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# Changes in air quality and tropospheric composition due to depletion of stratospheric ozone and interactions with changing climate: implications for human and environmental health

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UV radiation is an essential driver for the formation of photochemical smog, which includes ground-level ozone and particulate matter (PM). Recent analyses support earlier work showing that poor outdoor air quality is a major environmental hazard as well as quantifying health effects on regional and global scales more accurately. Greater exposure to these pollutants has been linked to increased risks of cardiovascular and respiratory diseases in humans and is associated globally with several million premature deaths per year. Ozone also has adverse effects on yields of crops, leading to loss of billions of US dollars each year. These detrimental effects also may alter biological diversity and affect the function of natural ecosystems. Future air quality will depend mostly on changes in emission of pollutants and their precursors, but changes in UV radiation and climate will contribute as well. Significant reductions in emissions, mainly from the energy and transportation sectors, have already led to improved air quality in many locations. Air quality will continue to improve in those cities/states that can afford controls, and worsen where the regulatory infrastructure is not available. Future changes in UV radiation and climate will alter the rates of formation of ground-level ozone and photochemically-generated particulate matter and must be considered in predictions of air quality. The decrease in UV radiation associated with recovery of stratospheric ozone will, according to recent global atmospheric model simulations, lead to increases in ground-level ozone at most locations. If correct, this will add significantly to future ground-level ozone trends. However, the spatial resolution of these global models is insufficient to inform policy at this time, especially for urban areas. UV radiation affects the atmospheric concentration of hydroxyl radicals, $^{\bullet}$OH, which are responsible for the self-cleaning of the atmosphere. Recent measurements confirm that, on a local scale, $^{\bullet}$OH radicals respond rapidly to changes in UV radiation. However, on large (global) scales, models differ in their predictions by nearly a factor of two, with consequent uncertainties for estimating the atmospheric lifetime and concentrations of key greenhouse gases and air pollutants. Projections of future climate need to consider these uncertainties. No new negative environmental effects of substitutes for ozone depleting substances or their breakdown-products have been identified. However, some substitutes for the ozone depleting substances will continue to contribute to global climate change if concentrations rise above current levels.

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## Introduction

The degradation of air quality is one of the major environmental hazards facing modern society. Human activities result in the emission of many chemicals to the atmosphere, which are either toxic themselves, or produce noxious compounds when exposed to ambient ultraviolet (UV) radiation. UV radiation is an essential driver for the generation of ground-level ozone ($O_3$) and some particulate matter (PM, frequently called aerosol) including sulfate, nitrate, and organic aerosols. These pollutants have major health implications for humans and the environment. Future changes in tropospheric UV radiation,

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whether from stratospheric ozone changes or other factors such as clouds, are likely to contribute to trends in air quality and associated health effects.

UV radiation makes hydroxyl ($^•OH$) radicals, the so-called cleaning agents of the troposphere. These radicals limit the atmospheric lifetime of many gases that are important to both tropospheric and stratospheric chemistry as well as climate change, including methane ($CH_4$), hydrogen-containing halocarbons (*e.g.* hydrofluorocarbons, hydrochlorofluorocarbons and hydrobromocarbons), and the oxides of sulfur and nitrogen ($SO_2$ and $NO_x$).

This paper provides an assessment of how UV radiation affects air quality, particularly ground-level $O_3$ and PM, in the context of the growing body of knowledge on their health impacts, geographic distributions, and long-term trends. It should be recognised that many factors drive these trends, including changes in both natural and anthropogenic emissions, as well as climate variability through changes in temperature, moisture, and atmospheric circulation patterns. Tropospheric UV radiation is one of these factors, and its effects can be approximately superimposed onto the effects of the other factors, but complex non-linear interactions must be considered to obtain reliable estimates.

Since the previous assessment of the interactions between ozone depletion, climate change, and air-quality in the troposphere,[10,11] significant advances are noted in: (i) understanding and quantifying the important consequences of poor air quality for human health, separating the effects of $O_3$ and PM; (ii) understanding changes in air pollution on urban and regional scales, in terms of changes in anthropogenic emissions (increases or decreases, depending on location) as well as long-range transport; (iii) understanding long-term changes of key tropospheric oxidants ($O_3$ and $^•OH$) on continental and global scales, as anthropogenic emissions continue in an environment where both stratospheric ozone and climate are also changing.

An equally important advance is a better understanding of uncertainties inherent in numerical models used to predict the future chemical composition of the atmosphere. These computer models endeavor to represent and integrate the many chemical, physical, and biological processes that control air quality as well as climate. Recent inter-comparisons among the models (see below) highlight important differences that cast some doubt on the reliability of future projections, while also indicating a path to model improvements.

Ozone-depleting substances (ODS) could also affect air quality. While the long-lived chlorofluorocarbons (CFCs) break down almost exclusively in the stratosphere, the halogenated replacements break down in the troposphere. The cycling of the halogenated species in the troposphere needs to be assessed to ensure that there are no other significant short- and long-term effects that will result from the replacements for the halocarbons. Health effects could result from exposure to these substances, and are therefore included in this assessment (previously this was included in the health assessment, which now focuses on UV-mediated effects).

This paper provides summaries of the state of knowledge on ground-level $O_3$, PM, and $^•OH$ radicals, and addresses some of the more complex but still largely unquantified interactions between air quality, climate change, and human activities. An important additional interaction between air quality and stratospheric ozone depletion is the introduction of substitute compounds for ODSs pursuant to international agreements. The last part of this paper provides an update on selected substitutes whose potential environmental and health impacts should be considered.

In summary, our assessment updates and reinforces several key conclusions. Air pollution is increasingly recognised as a major environmental hazard and a risk to human health, globally leading to several million premature deaths per year. Air pollution also damages vegetation and reduces agricultural yields, with associated economic losses estimated as \$10–20 billion annually. UV radiation is an essential ingredient for the formation of ground-level $O_3$ and some PM, and of $^•OH$ radicals that control the global self-cleaning capacity of the troposphere. Future trends in UV radiation will modulate future trends in air quality. Air quality is sensitive to other changes in the environment including atmospheric circulation, hydrological cycles, and temperatures, all of which are likely to change due to the combined effects of changing stratospheric ozone and climate. No new negative environmental effects of the substitutes for the ODSs have been identified.

## Ground-level ozone

**Health effects.** Tropospheric $O_3$ has significant effects on human morbidity and mortality. Premature mortality has been estimated in recent studies, which are summarised in Table 1. Ozone and particulate matter (PM) often co-occur in the troposphere and therefore their effects on human health are difficult to separate. However, there appears to be no interaction between these in terms of premature mortality. Earlier epidemiological studies (reviewed in ref. 12) have supported this conclusion and further studies by the same authors[13,14] on the individual components of PM have shown that there is no interaction between these and ozone. Thus for the purposes of protecting human health, PM and $O_3$ can be treated separately. Premature mortality associated with exposure to ground-level ozone, while lower than that from PM, is still substantial with several hundred thousand people affected globally each year (Table 1). Recent studies are broadly consistent on effects

Table 1 Premature mortality from ground-level ozone ($O_3$) and particulate matter (PM)

| | | | Premature mortality (millions per year) | |
|---|---|---|---|---|
| Source | Year | Area | From $O_3$ | From PM |
| OECD[19] | 2010 | Global | 0.35 | 1.4 |
| | 2050 | Global | 0.75 | 3.6 |
| Lim *et al.*[18] | 2010 | Global | 0.05–0.27 | 2.8–3.6 |
| Fang *et al.*[20] | 2000 | Global | 0.38 | 1.5 |
| Fann *et al.*[21] | 2005 | US only | 0.005 | 0.05–0.2 |

of ozone on mortality in humans from cardiovascular and respiratory diseases in Oporto, Portugal,[15] Taipei,[16] and Prague.[17,18]

Ozone-related morbidities manifested as acute and chronic bronchitis, asthma and/or atopic dermatitis,[22] appendicitis,[23] venous thromboembolic disease, and pulmonary embolisms[24] have been reported. Ozone may also interact synergistically with viral infections. A study in Hong Kong reported interactive effects between viral infections and concentration of $O_3$ that resulted in increased risks for hospitalisation for respiratory disease.[25] The mechanism for this apparent synergism was not reported.

A number of studies have extrapolated the effects of exposure to $O_3$ into the future. Based on the OECD[19] study, premature deaths from ground-level ozone will increase to about 0.75 million per year worldwide by 2050. The greatest increases are predicted in India (130 premature deaths per million per decade by 2050) but those in OECD countries will be almost as large (95 premature deaths per million per decade by 2050), mostly as a result of greater sensitivity in an ageing population.[19] Modelling of the interactions between concentrations of tropospheric ozone, precursors of ozone in the atmosphere, and climate change suggests that, by 2050, concentrations of $O_3$ will increase in developing countries and decrease in developed countries,[26] due to regional differences in future emissions.

**Effects on plants.** For plants, the most important air-pollutant is $O_3$;[27,28] particulates have not been observed to have substantial direct effects on plants. In our previous assessment,[11] we noted that damage to crops by air-pollutants is likely to become more severe in the future. Since the last assessment, further studies have reinforced this conclusion. Based on a scenario of a world population of 9.1 billion, concentration of $CO_2$ of 550 ppm,† a concentration of ozone of 60 ppb (about 10 ppb above current), and the climate warmer by *ca.* 2 °C by 2050, Jaggard *et al.*[29] postulated that yields of major crops (*e.g.* wheat, rice, soy, and maize) would be reduced by about 5% because of $O_3$. However, this may be compensated by an increase in yield for most crops by about 13% because of the increased concentrations of $CO_2$, depending on water availability.

In a review of studies on the effects of $O_3$ on plants, it was concluded that reductions in the yields of 18 to 27% result from exposure to $O_3$ at concentrations of 70 to 100 ppb, at the upper end of typical regional concentrations.[30] Not all crops are equally sensitive to ozone. In a sensitive crop, such as soybean, yields in several cultivars were shown to decrease by as much as a factor of 2 with long-term exposure to 20–30 ppb (24 hour mean) of added ozone.[31] Reductions in photosynthesis upon exposure to $O_3$ were estimated in three different forest types and found to be statistically significant for an orange orchard, and observable for ponderosa pine.[32] The potential for damage from $O_3$ in crop plants was assessed in relation to the IPCC (pessimistic) A2 scenario[33] for 2100.[1] Changes in gross plant productivity resulting from changes in tropospheric $O_3$ were projected to range from −40 to +15%, depending on location (Fig. 1). In another example, the ranges of global crop losses for wheat and soybean in 2030 as estimated from the IPCC A2 scenario were 5.4–26% and 15–19%, respectively.[34] In this same study, yield reductions in the B1 (optimistic) scenario were 4.0–17% for wheat and 9.5–15% for soybean, with monetised annual losses estimated to range from $12–21 billion (year 2000 dollar equivalents).

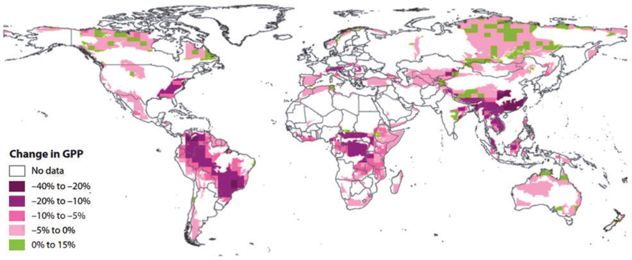

**Fig. 1** Global assessment of the projected percentage changes in gross primary productivity (GPP) due to $O_3$ under the Intergovernmental Panel on Climate Change A2 scenario in 2100 within the World Wildlife Foundation Global 200 priority conservation areas. From Ainsworth *et al.*[1] Reproduced with permission of the Royal Society.

Although most of the research on the effects of $O_3$ in ecosystems has been directed toward plants, effects on soil microorganisms have also been reported.[35] The abundance and diversity of methanogenic bacteria in soils of rice paddies were found to be reduced after exposure to elevated concentrations of $O_3$ (60 ppb) in ground-level air.

Overall, productivity and yields of crops will likely be reduced as a result of increases in concentrations of tropospheric $O_3$. There is some hope that genetic selection of plants tolerant to $O_3$ will mitigate these adverse effects on production of food and fibre but other plants in the ecosystem are likely to suffer greater adverse effects. These are expected to impact diversity and functions of natural ecosystems. Other effects of climate change, *e.g.*, mediated by temperature and precipitation, will also affect yields of crops.

**Photochemical processes.** Atmospheric ozone ($O_3$) is generated primarily in the atmosphere by photochemical reactions involving UV radiation. In the stratosphere, it is made directly by the photo-dissociation of molecular oxygen ($O_2$) into two oxygen atoms (2O), followed by the association of each of these atoms with remaining $O_2$ (see Table 2) to make two $O_3$ molecules. In the troposphere, this direct formation is not possible because photons of sufficient energy to dissociate $O_2$ ($\lambda < 240$ nm) are nearly completely absorbed by stratospheric $O_2$, and so are not available in the troposphere. Descent of stratospheric ozone to the troposphere does occur (*e.g.*, during stratospheric intrusions common during springtime at mid-latitudes) but accounts for only about 1/10th of the tropospheric production in global models,[6] and is only

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† A ppm of X, parts per million, is a mixing ratio of 1 molecule of X per million molecules of air. Similarly, ppb is parts per billion.

**Table 2** Atmospheric photochemical reactions

| Stratospheric ozone formation: | Reaction |
|---|---|
| $O_2 + h\nu\ (\lambda < 240\ \text{nm}) \rightarrow O + O$ | (1) |
| $O + O_2 \rightarrow O_3$ | (2) |
| Tropospheric ozone and $^{\bullet}OH$ formation: | |
| $O_3 + h\nu\ (\lambda < 330\ \text{nm}) \rightarrow O^* + O_2$ | (3) |
| $O^* + H_2O \rightarrow {}^{\bullet}OH + {}^{\bullet}OH$ | (4) |
| $^{\bullet}OH + VOC + O_2 \rightarrow HO_2$ (or organic analog $RO_2$) + other products | (5) |
| $HO_2 + NO \rightarrow NO_2 + {}^{\bullet}OH$ | (6) |
| $NO_2 + h\nu\ (\lambda < 420\ \text{nm}) \rightarrow NO + O$ | (7) |
| $O + O_2 \rightarrow O_3$ | (2) |
| Secondary tropospheric radical sources: | |
| $CH_2O + h\nu\ (\lambda < 340\ \text{nm}) + 2\ O_2 \rightarrow HO_2 + HO_2 + CO$ | (8) |
| $H_2O_2 + h\nu\ (\lambda < 350\ \text{nm}) \rightarrow {}^{\bullet}OH + {}^{\bullet}OH$ | (9) |
| $HONO + h\nu\ (\lambda < 395\ \text{nm}) \rightarrow {}^{\bullet}OH + NO$ | (10) |

a minor source of ozone found near the surface in polluted regions.

Formation of $O_3$ in polluted urban atmospheres has been recognised since the 1950s,[36] and occurs when mixtures of volatile organic compounds (VOCs) and nitrogen oxides ($NO_x$ = NO + $NO_2$) are exposed to the UV radiation available in the troposphere. The chemistry leading to tropospheric $O_3$ formation is generally complex because it (*i*) requires the absorption of multiple photons, (*ii*) is augmented by several catalytic cycles, and (*iii*) can be fuelled by many different VOCs, including those of anthropogenic and biogenic origin. Table 2 provides a highly simplified schematic of the major chemical pathways. The production of tropospheric $O_3$ is autocatalytic because photolysis of an initial amount of $O_3$ (Table 2, reactions 3 and 4) results in two $^{\bullet}OH$ radicals, each of which can then continue through the reaction sequence to regenerate more $O_3$. Note that two photons are required for this process (Table 2, reactions 3 and 7) with their combined minimum energy being more than sufficient to break $O_2$ directly.

Reaction 3 in Table 2, the photolysis of ozone to yield excited oxygen atoms O*, is the primary source of radicals ($^{\bullet}OH$, $HO_2$, and $RO_2$) involved in production of $O_3$. It is also very sensitive to the overhead ozone column (see Table 1 of McKenzie *et al.*[37]). Other sources of radicals include the photolysis of formaldehyde ($CH_2O$), hydrogen peroxide ($H_2O_2$), and nitrous acid (HONO). These latter compounds are typically the products of previous chemical reactions initiated by $O_3$ and $^{\bullet}OH$ and so they are sensitive to the production of primary radicals (Table 2, reaction 3) and therefore to UV-B radiation as affected by changes in stratospheric ozone.

**Distributions and trends.** Tropospheric ozone has increased since preindustrial times, mostly because of increasing anthropogenic emissions of the precursor gases, VOCs and $NO_x$. Relative to that, the effects of changing the UV radiation environment, *e.g.*, from mid-latitude stratospheric ozone depletion, have been smaller but remain important due to the very large number of people living in areas with poor air quality.

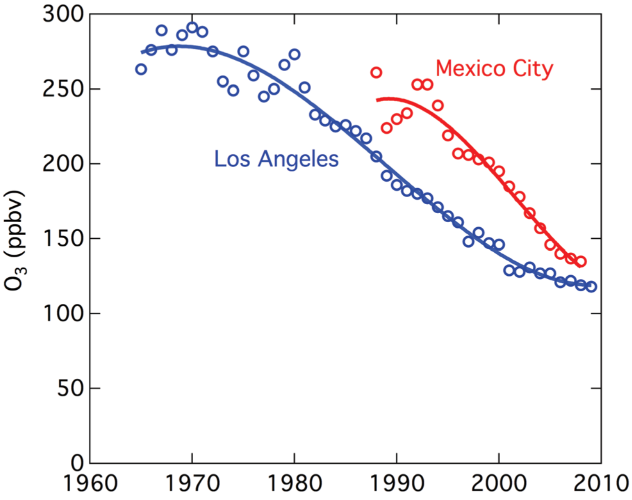

**Fig. 2** Improvements in air quality in Los Angeles and Mexico City. Plotted is the 3-year average of the 4th highest maximum ozone 8-hour average. (From Parrish *et al.*[2]).

Urban ozone trends differ in different cities. Considerable progress has been made in reducing urban $O_3$ in Europe, the United States, and some other locations.[2,38–40] Fig. 2 shows the reductions in ground level ozone achieved in Los Angeles and Mexico City over the past several decades. In Beijing, from 2005 to 2011, ground-based measurements give daytime average $O_3$ increasing at 2.6 ppb (5%) per year.[41] In comparison, increases of 3% per year over 2002–2010 have been reported for the tropospheric $O_3$ column above Beijing.[42] Other Asian cities showing increases include Hong Kong (0.55 ppb per year over 1994–2007), Seoul (about 5 ppb over 1991–2007), and Tokyo with a doubling of days with $O_3$ exceedances (incidences where air quality standards are exceeded).[40]

Regional ozone (ozone averaged over large areas extending well beyond cities) is increasing at some locations, particularly in densely populated areas, for example 6–7% per decade in the Indo-Gangetic Plains.[43] Regional production of ozone was also shown to be a factor limiting air quality improvements from local emission reductions during the Beijing Olympics.[44] Background ozone continues to increase at many locations, such as central and northwestern Europe, but is decreasing in eastern and southwestern Europe.[38,39] Increases of 0.25 ppb per year have been reported for ground-level ozone at Mace Head, Ireland.[45] In the western U.S., mid-tropospheric (3–10 km) ozone has increased by 0.6 ppb per year in the springtime over 1995–2008, and may be indicative of long range transport.[46] Changes in the seasonal cycle observed at various mid-latitude locations in the Northern Hemisphere are consistent with increasing emissions of precursors.[47] On the other hand, a review of measurements made with balloon-borne instruments (ozone sondes) and surface observations at remote locations showed that most of the increases in both hemispheres occurred in the early part of the 20–40 year

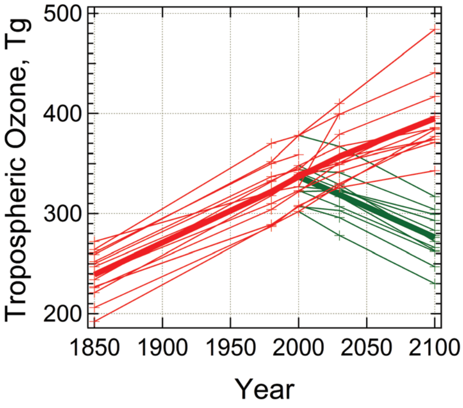

**Fig. 3** Global tropospheric ozone burden simulated by different models. Drawn from data in Table 1 of Young *et al.*[6] Thin lines are for individual model results, thick lines are multi-model averages, for two scenarios of future emissions, RCP2.6 (green) and RCP8.5 (red), as defined by the Intergovernmental Panel on Climate Change.[9]

record, with more recent changes characterised by little or no increase.[48]

Changes in atmospheric circulation are also likely to have affected trends of tropospheric ozone. Some increases may have been due to changes in the rate of stratosphere–troposphere air exchange.[49] Trends at Mauna Loa, Hawaii, were influenced by changes in circulation due to El Niño, transporting air masses from different regions of Asia to Hawaii.[50]

Prediction of tropospheric concentrations of $O_3$ *via* numerical models remains problematic, with large differences at regional[38] and global scales.[6,51] This is illustrated in Fig. 3, where several global models, represented by different lines, are seen to differ by as much as 25% for current conditions, and future predictions show a wider range depending on the choice of future scenario as well as model. However, it should be noted that future photochemical ozone formation will in any case depend to a large extent on details of future emissions, particularly those associated with different fuel choices (*e.g.* diesel, gasoline, or biofuels).

The specific response of tropospheric $O_3$ to future changes in stratospheric $O_3$ was modeled by Zeng *et al.*[52] and Zhang *et al.*[53] with both studies showing large-scale increases in tropospheric $O_3$, as a net result of slowing both production and loss in response to declining UV levels. However the low resolution of their models (several degrees latitude × longitude) is insufficient to discern urban effects where higher levels of $NO_x$ are expected to maintain an opposite (positive) relationship between UV radiation and ground-level ozone[54,55] that would indicate improvement in air quality in response to recovery of stratospheric ozone. Global models also do not agree well with measurements of the background atmosphere (*e.g.* ref. 56), indicating that there is still significant work to be done in understanding this chemistry. These uncertainties make it difficult to identify precisely which geographic regions will experience decreases in tropospheric ozone as stratospheric ozone recovers, and which ones will suffer increases.

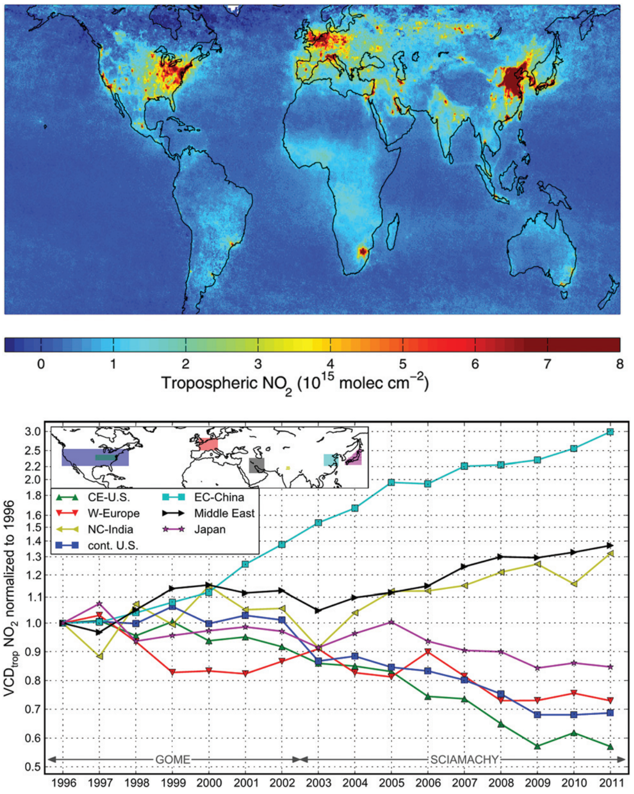

**Fig. 4** Tropospheric vertical column of nitrogen dioxide, a major air pollutant and precursor of tropospheric ozone. Top panel: global distribution averaged from May 2004 to April 2005.[3] Bottom panel: region-specific trends.[8]

Nevertheless, all models agree that over large regions tropospheric ozone will increase.

**Nitrogen dioxide.** The near-term outlook for tropospheric oxidants can also be surmised from satellite measurements of $NO_2$ (see Fig. 4), a precursor of tropospheric ozone and an important pollutant in its own right. The geographic distribution agrees with the general understanding of major emission sources, particularly over the U.S., Europe, and East Asia. Trends, also derived from satellite-based observations, are shown in the lower panel for specific regions. Notably, decreases in $NO_2$ are seen to have occurred over the U.S. and Europe, in accordance with $NO_x$ emission reduction policies, and consistent with the reductions in urban ozone reported for these regions. However, positive trends are noted for east-central China, the Middle East, and north-central India. It seems likely that such recent trends will also continue into the near-term future, with the associated expectation that ground-level ozone (and other photochemical pollutants) may increase in some areas and decrease in others.

## Particulate matter

Particulate matter (PM) in the atmosphere consists of small solid or liquid particles suspended in air, also called *aerosols*. The size of PM is recognised as important for health effects, with PM smaller than 2.5 μm (termed PM2.5) being inhaled deeper into lungs than larger particles, typically measured as all particles below 10 μm (PM10).

**Health effects.** Particulate matter in the troposphere causes significant adverse health effects. A large body of literature spanning decades of research has been reviewed and assessed confirming this causal relationship (*e.g.* ref. 57). Table 1 shows recent estimates of premature deaths from particulate matter. Recent studies have reported PM health effects from different locations. In the time-series analysis of hospitalisations for venous thromboembolic disease in Chile between 2000 and 2007 discussed for ozone above, an increase in concentration of PM2.5 of 20 μg $m^{-3}$ resulted in a relative risk (RR) of 1.05 (95% CI 1.03–1.06) for all hospitalisations.[24] A similar RR was observed for pulmonary embolism. In a study of 90 cities in China over 1981–2000, those north of the river Huai had total suspended particulates (PM of all sizes) higher by 100 μg $m^{-3}$ (95% CI = 61–307) than those south of the river, and were associated with a decrease in life-expectancy of 3 years (95% CI 0.4–5.6).[58] Much of the PM2.5 is due to particles generated in the atmosphere by UV-dependent photochemistry (*e.g.* sulfate, nitrate, and organics, see below), although other PM sources can be extremely important, *e.g.*, biomass burning plumes reaching densely populated urban areas (*e.g.*, van Donkelaar *et al.*[59]).

Where control of emissions into the troposphere has resulted in decreases in PM2.5, fewer health effects have been observed. In a study of life expectancy in 545 U.S. counties, reductions in PM2.5 of 10 μg $m^{-3}$ from 2000 to 2007 were associated with an increase in mean life expectancy of 0.35 years (SD = 0.16 years).[60]

Overall, the global relevance of particulates to human health is very large, and substantial changes are expected to occur in response to changes in climate.[61] Future predictions are uncertain due to limitations of atmospheric models and their assumptions[62] and, specifically for human health effects, the difficulty to clearly separate effects of $O_3$ and PM2.5.[63] Future changes in aerosols are uncertain but may be substantial regionally. A multi-model analysis of past and future trends in aerosol, described in Fig. 8 of Bais *et al.*,[64] indicates large changes in industrialised regions, particularly in China.

**Effects on plants.** Direct effects of PM on plants appear to be minor, for example through direct deposition of PM on foliage.[57] However, two important indirect effects should be recognised. The first is an increase in diffuse visible radiation from the scattering of solar photons by aerosol particles, altering photosynthetic efficiency within partly shaded canopies. The second is the surface deposition of some aerosol chemicals, for example, the heavy metals Cu, Ni, and Zn, with potential effects on soil chemistry, microbial communities, and nutrient cycling.[57]

**Atmospheric processes.** Particles in the atmosphere include those emitted directly, such as wind-blown dust and soil, combustion-generated soot (black carbon), and salt from sea-spray, as well as those formed *in situ* by condensation of vapours, such as sulfates, nitrates, and many organics. The latter, secondary, aerosols depend on UV-initiated reactions of $^{\bullet}OH$ radicals (see section on Global $^{\bullet}OH$ models), and thus are likely to be affected by changes in stratospheric ozone. However, we note the absence of specific studies addressing how changes in UV associated with stratospheric $O_3$ would affect the formation and removal of tropospheric particles.

The formation of sulfate and nitrate aerosols is well understood in terms of the $^{\bullet}OH$ oxidation of $SO_2$ and $NO_2$ giving sulfuric and nitric acids, respectively. While the majority of this production occurs in the gas phase, the sulfate and nitrate condense rapidly to form particles, particularly if ammonia is present. Chemical reactions in cloud and rain water can also contribute.[65]

Considerable progress has been made recently in understanding secondary organic aerosols (SOA), which previous observations had shown to be seriously underestimated by models. While many details remain poorly understood, numerous studies support the basic conceptual model that hydrocarbons are oxidised (by $^{\bullet}OH$ and $NO_3$ radicals, and $O_3$) into a myriad of heavier, more functionalised molecules as well as smaller fragments.[66] Molecules with multiple functional groups (*e.g.*, alcohols, ketones, aldehydes, organic acids, nitrates and peroxides) typically have lower vapour pressures and therefore are likely to condense onto particles. However, quantification remains a problem due to the large number of chemical species contributing to particle mass. Significant advances in modelling have been made by classifying these multifunctional compounds according to relevant properties, such as vapour pressure,[67,68] solubility,[69] oxidation state,[70] atomic ratios (O, C, H, *etc.*),[71,72] and carbon number and polarity.[73] In practice, for ambient aerosols many of these properties are not known and therefore cannot be used to constrain predictions. However, these modelling frameworks now allow exploratory sensitivity analyses to help identify the most important processes for more accurate parameterisation.

Removal of aerosols from the atmosphere is poorly understood. Ultimately removal from the atmosphere occurs by wet or dry deposition. Incorporation of aerosol particles into raindrops (wet deposition) leads to lifetimes estimated to range from 0.5 to 2 weeks.[74–76] Dry deposition of particles is generally slower.[65,77]

**Distributions and trends.** The global distribution of aerosols is shown in Fig. 5. Satellite observations and models agree on broad features, including the dust belt extending from N. Africa to S. Asia, biomass burning evident over tropical S. America, and high values over E. Asia. These optical depth values represent the entire aerosol vertical column and not necessarily those at ground level. Surface network data are available in many countries and have been used to show detailed geographical and seasonal distributions of major chemical constituents of collected particles (*e.g.* ref. 78 for the U.S.).

Heavily populated urban locations are of special interest, and some recently reported measurements in megacities are summarised in Table 3. World Health Organization (WHO) guidelines are frequently exceeded by all cities listed. Reductions in PM concentrations are occurring in many cities,

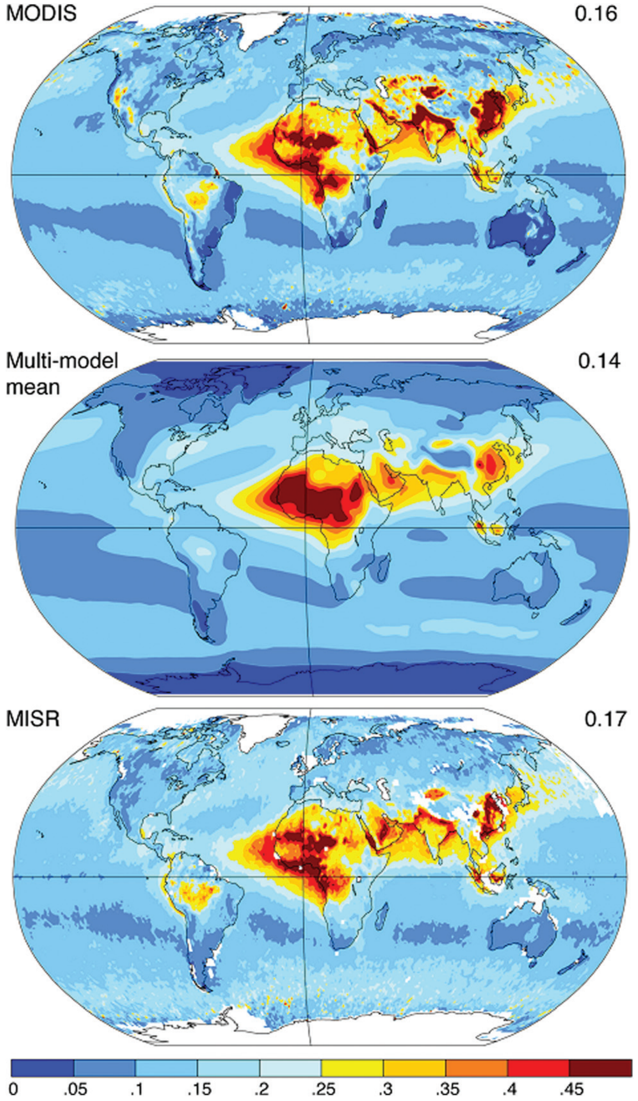

**Fig. 5** Annual average aerosol optical depth at 550 nm from the MODIS and MISR satellite instruments (top and bottom, for the years 2004–2006) and models (middle, for the year 2000). From Schindell et al.[4]

in some cases well-documented by long-term urban monitoring networks, and evidently related to emissions-lowering technologies for both fixed and mobile sources. However, measurements at many polluted locations are still sparse, making an assessment of trend difficult.

Future concentrations of aerosols are subject to similar scenario assumptions as other pollutants.[4,79,80] Globally averaged sulfate concentrations have already decreased over the last two decades and are expected to continue decreasing. Organic and black carbon are expected to continue to increase over the next few decades globally, but then decrease, with timing and magnitude depending on the specific scenario.

On smaller geographic scales, aerosol concentrations are sensitive to local and regional emissions, and may improve or worsen depending on regulatory strategies. For example, a multi-model analysis of past and future trends in aerosols, described in Fig. 8 of Bais *et al.*[64] shows strong regional reductions of aerosol concentrations by 2090, particularly in China.

**Table 3** Concentrations of particulate matter in megacities[a]

| City | PM10 (μg m$^{-3}$) | PM2.5 (μg m$^{-3}$) | Measurement period |
|---|---|---|---|
| *WHO guidelines* | *20* | *10* | *Annual mean* |
| | *50* | *25* | *24-hour mean* |
| Cairo | 90–260 | 30–220 | 1999–2002 |
| Dakar | | 30–60 | 2008–2009 |
| Bangkok | 40–90 (−) | | 1995–2008 |
| Beijing | 150–180 (−) | 95–155 | 1999–2008 |
| Delhi | 50–300 | 50–250 | 2004–2009 |
| Dhaka | >100 (+) | >30 (+) | 2002–2006 |
| Hong Kong | 40–50 (−) | 20–40 | 1998–2008 |
| Jakarta | 60–100 (−) | | 2001–2007 |
| Manila | 40–50 | 20–30 (−) | 2001–2008 |
| Seoul | 60–80 (−) | | 1995–2007 |
| Shanghai | 90–110 (−) | | 2002–2007 |
| Tokyo | | 15–30 (−) | 2001–2008 |
| Tehran | 65–370 | | 2003 |
| Santiago | 50–100 (−) | 20–30 (−) | 2000–2008 |
| Sao Paulo | 40–70 (−) | | 1996–2006 |
| Los Angeles | | 40–80 (−) | 1998–2008 |
| Houston | | 30–40 (−) | 1998–2008 |
| New York City | | 30–70 (−) | 1998–2008 |
| Mexico City | 50–180 (−) | 20–25 (−) | 1990–2010 |
| London | 20–35 | | 1994–2004 |
| Moscow | 35–50 (+) | | 2006–2008 |
| Milan | 35–60 (−) | | 2000–2009 |
| Istanbul | 45 | 20 | 2002–2003 |

[a] Positive (+) and negative (−) trends are indicated. Values shown are ranges observed over the measurement period. Compiled from data reported by Zhu *et al.*;[40] see original for details of the sampling intervals.

## Hydroxyl radicals

**Tropospheric self-cleaning capacity.** An important role of UV radiation in the troposphere is the production of $^{\bullet}OH$ radicals by photolysis of tropospheric ozone (Reaction 3 in Table 2) followed by reaction with $H_2O$ (Reaction 4, Table 2). The $^{\bullet}OH$ radicals react with many of the gases emitted at the Earth's surface, including carbon monoxide (CO), methane ($CH_4$) and other volatile organic compounds (VOCs), oxides of nitrogen and sulfur ($NO_2$ and $SO_2$), and hydrohalocarbons (HFCs and HCFCs). The reactions with $^{\bullet}OH$ determine the atmospheric residence time of these gases, as well as their amount in the atmosphere since this is directly proportional to the product of emission rates and lifetime.

Understanding $^{\bullet}OH$ is fundamental to understanding the chemistry of ozone and secondary aerosols as well. Cycling between $^{\bullet}OH$ and $HO_2$ (Reactions 5 and 6, Table 2) is essential for tropospheric ozone formation. Notably, $^{\bullet}OH$ itself has a lifetime of only seconds, but it affects $O_3$ on the time scale of hours to days, CO over months, and methane over a decade. For this reason, direct detection of $^{\bullet}OH$ has focused on local short-term measurements, while longer-term impacts, for example, on methane lifetimes, have been estimated from global models.

**Local measurements of ˙OH.** Direct measurements of ˙OH are difficult because of its high chemical reactivity. Within seconds of being produced, ˙OH reacts with various gases (see previous paragraph) limiting its concentration to low values (about $10^6$–$10^7$ mol cm$^{-3}$ during daytime, smaller at night) that are exceedingly difficult to detect and quantify. The high reactivity also implies that ˙OH has high spatial and temporal fluctuations, being sensitive to variations in production (*e.g.*, to variations in UV radiation, $O_3$, and $H_2O$) as well as loss (*e.g.*, *via* reactions with CO, $NO_x$, or VOCs). For this reason, it is important to note that locally measured ˙OH concentrations cannot be easily integrated spatially or temporally to estimate, for example, an annually averaged global ˙OH concentration. The main objective of direct local measurements is to evaluate whether the variations in ˙OH follow the expected variations in simultaneously measured meteorological (UV radiation, humidity) and chemical variables ($O_3$, $NO_x$, VOCs, *etc.*).

Several techniques have been developed over the past few decades to detect and measure concentrations of ˙OH. Measurements have been reviewed by Heard and Pilling[81] and more recently by Stone *et al.*[82] Most of the recent measurements are consistent with model calculations within a factor of approximately two, (*e.g.*, urban locations including New York City,[83] Tokyo,[84] Mexico City,[85,86] and Houston[87]). Studies in forested locations, specifically West Africa[88] and northern Michigan[89] also show reasonable agreement with models.

Measured ˙OH is much greater, by as much as an order of magnitude, than predicted by models in environments containing high concentrations of biogenic hydrocarbons (*e.g.*, isoprene, methyl butenol, and terpenes) and low concentrations of $NO_x$, including over the tropical forest of Suriname,[90–92] Borneo,[93,94] the Pearl River Delta (PRD),[95,96] and suburban Beijing during low-$NO_x$ episodes.[97] This apparent underestimation of ˙OH by models has led to a re-examination of the chemistry of isoprene at low $NO_x$, and to the suggestion that at least part of the ˙OH initially lost by reaction with isoprene is later regenerated by secondary reactions.[98,99] Simulations using an environmental smog chamber also indicate the need for some recycling of ˙OH by isoprene chemistry under very low $NO_x$ conditions, although not to an extent that would explain the large discrepancies between observations and models found over tropical Suriname (Fuchs *et al.*, 2013).[100]

Several inter-comparisons between different ˙OH instruments show good agreement in some circumstances but also disagreement in others.[82,101–103] The largest discrepancies appear to occur in environments dominated by biogenic hydrocarbons. For example, Mao *et al.*[104] found a factor of two difference between laser-induced fluorescence and a chemical analysis methods at Blodget Forest, California.

Instruments have been developed recently to measure the total ˙OH reactivity, *i.e.*, the rate at which ˙OH molecules are removed by reaction with the many constituents of sampled air (*e.g.*, CO, VOCs, and $NO_x$). The reactivity of ˙OH provides an important constraint on the budget of ˙OH since it must essentially balance the rate of production. Measurements show that this reactivity is larger than predicted from the simple sum of typically known constituents, indicating the presence of substantial but unmeasured amounts of other reactive compounds, by values ranging from 25–35% in Tokyo,[105] about 30% in a terpene-rich mid-latitude forest,[106] a factor of 2 in the Pearl River Delta[107] and 60–90% in a boreal forest.[108,109] The missing compounds are presumed to be a multitude of partly oxygenated organic compounds (aldehydes, ketones, *etc.*) formed during the ˙OH-initiated photo-degradation of VOCs.

Despite unresolved differences among various ˙OH instruments and models, some fundamental aspects of the photochemistry have been clearly demonstrated. Important in the present context is the theoretical expectation that, for relatively clean conditions, concentrations of ˙OH should scale more or less linearly with the photolysis of $O_3$ to generate O* (Reaction 3, Table 2), $j(O_3)$, which in turn is dependent on the amount of UV radiation. This linear correlation has now been re-confirmed by direct measurements of ˙OH and $j(O_3)$ over a year at Mace Head, Ireland[110] and is in agreement with earlier observations in the tropical Atlantic[111] and in the European Alps.[112] Because tropospheric $j(O_3)$ values are sensitive to the overhead ozone column, with a ~1.5% increase in $j(O_3)$ for each 1% decrease in the $O_3$ column (see Table 1 of McKenzie *et al.*,[37]), these studies reaffirm the importance of stratospheric ozone to tropospheric ˙OH and to the photochemistry of the lower atmosphere.

**Global ˙OH models.** Estimates of long-term changes in global ˙OH are uncertain and variable. Empirical estimates, based on the measured concentrations of trace gases, such as methyl chloroform, whose emissions and ˙OH kinetics are well known, are difficult due to large changes in emissions of suitable gases. An analysis of the decline in concentrations of methyl chloroform by Montzka *et al.*[113] concluded that globally averaged ˙OH varied by less than ±5% during 1997–2007. On the other hand, Monteil *et al.*[114] interpreted measurements of methane isotopes ($^{13}C$) to infer that the slowing of $CH_4$ trends in the early 2000s was due to increasing concentrations of ˙OH, at about 5% per decade, due to global increases in $NO_x$ emissions. Thus, the direction and magnitude of recent trends in global ˙OH remains unclear.

Estimates over longer time scales are largely based on models, which differ significantly. This was demonstrated by the recent intercomparison of 16 global chemistry-transport models for predictions of the methane lifetime, which is limited by reaction with ˙OH.[5,7] The modelled mean lifetime of methane was 8.6 ± 1.2 years (range 6.4–11.6 years) for the year 2000. Pre-industrial (1850) to present day (2000) changes in ˙OH were either positive or negative (see Fig. 6), depending largely on how each model specified relative changes in emissions of CO and $NO_x$. Pike and Young[115] showed that global concentrations of ˙OH (and therefore the lifetime of $CH_4$) were sensitive to how models represent ˙OH recycling by isoprene, which remains uncertain, as discussed above. If such buffering of ˙OH by biogenic VOCs is pervasive, it casts doubt

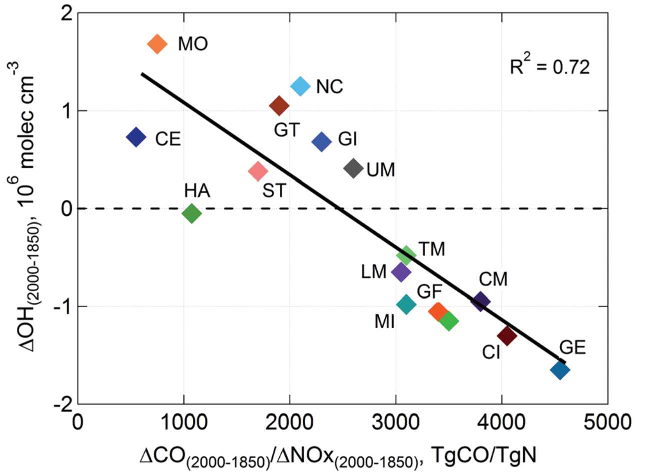

**Fig. 6** Changes in globally averaged hydroxyl radicals ($^{\bullet}$OH) between pre-industrial times (1850) and present day (2000) calculated by 16 different models (model-mean for the year 2000 $^{\bullet}$OH ~1.1x10$^6$ molec cm$^{-3}$) for relative changes in emissions of carbon monoxide (ΔCO) and nitrogen oxides (Δ$NO_x$) specified within each model (From Naik *et al.*[5]).

on the strong sensitivities to anthropogenic emissions of CO and $NO_x$ shown in Fig. 6 for current models.

An alternate approach to estimating changes in $^{\bullet}$OH based on sulfate isotopic studies suggested a 10% decrease in global $^{\bullet}$OH since pre-industrial times,[116] broadly in line with some of the models reported by Naik *et al.*[5] However, the accuracy of this method remains untested.

The multi-model mean changes in predicted $^{\bullet}$OH concentrations at the surface for the year 2100 and two different emission scenarios, RCP2.6 and RCP8.5, have been calculated[7] and are shown in Fig. 7. Substantial reductions in $^{\bullet}$OH are expected throughout much of the southern hemisphere due to large increases in methane ($CH_4$) in the RCP 8.5 scenario, while regional increases and decreases occur in both scenarios due to changes in shorter-lived precursors $NO_x$ and CO. Another model study focused on the recovery of stratospheric $O_3$ to 1980 levels (holding all other factors constant) predicted that global concentrations of $^{\bullet}$OH will decrease by 1.7% due to the lower tropospheric UV radiation levels.[53]

Global models are also sensitive to climate change, including changes in temperature, humidity, stratospheric ozone, and uncertain $NO_x$ emissions from natural sources such as biomass burning and lightning.[117–119] Thus, multi-model averages such as those shown in Fig. 7 do not truly reflect the model variability or actual uncertainties. However, in clean marine atmospheres, concentrations of $^{\bullet}$OH are well predicted by models,[120,121] but other unidentified oxidants appear to be important.[120] These other oxidants could be halogens.

## Climate-mediated changes in air quality

Air pollution is a complex, multifaceted problem that can only be correctly considered when integrated within the whole Earth system. Direct emissions from human activities are well recognized, but emissions that would otherwise be considered natural can also change due to, for example, deforestation, biomass burning, and even feedback between air quality, climate change (especially the hydrological cycle), and ecosystem health. Atmospheric transport of pollutants and their precursors is subject to circulation patterns that are likely to change under a changing climate. In particular, changes in the frequency of stagnation episodes that limit the dispersion of pollutants may have large impacts on air quality in affected areas. Chemical transformations, *e.g.*, those making ground-level $O_3$ from the photo-oxidation of hydrocarbons and nitrogen oxides, are sensitive to climate variables including temperature and moisture, as well as UV radiation. Removal of pollutants occurs mainly *via* contact with the Earth's surfaces (dry deposition) or scavenging by precipitation (wet deposition). Both could change significantly in the future, *e.g.*, changes in land-use altering rates of dry deposition, and

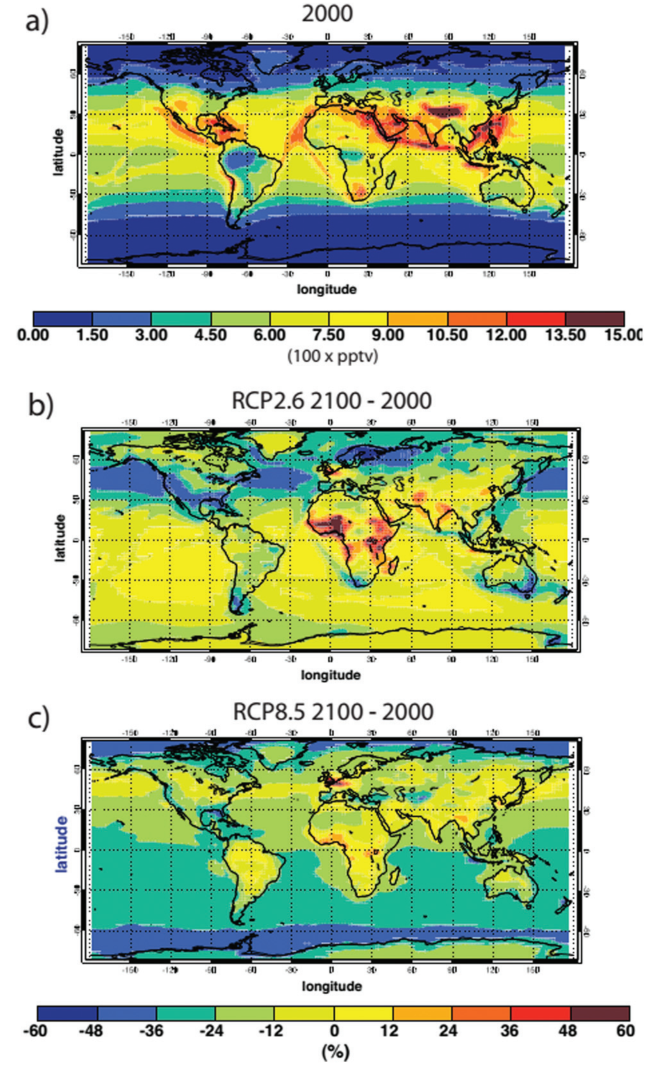

**Fig. 7** (a) Annual average surface $^{\bullet}$OH concentration, mean of 14 models, for the year 2000. (b) Model-mean % change in surface $^{\bullet}$OH concentrations in 2100 relative to 2000 for the IPCC RCP 2.6 emission scenario; (c) same for RCP 8.5 scenarios (From Voulgarakis *et al.*[7]).

changes in precipitation patterns modifying wet deposition rates.

Several potentially major interactions are discussed here. Many other feedback processes are possible and may be plausible but are not fully understood and cannot yet be quantified reliably. These are, by and large, outside the scope of the present assessment, except to the extent that we recognise their existence and therefore provide a cautionary note that the general aspects of our assessment need to be evaluated carefully for any given location with full consideration of these additional factors.

**Ozone.** Concentrations of ozone in urban environments are determined by a number of key factors. Firstly, the amount of ozone in the air entering the urban environment may be important. Then, within the urban airshed, reactions involving a range of emitted chemicals, most notably VOCs and $NO_x$, produce ozone as a result of UV-driven photochemistry. These chemicals arise from both anthropogenic and biogenic sources, the latter often being outside normal air quality management. Finally, a number of processes such as dry deposition (loss at the surface) might remove ozone from the atmosphere.

Background ozone concentrations can be influenced by long-range air transport, and this is likely to be an important factor in the future, transporting air between continents.[122] The background ozone concentrations can also be altered by changes in stratosphere/troposphere exchange and by the changes in global atmospheric composition, notably some greenhouse gases.[119] By analysing the natural variability of stratospheric transport, it has been estimated that changes in stratospheric circulation due to climate change will lead to around a 2% increase in tropospheric ozone in the northern mid-latitudes by the end of this century.[123] Although small, the significant geographic extent implies that this might be an additional factor affecting air quality.

Increased temperatures at ground level are expected to increase biogenic emissions of reactive organics (*e.g.*, ref. 124 and 125). However, emissions may well depend on other factors as well, such as water stress on the plants.[32] Indeed, changes in the climate, coupled to decreases in air quality, can substantially alter biogenic activity in ways that are difficult to predict.

Models suggest that other critical processes are also likely to be altered by climate change. Variations in cloudiness can alter the rate of photochemical production of ozone. Increased surface heating can result in changes in atmospheric movement (wind speed, both horizontal and vertical). Cloudiness can also be altered by human activity, with evidence that controls on air pollution have increased solar radiation at some locations.[126] Finally, changes in rainfall patterns and cloudiness can alter the rate of removal of both reactive precursors and ozone itself.[26] Estimates predict increasing ozone concentrations at ground level throughout the 21st century, driven by all of these meteorological factors, which are regionally dependent. This can be offset by changes in emissions from human activity, which may either augment or reverse the overall trend, depending on the levels of controls implemented.[26,127] Significant regional air quality changes may result, even if only episodically.[128]

**Particles.** The impact of climate change on aerosols remains highly uncertain. As mentioned above, increasing temperatures will increase biogenic gas emissions. The oxidation of these compounds will produce aerosols. Additional wild fires could become more important as a source of particulate matter.[129] These aerosols can scatter radiation and reduce warming (a negative feedback), and also impact upon cloud properties.[130] Changes in clouds in turn can alter the transformation (growth, chemistry) of aerosols in the atmosphere. In polluted environments the changes induced by climate will be overwhelmed by anthropogenic emissions, but in locations where anthropogenic emissions are small these changes could be significant. However, the net effect of climate change on aerosols remains unclear.[127,129] While there has been a lot of work in this area (*e.g.*, on climate/aerosol feedback models[131]) the level of scientific understanding remains very low.

**Biological interactions between air-pollutants and climate change.** Increased ambient temperatures may interact directly or indirectly to exacerbate the effects of pollutants such as $O_3$ in humans. A study of cardiovascular and respiratory mortality in 2002 to 2006 in Buenos Aires showed a relative risk of 1.0184 (95% confidence interval (CI) = 1.0139–1.0229) on the same day for each 1 °C increase in temperature.[132] Another study in several large cities in the UK reported that temperature increased mortality from cardiovascular and respiratory diseases and other non-accidental causes.[133] These authors also reported that the mean mortality rate ratio for $O_3$ was 1.003 (95% CI = 1.001–1.005) per 10 $\mu g\ m^{-3}$ increase in concentration. On hot days (greater than the whole-year 95th centile) this increased to 1.006 (95% CI = 1.002–1.009) but was only statistically significant for London. A study in older men in 2000 to 2008 in Boston showed that greater ambient temperature was associated with decreases in heart rate variability *via* dysfunction of the autonomic nervous system.[134] These warm-season associations were significantly greater when ambient ozone concentrations were above the median but were not affected by particulates (PM2.5). These studies are consistent with earlier analyses of the 2003 European heat wave episode[135,136] which attributed a significant fraction (20–60%) of excess mortality to the effects of elevated levels of $O_3$ and PM.

Change in climate also may affect human health indirectly. A study on allergic respiratory diseases and bronchial asthma showed that while exacerbation is related to air-pollutants, amounts of allergen in the air are also important.[137] The presence of allergenic pollens in the atmosphere might be prolonged by climate change and increase frequency and severity of these diseases.

### Halogenated organic and other substitutes in the troposphere

**Toxicity and risks of replacements for ozone depleting chemicals to humans and the environment.** The United States Environmental Protection Agency (USEPA) has a regulatory process for evaluating alternatives for Ozone Depleting Substances (ODS) prior to their wide-spread use in the U.S. Anyone planning to market or produce a new substitute must provide 90 days' advance notice to the Significant New Alternatives Policy (SNAP) program at USEPA of their intent as well as providing health and safety information before introducing it into interstate commerce in the U.S. Normally the health and safety information will include information on chemical and physical properties, flammability and basic toxicological information, and more recently, global warming potential. The SNAP program reviews the information in the context of the proposed use, and issues one of 4 decisions: acceptable; acceptable subject to use conditions; acceptable subject to narrowed use limits; and unacceptable. This information on a particular compound is continually updated so that compounds may be proposed for additional uses or additional information may be added to the portfolio for a particular use that could change the initial decision.

### Updates on selected halocarbons

*Brominated substances.* Natural bromo-carbons bromoform and dibromomethane are emitted from the oceans, and their emission strengths and role in the atmosphere are becoming better understood. These compounds release bromine upon oxidation in the atmosphere that is generally observed as bromine monoxide (BrO). The presence of bromine can lead to depletion of ground level ozone.[138] However, observations in other marine locations do not find such events occurring.[139] In the tropics, where sources are believed to be the biggest and vertical motion is enhanced, it has been estimated that these compounds have a lifetime in the atmosphere of 1 to 3 weeks. However, even with this relatively short lifetime, over 90% of the bromine that is transported to the stratosphere comes from these species.[140]

Bromine monoxide (BrO) is also calculated to be a significant oxidant for dimethylsulfide (20%) in the clean marine environment of the southern hemisphere.[141] This oxidation is a significant source of aerosol in this environment (nearly 20% of the total) and so has direct impacts upon cloud formation and light scattering, and hence climate. A large fraction of this BrO is derived from sea salt, and thus is an important part of the natural bromine background to which anthropogenic brominated organics are added. The overall significance of changes due to climate, as noted above, is not yet known.

n-Propyl bromide ($C_3H_7Br$), or 1-bromopropane, was introduced in the early to mid-1990s as an intermediate in a variety of closed commercial manufacturing processes for products such as pesticides, pharmaceuticals, and quaternary ammonium compounds. From the mid-1990s, it began to be used as a less toxic substitute for methylene chloride in open air uses such as vapour and immersion degreasing and cleaning of electronics and metals.[142] In 2003, it was first proposed by the SNAP program as an acceptable alternative for CFC-113 and methyl chloroform in a limited number of specific applications where emissions could be tightly controlled for both environmental and exposure concerns. Specifically, these included use as a solvent in industrial equipment for metals, electronics, and precision cleaning and in aerosol solvents and adhesive end-uses. However, the final rule issued in 2007[143] allowed use only as a solvent for industrial equipment; other uses such as aerosol solvents and adhesives are listed as unacceptable by the Agency.

The SNAP program decisions were based on health data related to reproductive and neurological end-points for which they considered a work place standard of an 8-hour time-weight acceptable exposure limit (AEL) of 25 ppm to be acceptable.[144] Subsequent to that information, reports have indicated that additional adverse effects have been added to the toxicological dossier for n-propyl bromide including immunotoxicity (significant decreases in a specific antibody) in rodents following 10 week inhalation exposures at levels of 125–500 ppm (mice) or 1000 ppm (rat)[145] and multi-site carcinogenicity following two-year chronic inhalation exposures at 250 or 500 ppm in rats and mice.[142]

*Chlorinated substances.* Chloroform ($CHCl_3$) has a number of poorly known natural sources as well as anthropogenic sources.[146] Peat bogs may be a large unrecognized natural source of chloroform (10% of the total).[147,148] Sources such as these are likely to be sensitive to both climate and land use change, and so represent an uncertainty in future predictions.

Production and consumption of carbon tetrachloride ($CCl_4$) are regulated under the Montreal Protocol. Observations show that atmospheric $CCl_4$ mixing ratios are decreasing at a rate slower than expected from assumed phase-out schedules[149,150] The sources and sinks of $CCl_4$, and their uncertainties, are beyond the scope of this paper, but it is probable that the slower decline is due to yet unidentified emissions. If such sources involve personal exposure, *e.g.*, in solvent use, potential health effects may be anticipated.[151]

*Chlorofluorinated substances.* Historically the first compounds developed as replacements for refrigerants, the largest sector where CFCs were used, were saturated hydrochlorofluorocarbons (HCFCs) and then saturated hydrofluorocarbons (HFCs), both classes of compounds which because of their hydrogen content, were susceptible to attack from hydroxyl radicals in the atmosphere, resulting in shorter atmospheric lifetimes than CFCs. Readers are referred to earlier reports for a review about the human and environmental risks for many of these replacements.

There is one compound in this category, *trans*-1-chloro,3,3,3-trifluoropropene (HCFO 1233zd(E)), which is just now being developed as a foam blowing agent, refrigerant, and solvent. A recent toxicology study[152] reported that HCFO 1233zd(E) was not acutely toxic and was not associated with any genetic toxicity in a battery of tests. The compound had an acute 4-hour 50% lethal concentration value ($LC_{50}$) of 120 000 ppm in rats, and a no observed effect level (NOEL) in canine cardiac sensitization studies of 25 000 ppm. The heart was identified as the apparent target organ on the basis of histopathological observations from a 2 week range finding study in male and female rats exposed levels of 0, 2000, 5700 and 20 000 ppm 6 hours per day for 5 days per week, Males at the mid and high doses and females at the high dose developed multifocal mononuclear infiltrates of cardiac tissue. In a 12-week study at 4000, 10 000 and 15 000 ppm, 6 hours per day for 5 days per week, a NOEL/lowest observed adverse effect level for multifocal mononuclear infiltrates of the heart was 4000 ppm. In a full inhalation developmental toxicity study at concentrations of 0, 4000, 10 000 and 150 000 ppm, HCFO 1233zd(E) was not associated with any effects on uterine, placental or fetal weights, nor were there any fetal abnormalities observed so that the study resulted in a NOEL for developmental toxicity of 15 000 ppm.

*Fluorinated substances.* Sulfuryl fluoride ($SO_2F_2$) is a substitute for the ozone-depleting fumigant methyl bromide used on crops and soils. Several reports on its use in agriculture have been published recently[153–156] and it will likely become more widely used in the future. As previously stated,[11] its atmospheric oxidation lifetime is estimated to be large (>300 years). However, $SO_2F_2$ is relatively soluble in water and is expected to partition into cloud water and ultimately rain out of the atmosphere with a half-life of about 2 weeks. The major sink is the oceans where the ultimate breakdown products are inorganic sulfate and fluoride. These breakdown products are not of concern for environment or health. However, $SO_2F_2$ has a large global warming potential (GWP) and its use is likely to increase in the future, so that monitoring of concentrations in the atmosphere should continue.

Hydrochlorofluorocarbons and hydrofluorocarbons (HCFCs and HFCs): As has been discussed previously,[11,157] several of the hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) used as substitutes for ozone-depleting CFCs and a new fluorinated olefin (HFO) can break down into trifluoroacetic acid (TFA). TFA is stable in the environment but is water soluble and accumulates in playas, land-locked lakes, and the oceans where it combines with cations such as sodium, potassium, calcium, and magnesium ($Na^+$, $K^+$, $Ca^{2+}$, and $Mg^{2+}$). More than 95% of the salts of TFA found in the oceans are naturally produced. These salts are inert and not of toxicological or environmental concern in the small concentrations ($\approx$200 ng $L^{-1}$) that are present in the oceans.

Perfluoro-*n*-butyl iodide (PFBI) is a compound being investigated as a substitute for CFCs. Its use is being explored as a replacement in aircraft maintenance operations as an alternative cleaner for liquid and gaseous oxygen aerospace systems and as a wipe cleaner solvent. A recent publication[158] summarised earlier preliminary toxicity testing results in which an acute inhalation of no observed adverse effect level (NOAEL) of 3900 ppm for cardiac sensitisation was established. Based on the results of a preliminary 4-week inhalation toxicity test, a 13-week inhalation study was conducted in which 15 male and 10 female rats per group were exposed by inhalation *via* nose-only exposure for 6 hours per day and 5 days per week to nominal concentrations of 500, 1500, and 5000 ppm PFBI. The 13-week inhalation exposure at 1500 ppm was associated with increases in concentrations of thyroid hormones and thyroid stimulating hormone in serum of male and female rats. These concentrations returned to control values following the 4-week recovery period without exposure in males (the only animals given a recovery period). The authors noted that, based on published information, they assumed that the return to normal following the recovery period indicated that the hormonal changes were only transient and not adverse and that the changes in female rats would also return to normal. Thus the NOAEL was selected to be 1500 ppm. The 3900 ppm from the earlier work served as an occupational acute exposure limit for PFBI, while the 1500 ppm NOAEL was converted to an occupational exposure limit (OEL) by adjusting it to an 8-hour/day time-weighted average exposure and applying uncertainty factors for animal to human, inter-human variability and subchronic to chronic extrapolation to arrive at a final value of 40 ppm.

Modelling of susceptibility of the analogous compound (perfluoro-*n*-propyl iodide) to photolysis suggested a half-life of a few hours in sunlight. Based on rapid degradation, PFBI has zero GWP and is not an ODS. Its atmospheric degradation is likely to produce TFA, analogously to many other fluorinated organics, *e.g.* some HCFCs and HFCs (see above).

*Hydrofluoroolefins (HFOs).* Among the other new compounds being used as substitutes are those belonging to the class known as hydrofluoroolefins (HFOs). Two examples currently being developed for use in the refrigeration, foam-blowing and/or aerosol sectors, 1,3,3,3 tetrafluoropropene (HFO 1234ze) and 2,3,3,3 tetrafluoropropene (HFO-1234yf) have recently been characterised toxicologically.[159–161] In the case of HFO 1234ze, the compound was not acutely toxic at levels as high as 207 000 ppm following 4 hours of exposure and showed no activity in a battery of genetic toxicity tests. In addition, the compound did not induce cardiac sensitization at levels as high as 120 000. Following a 2 week range finding study at 5000, 20 000 and 50 000 ppm 6 hours per day, 5 days per week, the liver and heart were identified as the target organs; however, in a subsequent 4 week study at 1000, 5000, 10 000, and 15 000, and a 90 day study at 1500, 5000, and 15 000, only the heart was identified as the target organ. The associated finding was multifocal mononuclear cell infiltrates with no evidence of fibrosis and no evidence of increased severity with increased duration of exposure.

No new papers on the relevance of TFA to human health and the environment have been published in the literature since the date of the previous assessment (2010). Thus, projected future increased loadings of TFA to playas, land-locked lakes, and the oceans due to continued use of HCFCs, HFCs, and replacement products are still judged to present negligible risks for aquatic organisms and humans.

## Gaps in knowledge

A key air quality constituent is ozone, and any future changes in ozone have significant outcomes for both human and environmental health. However, the direction and the magnitude of change in tropospheric ozone due to recovery of stratospheric ozone are still under debate, may depend on location, and need to be better quantified. Modulation by UV radiation will modify the impacts of climate change and regulation of local emissions. This represents a significant gap in our understanding. Computer modelling now has the potential to address this issue, but still requires the development and refinement of parameterisations for physical and chemical processes, as well as future scenarios under different socioeconomic assumptions.

Particulate matter (aerosol) plays a significant role in climate change and also in air quality. While the role of UV radiation in PM formation is known, the sensitivity of PM properties to changes in UV radiation has not been sufficiently quantified.

The oxidation capacity of the atmosphere remains poorly characterised in a number of environmentally sensitive regions, with an order of magnitude difference between measurements and models. Both measurements and our understanding of the key chemical processes have large uncertainties. One example of this lack of understanding is the uncertainty in future methane concentrations, with models predicting $^{\bullet}$OH driven lifetimes that differ by a factor of 2.

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