

Changes in air quality and tropospheric composition due to depletion of stratospheric ozone and interactions with climate

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Air pollution will be directly influenced by future changes in emissions of pollutants, climate, and stratospheric ozone, and will have significant consequences for human health and the environment. UV radiation is one of the controlling factors for the formation of photochemical smog, which includes tropospheric ozone (O₃) and aerosols; it also initiates the production of hydroxyl radicals ([•]OH), which control the amount of many climate- and ozone-relevant gases (*e.g.*, methane and HCFCs) in the atmosphere. Numerical models predict that future changes in UV radiation and climate will modify the trends and geographic distribution of [•]OH, thus affecting the formation of photochemical smog in many urban and regional areas. Concentrations of [•]OH are predicted to decrease globally by an average of 20% by 2100, with local concentrations varying by as much as a factor of two above and below current values. However, significant differences between modelled and measured values in a limited number of case studies show that chemistry of hydroxyl radicals in the atmosphere is not fully understood. Photochemically produced tropospheric ozone is projected to increase. If emissions of anthropogenic air pollutants from combustion of fossil fuels, burning of biomass, and agricultural activities continue to increase, concentrations of tropospheric O₃ will tend to increase over the next 20–40 years in certain regions of low and middle latitudes because of interactions of emissions, chemical processes, and climate change. Climate-driven increases in temperature and humidity will also increase production of tropospheric O₃ in polluted regions, but reduce it in more pristine regions. Higher temperatures tend to increase emissions of nitrogen oxides (NO_x) from some soils and release of biogenic volatile organic compounds (VOCs) from vegetation, leading to greater background concentrations of ozone in the troposphere. The net effects of future changes in UV radiation, meteorological conditions, and anthropogenic emissions may be large, thus posing challenges for prediction and management of air quality. Aerosols composed of organic substances have a major role in both climate and air quality, and contribute a large uncertainty to the energy budget of the atmosphere. These aerosols are mostly formed *via* the UV-initiated oxidation of VOCs from anthropogenic and biogenic sources, although the details of the chemistry are still poorly understood and current models under-predict their abundance. A better understanding of their formation, chemical composition, and optical properties is required to assess their significance for air quality and to better quantify their direct and indirect radiative forcing of climate. Emissions of compounds containing fluorine will continue to have effects on the chemistry of the atmosphere and on climate change. The HCFCs and HFCs used as substitutes for ozone-depleting CFCs can break down into trifluoroacetic acid (TFA), which will accumulate in oceans, salt lakes, and playas. Based on historical use and projections of future uses, including new products entering the market, such as the fluoro-olefins, increased loadings of TFA in these environmental sinks will be small. Even when added to existing amounts from natural sources, risks to humans or the environment from the historical use of CFCs or continued use of their replacements is judged to be negligible.

Introduction

Poor air quality (from the presence of pollutants in the atmosphere) plays a significant role in both human and environmental health. Globally, outdoor air pollution is estimated to lead to 850 000 premature deaths each year, mostly from respiratory and cardiovascular diseases.^{1,2} The cost of crop damage in the US

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was estimated between 3.5 and 6.1 billion dollars annually.³ These problems are expected to continue well into the future: Predictions based on numerical models indicate that annual deaths due to ground-level oxidants alone could reach 2 million in 2050,⁴ while the annual cost of crop damage is predicted to be of the order of US\$20 billion by 2030.⁵ Variations in stratospheric ozone and climate change are important drivers of changes in the production and fate of air pollutants.

Solar UV-B radiation (280–315 nm) and UV-A (315–400 nm) provide the energy for many of the chemical transformations that occur in the atmosphere. These wavelengths photo-dissociate (break down *via* photolysis) a number of important atmospheric gases, *e.g.* nitrogen dioxide (NO₂), formaldehyde (HCHO), and ozone (O₃). These processes will be altered by anything that changes the amount of UV radiation, including the elevation of the sun and attenuation by clouds and some air pollutants. Decreases in stratospheric ozone lead to enhanced UV-B radiation in the lower atmosphere (troposphere), and increase the rate of the photolytic processes.⁶ Increasing temperature from climate change also increases the rates of many reactions, leading to higher concentrations of surface O₃ in polluted regions, and causing increments in mortality that could exceed those resulting from climate-related increase in storminess.⁷ As a result, there is a direct link between stratospheric ozone depletion, climate change, and air quality.

The replacements for the original ozone-depleting chemicals (chlorofluorocarbons (CFCs)), such as the hydrochlorofluorocarbons (HCFCs) and the hydrofluorocarbons (HFCs), decompose primarily in the lower atmosphere. This decomposition can produce breakdown products, such as trifluoroacetic acid, that need to be considered for their impacts on humans and the environment.⁶

Here we present an assessment of recent work on our understanding of the impacts of ozone depletion, ozone-depleting chemicals and their replacements on atmospheric composition and how these may interact with climate change to adversely affect the environment and human health. This is an update of the information in the previous report.⁶

Photochemistry in the troposphere

Solar UV radiation is a major driver of tropospheric chemistry, causing photo-dissociation of various relatively stable molecules into more reactive fragments. These fragments initiate a series of chemical reactions that fundamentally change the composition of the atmosphere at all scales, from urban to regional to global, and affect many environmental issues including air quality, visibility, formation of particles and clouds, acidification of precipitation, and lifetimes of removal from the atmosphere of gases including sulfur and nitrogen oxides, methane, and other volatile organic compounds (VOCs), as well as HFCs and HCFCs that affect the ozone layer and climate.

A simplified schematic of tropospheric chemistry is given in Fig. 1. The key initiating reaction is the interaction of tropospheric O₃ with UV photons (shown as *hν* in Fig. 1) leading to the photo-dissociation, or photolysis, of O₃ to produce electronically excited oxygen atoms, O(¹D), and molecular oxygen O₂ (Fig. 1, reaction 1). A fraction of O(¹D) atoms can react with atmospheric water vapour, H₂O, to form hydroxyl radicals, [•]OH (Fig. 1, reaction 2).

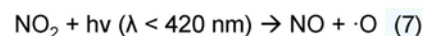
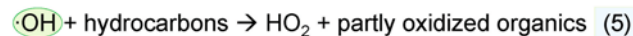
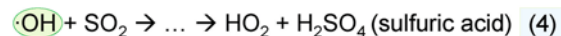
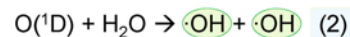
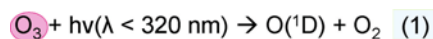


Fig. 1 Key reactions in the chemistry of air pollutants in the troposphere.

As shown in Table 1 in McKenzie *et al.*,⁸ for each percent decrease in the ozone column amount, the rate coefficient for reaction 1 (Fig. 1) increases by *ca.* 1.5%. This non-linear response means that tropospheric chemistry is very sensitive to the amounts of stratospheric ozone. This has been a clear stress point for change in stratospheric ozone as changes in concentration of [•]OH, globally averaged, could have significant impacts on the chemical composition of the atmosphere.

The hydroxyl radical is widely regarded as the cleaning agent of the atmosphere because it converts many atmospheric chemicals, including major air pollutants, into forms that are more water-soluble and therefore more easily removed from the atmosphere in precipitation. For example, [•]OH reacts with nitrogen and sulfur dioxides to make the corresponding nitric and sulfuric acids, and with hydrocarbons and other VOCs to make a variety of partly oxidized organics (aldehydes, alcohols, ketones, *etc.*) (Fig. 1, reactions 3–5). Many of the reactions involve multiple steps including catalytic cycles.⁹

Some of these gaseous products tend to have low vapour pressures and thus can condense to form air-borne particles (solid and liquid aerosols), with associated reductions in transparency of the atmosphere and damage to human health, especially in highly polluted urban areas. The hydroperoxy radical (HO₂) and its organic analogues, produced in the above reactions, are also the major source of tropospheric ozone, *via* the sequence shown in Fig. 1, reactions 6–8.

UV-B radiation is important for the initial production of [•]OH radicals (reaction 1 followed by reaction 2, Fig. 1), while UV-A radiation is important for the formation of ambient ozone (reaction 7 followed by reaction 8, Fig. 1). Although not shown in the simplified scheme of Fig. 1, the UV photolysis of several other molecules also can be important in specific environments, *e.g.* formaldehyde and nitrous acid in urban areas, peroxides in more pristine areas, and ketones in the upper troposphere.

In addition to UV radiation, other factors also influence the amounts of [•]OH, O₃, and aerosols in the atmosphere. These include emission of nitrogen oxides (NO_x = NO + NO₂) and VOCs, temperature, water vapour, and meteorological transport and mixing processes, some of which are also influenced by changes in climate.

Hydroxyl radicals in the atmosphere – a product of photolysis by UV

The UV-generated hydroxyl radical, $\cdot\text{OH}$, is central to the chemistry of the troposphere, as discussed above; yet accurate measurements of its amounts in the atmosphere are extremely challenging both to perform and to interpret. The measurement difficulty arises because $\cdot\text{OH}$ is highly reactive and therefore present in very small amounts, typically less than one part per trillion (ppt, equal to one $\cdot\text{OH}$ for every trillion molecules). Several techniques for $\cdot\text{OH}$ measurement have been developed and refined in recent years, and comparisons among them show that they are highly correlated, but calibration of such measurements remains an issue¹⁰ causing considerable uncertainty in absolute measurements of concentrations of $\cdot\text{OH}$.

The very short lifetime (<1 s) also means that the concentration of $\cdot\text{OH}$ is very variable, both in space and in time. This makes the interpretation of measurements difficult because amounts of $\cdot\text{OH}$ measured at any location or time are unlikely to be representative of large geographic scales (*e.g.* regional, continental, hemispheric, or global), of vertical distributions (near-surface *vs.* middle and upper troposphere), or of temporal variations (daytime *vs.* nighttime, seasonal cycles, *etc.*). Thus, even if the uncertainty of direct $\cdot\text{OH}$ measurements were reduced, such measurements would not be useful for assessing global changes in $\cdot\text{OH}$ concentrations (and the associated long-term changes in the global atmospheric self-cleaning ability), as a result of trends in UV radiation due to depletion of O_3 , climate change, or increased global pollution.

Alternative less direct methods for inferring globally averaged concentrations of $\cdot\text{OH}$ rely on observations of long-term changes in the concentrations of compounds whose lifetimes are determined by $\cdot\text{OH}$ radicals. A compound frequently used for this purpose is methyl chloroform, an industrial solvent present in the atmosphere. Methyl chloroform is anthropogenically produced and is removed from the atmosphere mainly by reaction with $\cdot\text{OH}$. In principle, the measurement of the amount of methyl chloroform in the atmosphere, coupled with self-reported estimates of the amount emitted by industry into the atmosphere should allow the global average concentration of $\cdot\text{OH}$ and any changes to be estimated. However, such estimates have differed, depending on details of the analysis (*e.g.* ref. 11 and 12). A recent assessment of the global concentration of $\cdot\text{OH}$ ¹³ determined from methyl chloroform warns that the uncertainties in quantifying the transport of compounds through the atmosphere could limit the ability of this method to detect changes in $\cdot\text{OH}$. New developments in modelling a range of chemicals simultaneously in the atmosphere¹⁴ and the addition of long-term records of volatile organic compounds¹⁵ offer opportunities to reduce some of these modelling limitations in the future.

Possible changes in $\cdot\text{OH}$ since pre-industrial times have been summarized recently.^{16,17} No reliable observational proxies are known for such long-term changes, requiring reliance on atmospheric chemistry-transport models and assumptions about historical emissions of the compounds that affect $\cdot\text{OH}$, especially nitrogen oxides (which tend to increase $\cdot\text{OH}$) and VOCs (which tend to decrease $\cdot\text{OH}$). The production of $\cdot\text{OH}$ in the atmosphere is estimated to have increased by 60 to 70% in the last century, approximately compensating for increases in the rate of removal.^{18,19} Depending on the model and assumptions used, concentrations

of $\cdot\text{OH}$ may have decreased by less than 10% or as much as 33% since pre-industrial times.

More recent changes in $\cdot\text{OH}$ in the last few decades have been influenced by varying emissions of precursors, changes in tropospheric UV radiation associated with stratospheric O_3 depletion, as well as interannual variability. The global concentration of $\cdot\text{OH}$ due to changes in atmospheric composition has been calculated to have decreased²⁰ (0.8% per decade over 1890–1990) and to have increased²¹ (0.8% per decade over 1990–2001), with a high degree of uncertainty.²² From a UV perspective, $\cdot\text{OH}$ has been calculated to have increased by 3.5% due solely to depletion of stratospheric ozone,²³ although this trend is expected to reverse in future decades as stratospheric O_3 returns to pre-1980 levels (see McKenzie *et al.*⁸).

The future of $\cdot\text{OH}$ in the atmosphere depends on a wide range of factors. As an example of possible changes, Wild and Palmer¹⁸ have taken a scenario (SRES A2p)²⁴ where, in 2100, the emission of VOCs, NO_x , CO, and methane has approximately doubled over 2000 levels. However, the meteorology and stratospheric ozone is held constant so that the results can isolate the impact of emissions. Under these conditions, the photochemically generated ozone increases also by a factor closer to two. The $\cdot\text{OH}$ concentration, as shown in Fig. 2, varies also by a factor of two, but with both significant increases and decreases. The net change in $\cdot\text{OH}$ is a 20% reduction of its global concentration. However, this change is likely to be reduced by climate change (increases in temperature and humidity). Isaksen *et al.*²² similarly conclude that the competing nature of the effects makes the overall trend of $\cdot\text{OH}$ in the future unclear. Future changes in UV-B radiation will modify both the trends and distribution of $\cdot\text{OH}$ in the troposphere. Global-scale reductions in $\cdot\text{OH}$ would have considerable implications for the concentrations of many climate- and ozone-relevant gases in the atmosphere, *e.g.* if $\cdot\text{OH}$ is reduced by 20%, methane and HCFCs concentrations would increase by about 20% even if their emissions were held constant.

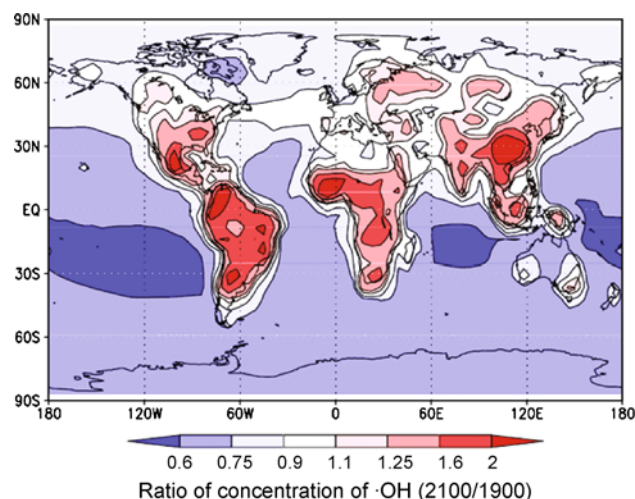


Fig. 2 Ratio of the concentration of $\cdot\text{OH}$ in 2100 to that calculated in 1900 at the surface (reproduced with permission from ref. 18).

Direct measurements of $\cdot\text{OH}$ can be useful for testing current understanding of photochemistry on short time scales, especially when ancillary observations (*e.g.*, of UV radiation, temperature,

humidity, O₃, NO_x, carbon monoxide, and VOCs) are available. Over the past several decades, a general understanding has been developed of the processes that control formation of [•]OH and its destruction (e.g., ref. 25–28). However, and due in part to the more advanced techniques for measuring [•]OH and related species (especially the closely coupled radicals HO₂ and RO₂), several recent studies have shown that, while some aspects of [•]OH chemistry are well understood, other aspects remain unexplained. Measurements in both polluted regions²⁹ and in unpolluted rainforest³⁰ show concentrations of [•]OH that are several times higher than those expected using accepted chemical pathways – see red and green (upper and middle) arrows in Fig. 3. The higher concentration of [•]OH is suspected to stem from enhanced regeneration of [•]OH by currently unidentified atmospheric compounds indicated by the yellow (lower) arrows in Fig. 3. Direct measurements of the total reactivity of [•]OH radicals also suggest a faster loss of [•]OH than would be computed from the sum of all individually measured compounds known to react with [•]OH.^{31,32} Similar problems exist with the hydroperoxyl radical HO₂, which, in urban environments with high concentrations of NO_x, is observed at much higher concentrations than predicted by models (e.g.,³³).

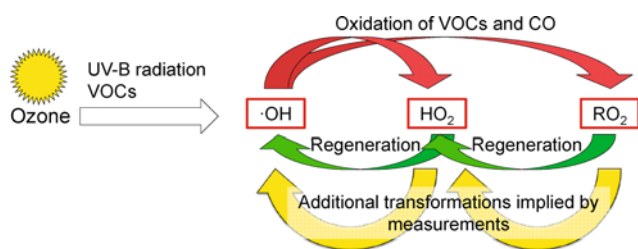


Fig. 3 Proposed changes in the chemistry of [•]OH in the atmosphere. The red (upper) and green (middle) arrows summarize the accepted reactions in a polluted atmosphere²⁹ and the yellow (lower) arrows show the additional transformations, implied by measurements, for regenerating [•]OH. VOC = volatile organic compounds, CO = carbon monoxide, [•]OH = hydroxyl radical, HO₂ = hydroperoxy radical, RO₂ = organic peroxy radicals.

These recently discovered discrepancies remain largely unexplained and are not yet considered in global chemistry-transport models (e.g., those reviewed by IPCC¹⁷) used to estimate past, current, and future trends of [•]OH. It is unclear to what extent the new chemical pathways, when finally unravelled and quantified, will change these estimates, and further studies will clearly be needed to re-evaluate how tropospheric [•]OH is responding to changes in stratospheric O₃, climate, and emissions of air pollutants.

Tropospheric ozone

Tropospheric O₃ is one of the most important regional-scale air pollutants, causing adverse effects on respiratory health of humans,^{1,2,34} and decreases in crop production.^{35,36} About 5–10% of the total atmospheric ozone column resides in the troposphere. Stratospheric ozone can affect the quality of air at ground level directly by transport from the stratosphere and indirectly *via* changes in photochemical processes.³⁷ The transport of stratospheric ozone and photochemistry within the troposphere can be significantly modified by increased temperatures and humidity resulting from

climate change, through changes in atmospheric circulation (including changes in stratosphere-troposphere exchange), changes in the hydrological cycle, and changes in emissions of precursors of air pollutants.

The environmental impact of increases in ozone at ground level is widely acknowledged.³⁸ The World Health Organization (WHO) recommended air quality guideline for protection of human health was reduced in 2005 to an 8 h time-weighted mean concentration of 50 parts per billion by volume (ppbv). WHO notes that O₃ from “natural causes” could occasionally exceed the guideline.¹ As a result, relatively small changes in ozone at ground level may have significant effects on measures of air quality through more frequent exceedances of the guideline.

Pre-industrial values of tropospheric O₃ were probably much lower than current values, especially in populated regions of the Northern Hemisphere.³⁹ Since the mid-1980s, concentrations of tropospheric O₃ in a number of locations have increased at rates of 0.3 to 0.5 ppbv per year, mostly as a result of anthropogenic activity.^{36,40,41} Such estimates are logically limited to sites where ground measurements exist. It would be better if more global estimates based on measurements from satellites were possible. These have been attempted using a number of satellites (e.g., ref. 42 and 43), although this process is difficult as it involves measuring the relatively small amount of O₃ that lies below stratospheric O₃. New satellite-borne instrumentation and analyses are making significant advances in this area.^{44,45} While the satellite observations are most sensitive to O₃ in the mid-troposphere (5–10 km above the surface), this method has the potential to provide significant information about ground level ozone levels.⁴⁶ Such information will be important in assessing the role of international impacts on regional air quality, an area of significant on-going research.⁴⁷

An analysis of air masses in the mid-troposphere (3–8 km above sea level) over western North America for the period 1995–2008, found significant increases in concentrations of O₃ (0.63 ± 0.34 ppbv per year) during the spring months.⁴⁰ During spring, intercontinental transport of O₃ is most efficient, particularly in the prevailing westerlies between Asia and North America. Even greater increases in concentrations of O₃ (0.80 ± 0.34 ppb per year) were observed in air masses of Asian origin. This suggests that the rise in anthropogenic emissions of precursors to O₃ over Asia may be partly responsible for increases in tropospheric O₃ over western North America. This has significant implications for human and environmental health as well as for the impacts of climate change, either where the O₃ forms, or in regions to which O₃ might be transported.

UV radiation exerts a strong influence on the formation and destruction of tropospheric ozone, through the system of photochemical reactions shown in Fig. 1. Increases in UV radiation are expected to decrease concentrations of tropospheric O₃ in clean environments, but increase concentrations of O₃ in polluted, NO_x-rich environments.⁴⁸ Recent work has examined changes in UV radiation due to particulate pollutants (aerosols). Reduction of UV radiation in urban areas due to the presence of aerosols has been observed, and this has been found to reduce the rate of formation of ozone.^{49,50}

Predicting future changes presents significant technical challenges, as there is a need to understand both global and small scale effects at the interface between the stratosphere and

troposphere and at ground level. Models have been improved to limit the tendencies to simulate too rapid transport of ozone from the stratosphere to ground level.^{51,52} Similarly, the impact of biases in temperature and humidity on modelled estimates of concentration of ozone has been estimated.⁵³ This work should improve confidence in performance of the models, although the importance of quantifying stratosphere-troposphere exchange reliably remains a challenge. In a number of regions in the northern hemisphere, an increase in temperature was found to be correlated with higher concentrations of ozone.⁵⁴ While very useful as an indicator of likely atmospheric behaviour in a warming climate, such observations do not allow the assessment of the relative importance of other contributing factors.

Detailed numerical models based on projections to 2050 (Fig. 4) and beyond, predict concentrations of tropospheric O₃ to further increase up to 4 ppbv in the mid-latitudes because of climate change and interactions of climate change with atmospheric chemistry.³⁵ The drivers for this are a doubling of CO₂, an assumed 50% increase in emissions of isoprene from plant-cover, and a doubling of emissions of soil-derived NO_x in conjunction with releases from human activity,⁵⁵ plants (see Ballaré *et al.*⁵⁶) and from the ocean.⁵⁷ However, other models predict different geographical and temporal distributions of the changes in tropospheric O₃. For example, another study⁵⁸ shows maximum increases in O₃

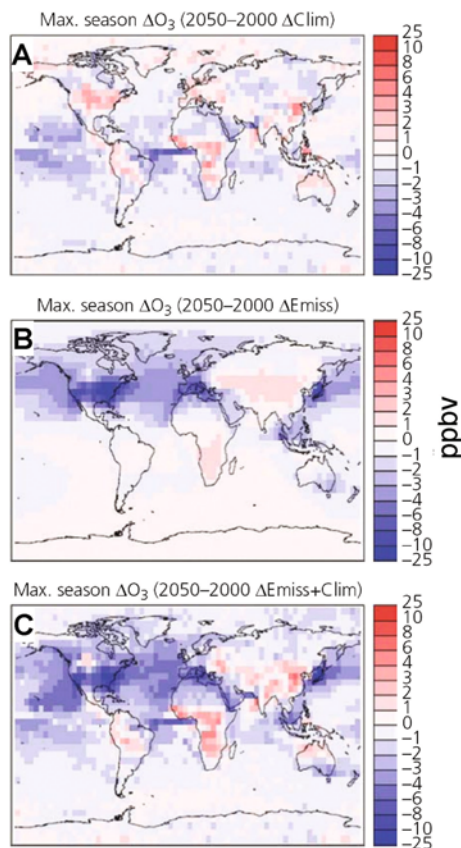


Fig. 4 Predicted changes in surface ozone between 2000 and 2050.³⁵ Panel A shows changes predicted for additional emissions of precursors. Panel B shows the change in ozone predicted to result from changes in climate. Panel C shows the result for the combined impact of increased emissions of precursors of O₃ and increases resulting from climate change (reproduced with permission from the Royal Society).

occurring by 2030 in the Middle East and Europe, in contrast to the more widespread changes shown in Fig. 4C.

Predictions of changes in tropospheric O₃ at a regional scale depend on the interplay of several factors. Rising global emissions of anthropogenic air pollutants will tend to increase O₃. However, climatic factors resulting in greater humidity will lead to greater rates of destruction of O₃ in the tropics but not in the mid-latitudes, which are predicted to be drier.³⁶ Changes in precipitation and local circulation can also be significant.⁵⁴ Increased temperatures of some soils can increase NO_x emissions, leading to increases in O₃.⁵⁹ Climate-induced changes in atmospheric circulation may increase the stratosphere-to-troposphere O₃ flux, leading to long-term changes in both stratospheric and tropospheric O₃. In addition, biogenic emissions are sensitive to other climate variables including temperature, CO₂ and solar radiation^{60,61} and may affect future budgets of O₃. As there is uncertainty in these predictions as well as in the interactions between O₃ and factors related to climate change, the final effects on O₃ in the troposphere and stratosphere are unclear and additional information will be needed to address this issue.

Changes in cloudiness could have a profound effect on both O₃ and [•]OH, and atmospheric photochemistry in general. Numerical models indicate that clouds currently have only a modest impact on global O₃ averaged over the troposphere, due to the offset between shading below cloud and radiation enhancement above cloud (Fig. 5).^{61,62} Regionally, however, the impact can be large, and climate variations could lead to both an increase or decrease in cloudiness. Changes in the vertical distributions of O₃ and [•]OH can also be large.⁶³

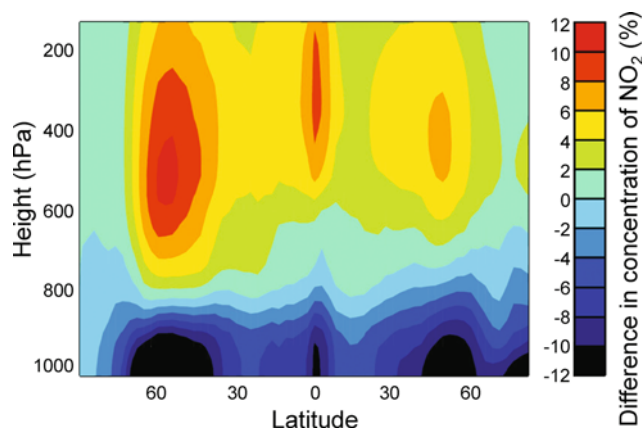


Fig. 5 Prediction of the change in the rate of photolysis of NO₂ from calculations that include and exclude clouds.⁶² At low altitudes, photolysis is decreased by the presence of clouds. At higher altitudes, the photolysis rates are increased due to the reflection from the cloud tops. The scale on the right shows the difference in annual mean concentration.

The impact on ground-level ozone of increased downward transport of stratospheric ozone due to the control of ozone-depleting substances under the Montreal Protocol and climate change has been estimated, assuming that there is no change in emissions into the atmosphere other than an assumed increase in greenhouse gases.⁶⁴ For simplicity, photolysis has also been assumed to be unaffected by stratospheric ozone change. While there is a large increase in transport of ozone into the troposphere (43%), the climate model predicts little change in O₃ in the northern

hemisphere at ground level. However, in the southern hemisphere winter, an increase of 8 ppbv of O₃, which represents an increase of *ca.* 50%, and little change in summer are predicted. This highlights the importance of including return of stratospheric ozone in estimates of future air quality. However, the magnitude of the overall changes will depend on the interplay of all the factors discussed here.

In contrast to the adverse direct effects of tropospheric O₃ on human health, in plants the physiological responses to future climate change (increased dryness and CO₂) will decrease uptake of O₃, mitigating the impact of increases in O₃ on crop production in these regions. In areas with greater warming and less drying, such as in northern latitudes, risks of ozone damage to crops have been projected to increase because of increasing hemispheric transport of pollution leading to greater concentrations of ozone in the growing season when plants are more sensitive.³⁶ Drying as a result of climate change could also have an impact on the frequency and extent of fires, and thus affect the regional atmospheric burdens of aerosols and other pollutants. These different regional vulnerabilities will need to be considered in future control strategies for sources of air pollution.

Aerosols in the troposphere

Aerosols (small air-borne particles) have a significant impact on human health through effects on respiratory and cardiovascular systems,¹ and can have a large impact on the physics and chemistry of the atmosphere. As noted previously,⁶ aerosols scatter and absorb incoming solar radiation, changing the atmospheric energy balance and the rate of photochemical reactions. They also affect the formation of clouds, modifying their optical properties, their precipitation efficiency, and lifetimes. The IPCC¹⁷ has recognized the effects of aerosols as the highest uncertainty in the radiative forcing budget of the atmosphere.

Aerosols can be generated from a wide range of sources and can be primary (directly emitted) or secondary (generated in the atmosphere). While sea-salt and dust are major sources by mass, both biogenic sources (such as emissions from plants) and anthropogenic activities represent significant sources of organic material. Soot and primary organic aerosols (POAs) are emitted during burning of fossil fuels and biomass. For example, a recent study found that, in Beijing, concentrations of POAs were due mostly to biomass burning, cooking, vehicular exhaust, and coal burning.⁶⁵ Secondary aerosols include sulfate, produced from the oxidation of SO₂ in the gas phase by [•]OH radicals and in the aqueous phase by peroxides, nitrates, and secondary organic aerosols (SOAs) from the photo-oxidation of hydrocarbons (reactions 3–4, Fig. 1).⁹

The formation of SOAs has received much attention in the past few years, following the realizations that (i) traditional models fall short of explaining the observed concentrations of SOA, with discrepancies ranging from a factor of three to two orders of magnitude,⁶⁶ and (ii) the atmospheric concentrations of SOAs are frequently as large as, or larger than, those of other aerosols including sulfate.⁶⁷ While many of these studies took place in urban areas, SOAs from forested regions were also identified as important,⁶⁸ and even the ubiquitous biogenic hydrocarbon isoprene was shown to produce significant yields of SOAs.⁶⁹ In urban areas, a likely source for the previously unexplained SOAs may be the evaporation of primary organic aerosols (POAs) followed

by the gas phase reaction with [•]OH radicals and condensation of the reaction products as SOAs.^{70,71} Other studies have shown that the anthropogenic and natural sources of aerosols may be linked intrinsically through the gas phase photochemistry, for example, with anthropogenic NO_x accelerating the production of SOAs from biogenic (non-anthropogenic) hydrocarbons.⁷² Analysis of the ratios of carbon isotopes (¹⁴C/¹²C) shows that, even in polluted urban areas, a significant fraction of the particulate carbon is not from fossil fuels but is rather from biogenic emissions and burning of biomass, *e.g.* 30% in Los Angeles,⁷³ 30–50% in Beijing,⁷⁴ 30–40% in Tokyo,⁷⁵ and 30–60% in Mexico City.^{76,77}

Neither anthropogenic nor biogenic organic aerosols are well simulated by current numerical models, although it is clear that UV radiation initiates the cascade of chemical reactions resulting in the formation, *via* photo-generation of [•]OH radicals and their reactions with VOCs to yield condensable organic compounds. Wet and dry deposition is believed to be the major removal process, although there is increasing evidence that UV radiation may have a role in the destruction of SOA, by the photolysis of surface-bound carbonyl compounds and the subsequent release of gases such as carbon monoxide, formaldehyde, and formic acid^{78,79} (see action spectra in Fig. 6 of McKenzie *et al.*⁸).

Some models for studying the evolution of organic aerosols in specific, relatively simple environments are in early stages of development. For example, a numerical model has been developed that reproduces observed aerosol production over a conifer forest, using observed changes in the environment including temperature and UV-B radiation.⁸⁰ This model has then been applied to predicting particle formation in future climate scenarios. Changes in O₃, temperature and water vapour were considered. Temperature is the independent variable, with changes in O₃ assumed to be driven by increased release of volatile organic compounds from trees. Unfortunately, due to the uncertainties, the impact of changes in UV-B radiation has not been estimated. Another model of changes in aerosol production over the US includes changes in cloudiness but does not explicitly include UV-B radiation.⁸¹

Even for inorganic aerosols, future changes are difficult to calculate because they depend not only on stratospheric ozone, but also on tropospheric chemical processes and on climate change. For example, numerical models show that future concentrations of sulfate and nitrate aerosols will depend sensitively on [•]OH radical concentrations, which in turn depend on emissions of NO_x, methane, and other VOCs.⁸² Wind is also a major factor determining dust and sea spray emissions, size distributions, and transport,^{83,84} and higher wind speeds over oceans and land will increase their concentrations. Mulcahy *et al.*⁸⁵ found a strong increase of the optical depths of sea spray with wind speed, leading to reductions in direct solar radiation equivalent to or greater than that seen in significant pollution events.

Some advances have been made in the past few years in determining the optical properties of aerosols at UV wavelengths. One previously unexpected result was that the absorption of these short wavelengths by aerosols is quite large, and cannot be explained by their known chemical composition.^{86–89} A possible explanation is that this absorption is due to organic compounds contained within the SOA particles, but which are not yet fully understood as discussed above.^{86,88} These UV properties of the aerosols can provide a significant feedback on to the photochemistry: absorbing aerosols tend to reduce the available UV radiation and thus slow

the production of tropospheric O₃,⁴⁹ while scattering aerosols can increase the effective pathlength of UV photons and lead to more rapid production of O₃.⁹⁰

Halogens in the troposphere

As both measurement techniques and the understanding of possible chemical processes are improving, new information shows that the roles that halogens play in the lower atmosphere are more diverse than previously thought. Knowledge of the impacts of these halogens on tropospheric ozone and how they interact with changes in UV-B radiation will be important for a more accurate prediction of risks from tropospheric ozone in the future.

Bromine and brominated substances

Bromine-containing compounds, such as bromoform (CHBr₃), are a well-known source of reactive halogen with relevance to both tropospheric and stratospheric ozone. Recent studies have further highlighted the likely significance and variety of oceanic sources.^{91,92} Ocean surveys of bromine oxide (BrO), produced by the oxidation of compounds such as bromoform, have shown that coastal regions⁹³ and passively venting volcanoes⁹⁴ can be significant sources likely to affect concentrations of ozone in these regions.⁹⁵

Studies of the atmosphere around the Dead Sea have reported events of unexpectedly large depletions of surface concentrations of O₃ (up to 93% loss). The co-occurrence of significant amounts (176 pmol mol⁻¹) of BrO in the surface boundary layer did not fully explain the loss of ozone.⁹⁶ A partial explanation may be provided by newly identified reaction mechanisms of halogen-containing compounds and aerosols.⁹⁷ While these studies have focused on polluted atmospheres, the particle-based reactions may also explain observations of reactive halogen species in the upper troposphere.⁹⁸ In the future, increasing surface temperatures of tropical seas are expected to increase the movement of these reactive species from the troposphere to the stratosphere⁹⁹ and contribute to depletion of stratospheric ozone, through changes in atmospheric circulation.

Iodine and iodinated substances

The species of iodine equivalent to those of bromine (discussed above) have been detected in marine coastal atmospheres at similar concentrations to the bromine compounds,¹⁰⁰ although the concentrations of precursors appear to be less than those of the bromine species¹⁰¹ and it is not clear how widespread the sources of these compounds are. The significance of iodinated substances in terms of air quality is unclear at this time.

Chlorine and chlorinated substances

In contrast to other halogens, chlorine-containing species have been considered relatively unimportant for ozone in the troposphere even though there are a few pathways that were known to produce Cl atoms.¹⁰² Any Cl atoms will react rapidly to form HCl, which is then washed out of the atmosphere. However, studies on the surface chemistry of hydrochloric acid (HCl) and oxides of nitrogen (NO_x) have shown that when HCl and NO_x are adsorbed

on surfaces (formerly thought of as a removal mechanism) they react to generate gaseous nitrosyl chloride (ClNO) and nitryl chloride (ClNO₂).⁹⁷ When these absorb UV and visible radiation, they break down to form highly reactive chlorine atoms that react with VOCs and result in increases in the concentrations of O₃ in the troposphere. In modelling this process in the South Coast Air Basin of California, the addition of the interaction between HCl from sea salt, NO_x, and solar radiation increased concentrations of O₃ by 40 ppbv (20%) at peak periods. Evidence from atmospheric observations is needed to assess the environmental importance of this mechanism.¹⁰³

Anthropogenic emissions of halocarbons, *e.g.* methyl chloroform (C₂H₃Cl₃),¹⁰⁴ continue and also will contribute to depletion of stratospheric ozone. A study of emissions of HCFC-22 inferred from atmospheric observations indicated that the storage time was significant, delaying emissions and therefore delaying the impact of the production and release of these substances and the final recovery of stratospheric O₃.¹⁰⁵

Fluorinated substances in the troposphere

Historically, the fluorinated substances, such as the chlorofluorocarbons (CFCs) had a major impact on stratospheric O₃. For this reason, there is still strong interest in this class of compounds, new products, their replacements, and their degradation products. Sulfuryl fluoride (SO₂F₂) is an industrial chemical released into the atmosphere in significant quantities (kilotonnes (kt) per year). Sulfuryl fluoride has been suggested as a substitute for methyl bromide, a depletor of stratospheric ozone, in fumigation of crops and soils.¹⁰⁶ Global production in 2006 and 2007 was 3.5 and 2.3 kt, respectively but has increased steadily since 1960 when it was only 57 t and will likely increase into the future, especially if used more widely. The potential impact of sulfuryl fluoride in the atmosphere is now becoming clearer. Estimates of atmospheric lifetimes are >300, >5000, and >10⁷ years for removal processes driven by ·OH, ·Cl and O₃, respectively.¹⁰⁶ Although SO₂F₂ is relatively soluble in water,¹⁰⁷ at this time the significance of other potential removal processes such as partitioning to cloud water (followed by deposition) is not known. The rate of hydrolysis in water with pH similar to cloud water (5.9) is small (2.6 × 10⁻⁶ s⁻¹),¹⁰⁷ which is consistent with lack of observed hydrolysis in the atmosphere.¹⁰⁸ The rate under alkaline conditions (pH 8.3) is 100 times faster, suggesting that it will not accumulate in surface waters unless these have pH < 6. The ultimate hydrolysis products (inorganic sulfate and fluoride) are judged to present negligible risks to the environment. Recently published measurements of SO₂F₂ in current and archived atmospheric samples show that the global tropospheric background concentration is smaller in the southern than in the northern hemisphere but has increased by 5 ± 1% per year from 1978 to 2007.¹⁰⁹ Models have predicted global atmospheric lifetimes of 36 to 40 years with a major sink in the oceans. Modelled emissions underestimated production by 33%, suggesting that, during use as a fumigant, about one third is destroyed and does not enter the atmosphere.¹⁰⁹ Based on uncertain data, the GWP for SO₂F₂ (*i.e.*, its global warming potential relative to CO₂) is estimated to range from 120–7600 for a 100 year time horizon.¹⁰⁶ This, and likely increases in use of SO₂F₂ in the future, suggest that monitoring concentrations in the atmosphere needs to be continued.

As has been discussed previously,⁶ several of the hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) used as substitutes for ozone-depleting CFCs, can break down into trifluoroacetic acid (TFA). Two new fluorinated olefins (HFOs) that are entering the market may also break down into TFA.^{110,111} HFO-1234yf (2,3,3,3-tetrafluoro-1-propene, Fig. 6) is a refrigerant, particularly for air-conditioning in vehicles.^{110,111} HFO-1234ze (1,3,3,3-tetrafluoroprop-1-ene, Fig. 6) is a new agent used for blowing of insulating and structural foams. An analysis of emissions and subsequent production of TFA from HFO-1234yf, based on penetration in the US domestic market up to 2050, was combined with three-dimensional air quality modelling to estimate the concentrations of TFA in rainwater and to predict the potential increase in ground level O₃.¹¹¹ This analysis concluded that the projected maximum concentration of TFA in rainwater should not result in a significant risk of adverse effects in the environment and that production of O₃, resulting from emissions of HFO-1234yf, is unlikely to be a major concern for local air quality in most locations. A similar analysis of HFO-1234ze concluded that little or no TFA would be produced, because of structural differences between the two molecules that would prevent the formation of TFA from HFO-1234ze (Fig. 6). However, there are no experimental data in the literature to test this theory.¹¹²

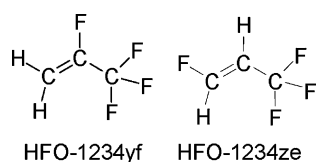


Fig. 6 Structures of the refrigerant HFO-1234yf and blowing agent HFO-1234ze.

The final environmental sink for TFA is in the oceans, playas, and landlocked lakes. Concentrations of TFA in rainwater range from <0.5 to 350 ng L⁻¹, depending on location and proximity to human activity¹¹³ and this source is predominantly anthropogenic. As TFA is very stable and very water soluble, it accumulates in the oceans where concentrations, largely from natural sources, are *ca.* 200 ng L⁻¹.¹¹⁴ Based on historical production of HFCs and HCFCs as potential sources of TFA, as well as projections of future uses, a worst-case estimate of release of TFA from complete conversion of HFCs and HCFCs yielded a global increase of 22 000 kt of TFA by the time of planned phase-out of the HFCs and HCFCs (2030–2045). Assuming release of 50–100 kt HFO-1234yf per year for 100 years from 2015, complete conversion to TFA (50–100 kt per year, as they have the same molecular weight) would increase concentrations in the oceans by 3.7–7.4 ng L⁻¹, a small increase above the background concentration of 200 ng L⁻¹ as estimated by Frank *et al.*¹¹⁴

Because of high water solubility, low octanol/water (K_{OW}), and octanol/air (K_{OA}) partition coefficients, TFA does not accumulate in aquatic or terrestrial organisms and does not bioaccumulate in food chains. As TFA is a strong acid (dissociation constant $pK_a = 0.3$), it is completely ionised at normal environmental pH and is present as a salt form in the soils, surface water, and oceans. No adverse effects of salts of TFA in mammals or humans were identified in earlier reviews¹¹⁵ or in the peer-reviewed literature up to August 2010. Concentrations of salts of TFA causing measurable effects in organisms in the environment are

large (222 000 to 10 000 000 ng L⁻¹)^{116,117} and provide an estimated 10 000-fold margin of safety for worst-case scenarios. Projected future increased loadings to playas, land-locked lakes, and the oceans (*via* precipitation and inflow of fresh water) due to climate change and continued use of HCFCs, HFCs, and replacement products,^{6,111} are still judged to present negligible risks for aquatic organisms and humans.

Some questions have been raised about the formation of monofluoroacetic acid (MFA). MFA is a naturally occurring compound that is a toxic constituent of the poisonous South African plant *Dichapetalus cymosum*, also known as gifblaar, and several other poisonous plant species.¹¹⁸ MFA is highly toxic to animals because it inhibits the energy-producing Krebs (citric acid) cycle by blocking the action of a key enzyme, aconitase. MFA is not formed from TFA except in very unusual situations where dehalogenation could occur, such as in anaerobic sediments.¹¹⁸ Small amounts of MFA are produced from the heating of Teflon (600 °C)¹¹⁹ but there is no evidence to suggest that it is formed from CFCs or their replacement HFCs. If it were formed, MFA would be degraded rapidly by microorganisms and, in soil, has a short half-life, and no potential for accumulation in the environment.¹¹⁸

Conclusions

The impacts of air pollution on human health and the environment will be influenced directly by future changes in emissions of pollutants, climate, and stratospheric ozone. UV radiation is one of the controlling factors for the formation of photochemical smog, which includes tropospheric O₃ and aerosols; it also initiates the production of [•]OH, which controls the amount of many climate- and ozone-relevant gases, such as methane and HCFCs in the atmosphere. Uncertainties still exist in quantifying the chemical processes and wind-driven transport of pollutants. The net effects of future changes in UV radiation, meteorological conditions, and anthropogenic emissions may be large but will depend on local conditions, thus posing challenges for prediction and management of air quality. Numerical models predict that future changes in UV radiation and climate will modify the trends and geographic distribution of [•]OH, thus affecting the formation of photochemical smog in urban areas and regions with greater concentrations of precursors. This will also affect concentrations of greenhouse gases in the atmosphere. Concentrations of [•]OH are predicted to decrease globally by an average of 20% by 2100, with local concentrations varying by as much as a factor of two above and below current values. However, significant differences between modelled and measured values in a limited number of case studies show that chemistry of [•]OH radicals in the atmosphere is not fully understood. Therefore, consequences for human health and the environment are uncertain.

Photochemically produced tropospheric O₃ is projected to increase. If emissions of anthropogenic air pollutants from combustion of fossil fuels, burning of biomass, and agricultural activities continue to increase, concentrations of tropospheric O₃ will increase over the next 20–40 years in certain regions of low and mid-latitudes because of interactions of emissions, chemical processes, and climate change. Climate-driven increases in temperature and humidity will also increase production of tropospheric O₃ in polluted regions, but reduce it in more pristine regions. Higher temperatures will tend to increase emissions

of NO_x from some soils and release of biogenic VOCs from plants, leading to greater background concentrations of O₃ in the troposphere. For the future protection of human health and the environment, more effective controls will need to be considered for emissions of NO_x and VOCs related to human activities. In addition, the development of ozone-tolerant crops will ameliorate the effects of O₃ on the production of food and fibre.

Aerosols composed of organic substances have a major role in both climate and air quality, and contribute a large uncertainty to the energy budget of the atmosphere. Aerosols are mostly formed via the UV-initiated oxidation of VOCs from anthropogenic and biogenic sources, although the details of the chemistry are still poorly known and current models under-predict their abundance. A better understanding of their formation, chemical composition, and optical properties is required to assess their significance for air quality and to better quantify their direct and indirect radiative forcing of climate.

Emissions of compounds containing fluorine will continue to have effects on the chemistry of the atmosphere and on climate change. Models predict global atmospheric lifetimes of 36 to 40 years for sulfuryl fluoride (SO₂F₂), a substitute for the fumigant methyl bromide. Based on the estimated GWP for SO₂F₂ and likely increased use in the future, there is a potential for adverse effects that should be considered in the future. The hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs), used as substitutes for ozone-depleting CFCs, can break down into trifluoroacetic acid (TFA), which is very stable and will accumulate in the oceans, salt lakes, and playas. Based on historical use and projections of future uses, including new products entering the market such as the fluoro-olefins, increased loadings of TFA in these environmental sinks will be small. Even when added to existing amounts from natural sources, risks from TFA to humans and organisms in the aquatic environment are judged to be negligible. There is no indication that the highly toxic chemical, monofluoroacetic acid would be produced in toxicologically significant amounts by degradation of trifluoroacetic acid or directly from hydrochlorofluorocarbons and hydrofluorocarbons used as substitutes for ozone-depleting chlorofluorocarbons (CFCs). The resulting risk to humans or the environment from the historical use of CFCs or continued use of their replacements is judged to be negligible.

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