</sup>). Thus caution is required before encouraging people to expose themselves to full sunlight in order to reduce their risk of developing these types of diseases. More research is needed in this challenging and complex area.

### **Additional diseases and conditions have been identified that may be adversely affected by exposure to UV-B**

There is evidence that UV-B exposure may induce the skin lesions characteristic of the autoimmune disease, systemic lupus erythematosus, in patients with gastrointestinal cancer (adenocarcinoma) who have been treated with the anti-cancer drug, fluorouracil.<sup>81</sup> In addition, based on the results of animal experiments, individuals exposed to arsenic may experience an increase in skin cancer incidence,<sup>82</sup> while those undergoing chronic stress may experience an accelerated development of skin cancer<sup>83</sup> when exposed to UV-B.

### **Concerns have arisen about unintended environmental consequences from the increased use of sunscreens to protect against UV-B**

A number of the UV-B absorbing components in sunscreens have been shown to have weak estrogenic activity (potencies in one report of 1/600 000 or less compared to the reference estradiol<sup>84</sup>) and thus may have adverse consequences for reproductive function when released into the environment, concomitant with other endocrine disrupting chemicals.<sup>85</sup> These observations lend strength to the recommendation that protection from UV-B may need to rely on strategies other than sunscreen use.<sup>84,86-92</sup>

## **Terrestrial ecosystems**

### **Biodiversity may be altered by UV-B radiation even though total community production and biomass are not necessarily affected**

A further recent report of this nature shows changes in the species composition and biodiversity of micro-fungi growing in peat bogs of Tierra del Fuego.<sup>93</sup>

### **New research in Antarctica shows that some native species are adversely affected by current levels of UV radiation**

An endemic species of moss was found to have reduced levels of photoprotective pigments (compared to other widely distributed moss species), and current levels of UV radiation were reported to cause increased frequency of abnormalities in leaf morphology.<sup>94</sup> These results are consistent with previous findings showing reduced growth as a result of exposure to ambient UV-B in native species of Antarctica and Tierra del Fuego.

### **The interplay between UV radiation and periodic drought conditions may result in altered species composition in shortgrass-steppe ecosystems**

In a field study in which solar UV was manipulated by filters,<sup>95</sup> productivity was decreased and forage quality increased by UV radiation for the dominant grass species in a dry, but not in a wet year. In another grass species, productivity decreased due to UV, but only in wet years. Forage quality of this species did not change. Since forage quality increases decomposition, UV radiation and drought would reduce biomass and soil organic matter. The variable response observed among species grown under changing conditions of soil moisture availability and UV suggests that as drought becomes more prevalent with global

change in the shortgrass-steppe ecosystem, the structure and function of this ecosystem may change substantially.

### **Increasing nitrogen supply to plants may result in additional sensitivity to UV-B**

In field experiments, supplemental UV-B simulating ozone depletion caused reductions in total biomass, nitrogen content and specific pigment concentrations for a South African legume species (*Cyclopia maculata*), but the UV-B effect was much more pronounced if the plants were supplied with supplemental nitrate.<sup>96</sup> In another field study with simulated ozone reduction over Portugal, net photosynthesis of maize was less affected by UV-B at low nitrogen supply than at higher nitrogen levels.<sup>97</sup> Interactions of nitrogen and UV-B may be important in regions experiencing nitrogen deposition or in agricultural systems with nitrogen applications.

### **In a study with soybean, increased UV-B radiation, elevated CO<sub>2</sub> and high temperature resulted in smaller flowers with less pollen and lower pollen germination rates<sup>98</sup>**

Many earlier studies have shown that elevated CO<sub>2</sub> ameliorates many injurious effects of UV-B. In another study with cotton, no interactive effect was found for elevated UV-B and CO<sub>2</sub>.<sup>99</sup> These experiments were performed in sunlit, controlled-environment chambers that may have compromised the realism in relation to field conditions.

### **UV-B radiation can alter plant responses to extreme temperatures**

UV-B radiation increased heat tolerance considerably in cucumber plants grown in growth chambers.<sup>100</sup> Freezing tolerance of jack pine was similarly increased by UV-B and this was linked to induction of secondary compounds (phenols) in plant tissues.<sup>101</sup> These studies were conducted in growth chambers and may not necessarily apply to field conditions. However, in a field study, low-temperature tolerance was increased.<sup>102</sup>

### **New studies on the genetic basis for plant responses to UV-B radiation contribute more detailed information on the effects of UV-B radiation, from the gene to the whole plant level**

Recent studies confirm earlier reports that a sizeable portion of the plant genome can exhibit changes in gene expression due to UV-B and that many of the UV-B-regulated genes are plant organ-specific.<sup>103,104</sup>

## **Aquatic ecosystems**

### **Climate change may increase the sensitivity of aquatic organisms to UV-B radiation**

In the oceans, future warming is likely to alter the spatial distribution of productivity, affecting ecosystems and placing additional stress on already depleted fish stocks and other marine resources.<sup>105</sup> Field observations suggest that climate forcing plays a strong role in determining UV exposures to communities in snow and ice-covered environments.<sup>106</sup> Climate change and ozone layer thinning simultaneously expose polar organisms to increasingly stressful conditions, including changes in temperature, salinity

and UV radiation.<sup>107</sup> Further, polar ecosystems may be more vulnerable to UV radiation because of the inhibiting effects of low temperatures on cellular repair of UV-B damage,<sup>108,109</sup> decreases in protective sea ice coverage in areas of recent rapid warming<sup>110,111</sup> and possible changing cloud cover.<sup>112</sup>

### **Changes in underwater UV-B and temperature can significantly influence the composition of the zooplankton community and ultimately food web dynamics<sup>113</sup>**

Laboratory studies on molluscan larvae have demonstrated that the effects of ultraviolet radiation were particularly marked, with mortality increasing up to 12-fold under temperature and salinity stress associated with climate change as compared with UV-B or temperature and salinity stress alone. It is likely that we are consistently underestimating the ecological impacts of climate change and enhanced UV-B radiation by failing to consider the complex interplay of environmental variables and their impact on organisms.<sup>114</sup>

### **There remains a lack of consensus regarding the role of UV-B and other environmental stresses with respect to the causes of the worldwide decline in amphibian populations**

Various experiments have led researchers to propose several potential causes for these declines, including disease, habitat destruction, environmental contaminants, introduced exotic species, global climate change and increased levels of UV-B radiation. Accumulating evidence suggests that high levels of UV-B radiation are harmful to many amphibian species. However, often in the natural environment where exposure is limited, UV-B radiation is less of a factor, although UV-B is believed to exacerbate a variety of these other listed stresses.<sup>115-117</sup>

### **Long-term studies conducted in the South Atlantic Ocean have shown seasonal sensitivities of phytoplankton to solar UV radiation**

Pre- and post-bloom phytoplankton assemblages are mainly composed of small-sized cells that are sensitive to and strongly inhibited by solar UV-B.<sup>118</sup> During the bloom in winter and early spring, microplankton diatoms, which are likewise sensitive to solar UV-B, dominate, but due to low solar irradiances, inhibition of photosynthesis and DNA damage are low. In these Patagonian waters, the exposure to detrimental radiation is mainly governed by the nutrient status and high wind speeds that affect the depth of the upper mixed layer and, by this, the mean irradiance affecting phytoplankton. Vertical circulation of the phytoplankton within the mixed layer reduces the exposure of solar UV radiation to individual organisms.

### **Recent investigations have revealed mechanisms for UV-B stress induction and avoidance by aquatic producers and consumers**

In addition to direct DNA damage by solar UV-B,<sup>119-121</sup> generation of reactive oxygen species (ROS) is a major factor in induced damage and mutation by UV-B.<sup>122</sup> Significant advances in understanding the molecular mechanisms have been achieved by identifying genes responsible for UV induction of damage and repair mechanisms,<sup>123</sup> as well as enzymes involved in ROS detoxification and defense mechanism induction.<sup>124</sup>

### **Results of modeling, evaluation of paleorecords, and studies using microcosms and field research all suggest a complex influence of UV-B radiation at the ecosystem level**

Paleorecords in the circumpolar Arctic reveal widespread changes in algal and invertebrate communities that are driven by climate warming.<sup>125</sup> Predicted increases in warming and precipitation for polar regions will influence freshwater and oceanic systems. Shifts in temperature and likely increased input of dissolved organic carbon, and consequent changes in the penetration of UV radiation, have an impact on Arctic lakes and ponds.<sup>126</sup> Modelling results are consistent with paleorecords. This suggests that global ocean productivity is sensitive to changes in whole ocean circulation<sup>127</sup> and to large-scale iceberg discharges from Northern Hemisphere ice sheets as during the last ice age.<sup>128</sup> The underlying processes linking these events with subantarctic productivity remain unclear but underpin the complexity of these extreme climate perturbations and their consequent influence of enhanced solar UV-B on aquatic systems.

### **Biogeochemical cycles**

#### **UV-B accelerates the production of CO<sub>2</sub> from organic matter that runs off from the land into freshwaters and the ocean**

Global warming and precipitation changes can alter the transport of dissolved organic matter (DOM) from terrestrial to freshwater and marine systems (Fig. 3). Increased UV-B radiation can enhance CO<sub>2</sub> production from DOM *via* direct and iron-catalyzed DOM photo-transformations.<sup>129-131</sup> The net result could be a UV-mediated positive feedback to CO<sub>2</sub> accumulation in the atmosphere.

#### **Climate change causes increased stratification of lakes and the ocean, which intensifies UV effects on biogeochemistry in the surface layer**

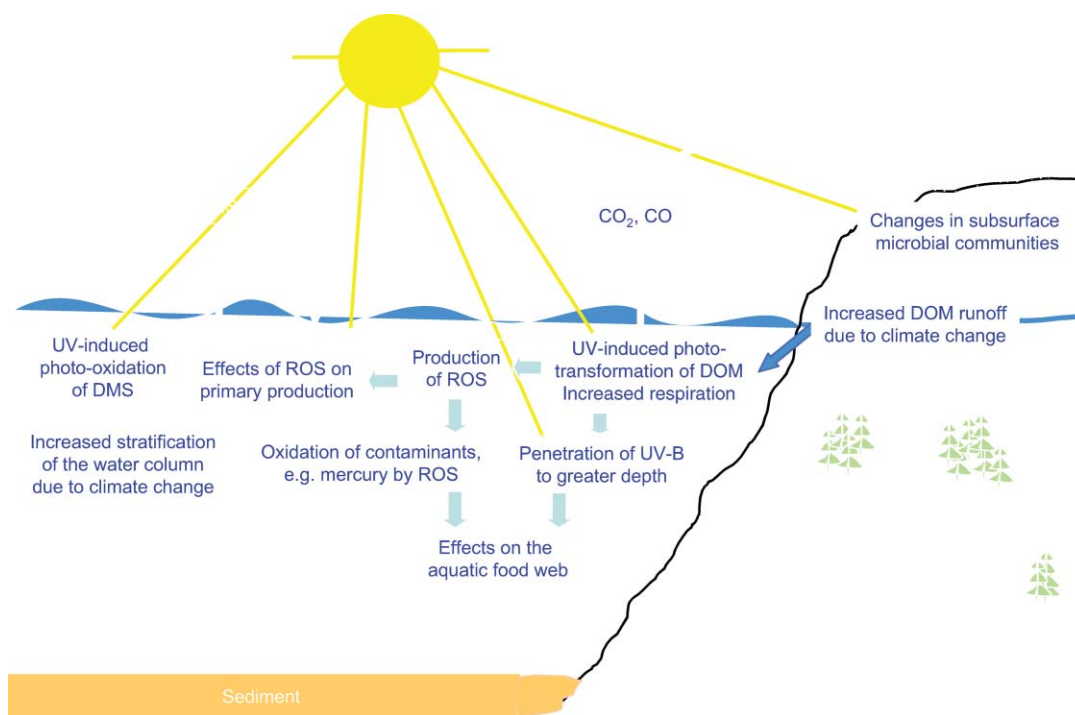
This important effect is illustrated by the extensive increase in transparency of the water to UV-B in the upper layer of stratified aquatic environments.<sup>132</sup> Warming affects the quality of the DOM produced by microbial decomposition of seagrass, rendering DOM more susceptible to UV-induced degradation. These effects of climate change will amplify UV impacts on biogeochemical cycles in the upper part of aquatic systems, thus partially offsetting the beneficial effects of an ozone recovery.

#### **The toxicity of metals depends on their biological availability, which can be enhanced by reactions involving UV-B**

For example, UV-induced oxidation of mercury has been demonstrated.<sup>133,134</sup> This process increases the concentration of methylmercury,<sup>135</sup> which bioaccumulates in the aquatic and terrestrial food chain.<sup>136</sup>

#### **UV radiation drives photoreactions that play an important role in marine sulfur cycling and thus in the production of atmospheric aerosols**

Aerosols that influence atmospheric radiation and climate are affected by the UV radiation that penetrates into the ocean. Oceanic emissions of dimethyl sulfide (DMS) produce aerosols.



**Fig. 3** Diagrammatic representation of the effects of increased UV-radiation and climate change on biogeochemical cycles.

Photolysis is an important transformation process for DMS in the upper ocean and the UV component of solar radiation induces this process.<sup>137</sup> Marine photoproduction of carbonyl sulfide also is induced by solar UV-B that interacts with chromophoric DOM and dissolved organic sulfur in the upper ocean.<sup>138</sup>

#### **Climate change and UV-B influence the budget of halogen-containing compounds that alter ozone chemistry in the atmosphere**

Generation of halogen atoms in atmospheric aerosols can be driven by processes involving UV radiation in the marine boundary layer.<sup>139,140</sup> Emissions of halomethanes related to climate change may be interacting with the flux of UV-B to the Earth's surface to modulate trends in atmospheric ozone concentrations. For example, increased temperatures strongly influence emissions of methyl bromide and methyl iodide from rice; an increase of ~10% was observed with warming of 1 °C.<sup>141</sup> In contrast, photoreactions involving UV-B can degrade brominated and iodinated methanes in water.<sup>142,143</sup>

#### **UV-B increases the oxidative activity of aquatic environments, thereby affecting biogeochemical cycles and the fate of contaminants**

Reactive oxygen species (ROS), important in the processing of natural and anthropogenic compounds, are produced by UV-induced photoreactions of organic matter,<sup>130,131,144</sup> inorganic nitrogen and/or iron. Reactions involving ROS oxidize aquatic contaminants such as pharmaceuticals,<sup>145-147</sup> certain herbicides<sup>148</sup> and commercial dyes<sup>149</sup> as well as naturally-occurring organic substances such as lignin<sup>150</sup> and DOM.<sup>131,151</sup> ROS can affect

biogeochemical cycles by damaging aquatic microbiota and also by producing toxic species such as methylmercury.

#### **Carbon cycling in terrestrial systems can be affected by vegetation exposure to UV-B leading to alterations in subsurface microbial communities in the rhizosphere (soil around root systems)**

Microbial communities in the rhizosphere play a key role in controlling plant nutrient supply. UV-B effects on plant root exudation and/or changes in litter quality were likely responsible for the alterations.<sup>94,152,153</sup> These changes may modify utilization of different carbon substrates by the microbial communities.

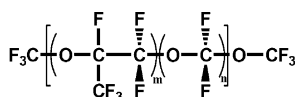
#### **Air quality**

##### **Tropospheric ozone is influenced by UV-B radiation as well as by local stagnant high pressure systems and pollutant concentrations**

A global chemical transport model study and analyses of measured total ozone and lower tropospheric ozone at three selected stations in Samoa, Hawaii, and Germany between the 1970s and 1990s agreed in terms of the dependency of lower tropospheric ozone on stratospheric ozone change.<sup>154</sup> These studies showed that, in unpolluted air (marine locations—Samoa and Mauna Loa, Hawaii), a decrease in stratospheric ozone led to a decrease in ozone at ground level. However, in a more polluted continental site (Hohenpeissenberg, Germany), a decrease in stratospheric ozone led to an increase in ground level ozone. It was concluded that the sensitivity of lower tropospheric ozone to reduced total ozone column amounts was strongly linked to the large-scale weather situation (stagnant high pressure systems) as well as local emissions of pollutants.<sup>154</sup> Thus, these factors must be considered in predicting effects of ozone depletion on lower tropospheric ozone concentrations.

## The changes in tropospheric hydroxyl radical (OH) caused by UV-B are now much better quantified

OH is one of the major oxidizing agents in the atmosphere, destroying about 3.7 petagrams (3 700 million tonnes) of trace gases each year, including many gases involved in ozone depletion, the greenhouse effect, and urban air pollution. The anomalously low global concentrations of OH from 1997–1999 may be explained by massive forest fires in Indonesia, Russia, and North America at these times.<sup>155</sup> The sources and sinks of methyl chloroform, the primary molecule used to detect OH changes, are now better characterized,<sup>156,157</sup> giving greater certainty to the analysis. Further, a second estimation method using carbon monoxide containing radiocarbon (<sup>14</sup>CO) agrees with the analysis based on methyl chloroform. The global averaged OH is observed to change on short time scales (months–years) but not in the longer term.<sup>158</sup> Thus, the estimate for the long term trend in the change in OH (1979/1980–2003/2004) is small, and could be explained by changes in tropospheric composition rather than by UV-B radiation.



Generalized structure of PFPEs

## Perfluoropolyethers, substances proposed as chloro-hydrofluorocarbon (CHFC) substitutes that have very large global warming potential show great stability to chemical degradation in the atmosphere

Perfluoropolyethers (PFPEs) are commonly used industrial heat transfer fluids that may be released to the atmosphere. In smog chamber studies on a PFPE, found in the commercial mixture of the heat-transfer fluid, Galden HT70®, reactivity with OH radical was very small ( $<2.28 \times 10^{-16} \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ ) and that with Cl radical 10 times less.<sup>159</sup> The minimum atmospheric lifetime was estimated to be about 1000 years. Over a 100 year time-frame, the global warming potential (GWP) of the PFPE was calculated to be 8 400 (compared to the GWP of carbon dioxide of one), a value exceeded by only a few hydrofluoro ethers. These substances have been suggested as substitutes for CHFCs<sup>160</sup> but they are very persistent and may be important contributors to global warming. They should be considered for further evaluation.

## Although iodine-containing compounds have not been considered to be significant ozone-depleting substances (ODS), a recent assessment suggests that they may be important in ozone depletion in the polar boundary layer in synergy with other ODSs

It has been suggested that iodine-containing compounds are minor contributors to ozone depletion ( $<1\%$  reduction of stratospheric ozone).<sup>161</sup> However, recent modeling studies have suggested that iodine and iodine-containing substances from natural sources, such as the ocean, may increase ozone depletion in polar regions during spring.<sup>162</sup> Measurements of IO- and I-containing precursor molecules as well as those of the important trace gasses, O<sub>3</sub>, CH<sub>2</sub>O, BrO, and Br-containing precursors may allow a realistic accounting to be made of the actual pathways that lead to the observed ozone depletion. Given the uncertainty of the fate of

iodine in the stratosphere,<sup>161</sup> these results may also be relevant for stratospheric ozone depletion and measurements of these substances should be considered in the future.

## Materials

### Photodegradation in plastic-wood composite materials by solar UV radiation increases with their lignin content

Composites of plastics and wood, especially those with polyethylene and polypropylene as the plastic component, are being increasingly used outdoors.<sup>163</sup> In these materials, the lignin chromophores in the wood powder were found to accelerate the photodamage to the plastics component.<sup>163</sup> The acceleration increases with the fraction of wood in the composite. Conventional UV stabilizers can control the photodegradation of wood to a limited extent. For instance, UV absorbers used in mechanical pulps (newsprint paper) were found to be effective in significantly reducing the UV-induced loss in brightness of newsprint paper.<sup>164</sup>

### The role of additives in modifying the rates of photodegradation in common polymers is now better understood

Additives such as flame retardants,<sup>165</sup> recycled plastics,<sup>166</sup> and certain copolymers,<sup>167</sup> are routinely used in plastics formulations. The mechanism by which each of these enhances the photodegradation of plastics has been better elucidated in recent findings. The use of certain UV stabilizers (sterically hindered-amine) along with bromine-containing flame retardants in the same formulation was shown to reduce stabilizer effectiveness and also promote photodegradation of the polypropylene plastics matrix.<sup>168</sup> This new information can help in selecting additives for improved UV stability in common plastics formulations.

Fillers generally retard the photodegradation of plastics. The newer nano-scale titanium dioxide filler, for instance, was shown to be particularly effective in stabilizing model epoxy polymers exposed to UV radiation.<sup>169</sup>

### Recent studies confirm the synergistic interaction of solar UV and higher ambient temperatures acting together to cause increased photodamage to plastics

Polycarbonates undergo discoloration, weakening and changes in materials chemistry on exposure to solar UV radiation. This reduces both the transparency and strength of the glazing material. At higher temperatures (45 °C and 60 °C) an increase in such damage, by as much as 2–3 times compared to that at 25 °C, was obtained. The finding confirms synergistic effects of UV and temperature acting together causing increased photodamage to plastics.<sup>170</sup>

### New techniques allow more accurate modelling of photodamage at different depths in plastics exposed to UV radiation

Recent improvements in depth profiling techniques,<sup>171</sup> especially those based on confocal microscopy, allow better quantification of the photodamage at different depths below the irradiated surface. The improved models allow for better design of plastic products as well as new stabilizer systems intended for materials destined for routine outdoor use.

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