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Changes in tropospheric composition and air quality due to stratospheric ozone depletion and climate change

Stephen R. Wilson
University of Wollongong, swilson@uow.edu.au

Keith R. Solomon
University of Guelph, ksolomon@uoguelph.ca

Xiaoyan Tang
Peking University, xytang@ces.pku.edu.cn

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Abstract

It is well-understood that reductions in air quality play a significant role in both environmental and human health. Interactions between ozone depletion and global climate change will significantly alter atmospheric chemistry which, in turn, will cause changes in concentrations of natural and human-made gasses and aerosols. Models predict that tropospheric ozone near the surface will increase globally by up to 10 to 30 ppbv (33 to 100% increase) during the period 2000 to 2100. With the increase in the amount of the stratospheric ozone, increased transport from the stratosphere to the troposphere will result in different responses in polluted and unpolluted areas. In contrast, global changes in tropospheric hydroxyl radical (OH) are not predicted to be large, except where influenced by the presence of oxidizable organic matter, such as from large-scale forest fires. Recent measurements in a relatively clean location over 5 years showed that OH concentrations can be predicted by the intensity of solar ultraviolet radiation. If this relationship is confirmed by further observations, this approach could be used to simplify assessments of air quality. Analysis of surface-level ozone observations in Antarctica suggests that there has been a significant change in the chemistry of the boundary layer of the atmosphere in this region as a result of stratospheric ozone depletion. The oxidation potential of the Antarctic boundary layer is estimated to be greater now than before the development of the ozone hole.

Recent modeling studies have suggested that iodine and iodine-containing substances from natural sources, such as the ocean, may increase stratospheric ozone depletion significantly in polar regions during spring. Given the uncertainty of the fate of iodine in the stratosphere, the results may also be relevant for stratospheric ozone depletion and measurements of the influence of these substances on ozone depletion should be considered in the future.

In agreement with known usage and atmospheric loss processes, tropospheric concentrations of HFC-134a, the main human-made source of trifluoroacetic acid (TFA), is increasing rapidly. As HFC-134a is a potent greenhouse gas; this increasing concentration has implications for climate change. However, the risks to humans and the environment from substances, such as TFA, produced by atmospheric degradation of hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) are considered minimal. Perfluoropolyethers, commonly used as industrial heat transfer fluids and proposed as chloro-hydrofluorocarbon (CHFC) substitutes, show great stability to chemical degradation in the atmosphere. These substances have been suggested as substitutes for CHFCs but, as they are very persistent in the atmosphere, they may be important contributors to global warming. It is not known whether these substances will contribute significantly to global warming and its interaction with ozone depletion but they should be considered for further evaluation.

Keywords

Changes, tropospheric, composition, air, quality, due, stratospheric, ozone, depletion, climate, change, GeoQUEST

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Changes in tropospheric composition and air quality due to stratospheric ozone depletion and climate change

S. R. Wilson^a, K. R. Solomon^b, and X. Tang^c

^a*Department of Chemistry, University of Wollongong, NSW, 2522, Australia*

^b*Centre for Toxicology, University of Guelph, ON, N1G 2W1, Canada*

^c*Peking University, Center of Environmental Sciences, Beijing 100871, China*

Summary

It is well-understood that reductions in air quality play a significant role in both environmental and human health. Interactions between ozone depletion and global climate change will significantly alter atmospheric chemistry which, in turn, will cause changes in concentrations of natural and human-made gasses and aerosols. Models predict that tropospheric ozone near the surface will increase globally by up to 10 to 30 ppbv (33 to 100% increase) during the period 2000 to 2100. With the increase in the amount of the stratospheric ozone, increased transport from the stratosphere to the troposphere will result in different responses in polluted and unpolluted areas. In contrast, global changes in tropospheric hydroxyl radical (OH) are not predicted to be large, except where influenced by the presence of oxidizable organic matter, such as from large-scale forest fires. Recent measurements in a relatively clean location over 5 years showed that OH concentrations can be predicted by the intensity of solar ultraviolet radiation. If this relationship is confirmed by further observations, this approach could be used to simplify assessments of air quality. Analysis of surface-level ozone observations in Antarctica suggests that there has been a significant change in the chemistry of the boundary layer of the atmosphere in this region as a result of stratospheric ozone depletion. The oxidation potential of the Antarctic boundary layer is estimated to be greater now than before the development of the ozone hole.

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In agreement with known usage and atmospheric loss processes, tropospheric concentrations of HFC-134a, the main human-made source of trifluoroacetic acid (TFA), is increasing rapidly. As HFC-134a is a potent greenhouse gas; this increasing concentration has implications for climate change. However, the risks to humans and the environment from substances, such as TFA, produced by atmospheric degradation of hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) are considered minimal. Perfluoropolyethers, commonly used as industrial heat transfer fluids and proposed as chloro-hydrofluorocarbon (CHFC) substitutes, show great stability to chemical degradation in the atmosphere. These substances have been

suggested as substitutes for CHFCs but, as they are very persistent in the atmosphere, they may be important contributors to global warming. It is not known whether these substances will contribute significantly to global warming and its interaction with ozone depletion but they should be considered for further evaluation.

Introduction

Reductions in air quality (from the presence of pollutants in the atmosphere) play a significant role in both environmental and human health. Poor air quality can lead to many adverse outcomes such as acid rain and respiratory disease. In the context of this assessment, it is recognized that increases in concentrations of tropospheric ozone and harmful substances generated from ozone have been shown to have significant impacts on human health as well as in the environment, particularly on plants. These effects have been widely reported and reviewed¹⁻⁷ and are not discussed further here. The quality of the air depends on a wide range of factors, including how rapidly chemicals are released and the reactions these substances undergo once they are released into the atmosphere. Solar UV-B radiation (280 – 315 nm) provides the energy for many of the chemical transformations that occur in the atmosphere. For example, the energy provided causes photolysis of a number of important atmospheric trace gases, such as sulfur dioxide (SO₂), formaldehyde (HCHO), and ozone (O₃). These processes will be altered by anything that changes the amount of UV-B radiation, including the elevation of the sun, clouds, and attenuation by some air pollutants.

The release of Ozone Depleting Substances (ODS), when transported to the stratosphere, reduces the amount of ozone. Decreases in stratospheric ozone lead to enhanced UV-B radiation in the lower atmosphere (troposphere), increasing the rate of the photolytic processes.^{8,9} As a result, there is a direct link between stratospheric ozone depletion and air quality.

There are other factors that change the reactive chemistry of the atmosphere, including increased air pollution and the emissions of climatically important greenhouse gases. Changes in climate can also dramatically change the chemistry of the atmosphere. Higher temperatures can lead to increases in the rates of chemical reactions, in the amount of water vapor present, and thus OH production¹⁰ as well as enhance emissions of volatile organic compounds such as isoprene from biological sources.¹¹ All of these factors then potentially interact in determining the actual atmospheric condition.^{12, 13} Thus, while change in atmospheric composition and circulation are observed, assigning cause and effect requires careful assessment.

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 chemicals that impact air quality.⁸

Here we present a summary of recent work on understanding the impacts of ozone depletion, ozone depleting chemicals and their replacements on atmospheric composition and how these may interact with climate change. This is an update of the information in the previous report.⁸

Stratosphere – Troposphere Exchange

One direct impact of stratospheric ozone depletion is a potential reduction in the amount of ozone transported into the troposphere (Stratosphere Troposphere Exchange, STE). It has been

estimated that there has been an approximate 30% reduction in the amount of ozone transported from the stratosphere to the troposphere due to stratospheric ozone depletion.¹⁴ While there is agreement that ozone concentrations in the upper troposphere are very sensitive to change in stratospheric ozone, there remains a divergence of opinion on the sensitivity of ground-level ozone. Some calculations have predicted that up to 40% of ground-level ozone is due to transport of ozone from the stratosphere, depending on season and location,^{15, 16} but other estimates are a factor of two lower.¹⁴ All three models estimate that the contribution of vertically transported ozone to ground-level ozone concentrations is smallest in summer compared with other season in both hemispheres.

The mixing of stratospheric air (and hence ozone) into the troposphere is critically dependent on atmospheric circulation. A modeling study of the chemistry-climate interactions showed that the rate of ozone transport into the troposphere is affected by El Niño Southern Oscillation (ENSO) events.¹³ An analysis of satellite ozone measurements also detected a dependence on ENSO, although they suggest it is due to the impact of circulation changes on *in situ* production.¹⁷ Climatic variability can therefore mask changes in the contribution of stratospheric ozone to the troposphere due to stratospheric ozone depletion.

The situation is further complicated as stratospheric ozone depletion appears to explain most of the cooling observed in the lower stratosphere over the last two decades.¹⁸ Such a cooling will modify STE, although it is not clear that this has been explicitly included in most current atmospheric models. We can conclude, however, that stratospheric ozone depletion will have a significant but small impact on tropospheric ozone amounts to date due to STE.

Significant longer-term increases in the amount of ozone brought into the troposphere from the stratosphere have been predicted due to climate change (80% by 2100).¹⁹ This calculation ignored the increase in stratospheric ozone, which would increase the stratospheric-tropospheric transport further. Such changes in the upper troposphere are not directly convertible into ground-level concentrations due to possible changes in chemical processes in the troposphere. However, predictions indicate that ground-level ozone is likely to increase significantly in the next century,^{14, 15} a trend enhanced by increases in stratospheric ozone. The predictions of these models could be verified against measured concentrations. However, the number of sites with long-term temporal and spatial measurements is few. This is an obvious data gap that could be addressed with collection of additional monitoring information.

Atmospheric photolysis

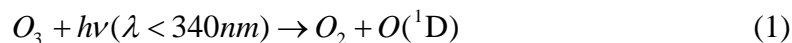
There has been ongoing work studying the fundamental atmospheric processes that are driven by solar radiation and, in particular, by UV-B radiation. Syntheses of data (photolysis cross sections and reaction rates) have recently been produced.²⁰⁻²² This section summarizes some of the key recent outcomes of this work.

Ozone in the troposphere. Ozone in the lower atmosphere plays a number of key roles. Due to its adverse impact upon both human and environmental health in many regions (e.g., European Union²), it is used as a key indicator of air quality.

Photolysis of ozone in the lower atmosphere is the primary source of the hydroxyl radical (OH) in unpolluted, humid environments, and OH initiates the removal process for most organic chemicals in the atmosphere, including methane and CO. It is estimated that OH initiates the destruction of 3 700 million tonnes of trace gases each year, including many gases involved in

ozone depletion, the greenhouse effect, and urban air pollution.²³ These reactions lead to the formation of products which are subsequently taken up by cloud droplets and precipitation and washed out of the atmosphere. OH therefore plays a dominant role in the ability of the atmosphere to “cleanse” itself.

The formation of OH radical in clean environments is described by the following two reactions:



The key ozone photolysis product for the formation of OH is the O(¹D) atom. O(¹D) is an oxygen atom that has sufficient energy to react with H₂O. Another possible product of light absorption by ozone is the less energetic O(³P) oxygen atom which has insufficient energy to react with water (reaction (2)) and primarily reacts with oxygen again to form ozone. The chemical reactions have been discussed in more detail elsewhere.⁹

The production rate of O(¹D) depends critically on the amount of UV radiation which, in turn, is dependent upon stratospheric ozone. As stratospheric ozone depletion increases solar radiation in the critical wavelength region, the loss of stratospheric ozone would be expected to lead to an increase in tropospheric O(¹D), if nothing else changed. The total rate of production of O(¹D) is determined by the concentration of ozone and the photodissociation constant J , which is given by

$$J = \int F(\lambda) \cdot \sigma(\lambda, T) \cdot \phi(\lambda, T) d\lambda, \quad (6.1)$$

where the integral is over wavelength (λ) at the temperature T . Here $F(\lambda)$ is the actinic flux, a measure of the amount of solar radiation available for initiating the chemical reaction, $\sigma(\lambda, T)$ is the strength of ozone absorption (cross section) and $\phi(\lambda, T)$ is the efficiency (quantum yield) of O(¹D) production. The wavelength dependence of these is shown in **Figure 1**. With decreasing wavelength, the actinic flux ($F(\lambda)$) of solar radiation decreases dramatically due to the absorption by (mainly stratospheric) ozone, but the efficiency of production increases (given by the product $\sigma(\lambda, T)\phi(\lambda, T)$). This results in a small range of wavelengths (primarily in the UV-B region) where the maximum production of O(¹D) occurs. The wavelength of maximum O(¹D) production shifts depending on the amount of stratospheric ozone, the elevation of the sun above the horizon, and environmental parameters such as temperature.

There have been significant advances in the determination of the actinic flux (see ²⁴), which is more formally defined as the amount of solar radiation available at a point in the atmosphere. There are instruments designed to measure actinic flux directly.^{25, 26} However, most measurements are of irradiance (the solar energy falling on a horizontal surface – see **Figure 2**). Methods have now been developed for converting irradiance to actinic flux.²⁷⁻³² The uncertainty in irradiance-derived actinic flux for $J(O^1D)$ is greater than for directly measured values. The uncertainty in the conversion of irradiance into actinic flux depends on the solar zenith angle, wavelength, and ambient conditions, but can be as low as 7% (95% confidence).²⁸

The quantum yield ($\phi(\lambda, T)$) for production of O(¹D) in the wavelength region around 308 nm is crucial. First, this is the wavelength of maximum production. Secondly, many of the estimates of the quantum yield at other wavelengths have been made relative to the quantum

yield at 308 nm. Recent work has reduced the uncertainty in the quantum yield at 308 nm (298K = 25°C) by nearly a factor of two.³³ These new values agree closely with previous best estimates based on the average of various laboratory measurements.²⁰

It is now realized that the quantum yield for O(¹D) production is non-zero up to at least 340 nm. While at these longer wavelengths the product $\sigma(\lambda, T)\phi(\lambda, T)$ is small (**Figure 1**), this longer wavelength dependence does reduce the dependence of O(¹D) on the amount of stratospheric ozone.^{20, 22} This has resulted in very good agreement between chemical and spectroradiometric measurements of the photolysis rate.³⁴ Measurements and models of UV actinic flux at the surface now show good agreement.³⁵ Similarly, measurements of OH and chemical model predictions of OH based on UV radiation measurements now normally agree to within measurement accuracy in remote, clean observation sites.^{36, 37} As discussed in ²⁴, the impact of clouds on actinic flux can be as large.³⁸ With such large variations, any future changes in cloud amount due to climate change could significantly change photochemically induced atmospheric processes.

In air substantially affected by land, other sources of OH have now been recognized as important, such as the photolysis of nitrous acid (HONO) (predominantly by UV-A radiation) in both urban environments³⁹ and in forests.⁴⁰ The wide variety of compounds present and variability of the atmospheric composition in continental air makes modeling assessments, like those described above for clean remote sites, very difficult.

Observed changes in OH. The OH radical has a very short atmospheric lifetime and is present in very small amounts, making direct detection of long term trends impossible. Two alternative methods have been used to determine global trends in OH indirectly.

The main method used for OH-trend detection involves interpretation of the long-term record of methylchloroform (Cl₃C-CH₃; 1,1,1-trichloroethane). Its only source is anthropogenic and the dominant sink is reaction with OH. With a good knowledge of the source, it is possible to infer the removal rate, and hence the amount of OH. Original estimates based on this technique suggested that there was little change in OH since 1980.⁴¹ More recent analysis suggested substantial changes in the amount of OH occurred during the 1990s.⁴² The issue of unaccounted emissions of methylchloroform has been raised. The magnitude of methylchloroform emissions from landfills has been debated as a result of measurements in Europe^{43, 44} and the US.^{45, 46} Consideration has also been given to the magnitude of ocean exchange,⁴⁷ which illustrates how difficult it is to account for the complexity of the atmosphere.⁴⁸ The most recent assessment, including a consideration of these factors, indicates that OH concentrations in 2003 are very similar to those of 1978, with the major alterations in the global OH concentration being driven by wildfires and climatic variations.²³ Global increases in the OH concentration due to stratospheric ozone depletion^{49, 50} are therefore masked by other factors or are smaller than the uncertainties of the measurements themselves.

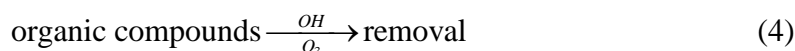
A second method of estimating OH has recently been developed using ¹⁴CO.⁵¹ No significant trend in OH for the Southern Hemisphere in the 1990s could be detected. Unfortunately, the data do not extend back far enough in time to be especially sensitive to changes induced by stratospheric ozone depletion.

A five-year study of OH at a European mountain site⁵² found no detectable long term trend in OH concentration, and highlighted that, in this somewhat polluted site, there were clearly factors that were affecting OH concentration that were not part of existing atmospheric chemical

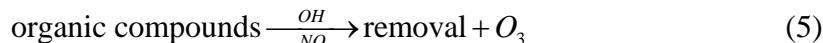
models.^{52, 53} Rohrer and Berresheim⁵² concluded that OH concentration is essentially proportional to $J(O^1D)$ and that scaling of OH by $J(O^1D)$, which depends on solar UV radiation, eliminated most of the diurnal and seasonal variation, and transformed OH into a parameter with significantly reduced variability, provided that factors dependent on local conditions are considered.⁵² Rohrer and Berresheim⁵² proposed that regional or even global OH distributions could be characterized by a simple set of coefficients for timescales on the order of months or even years and suggested that this approach may be used to define an ‘OH index’ that characterizes the oxidation efficiency of the troposphere in different chemical regimes. This would establish a direct link between stratospheric ozone concentrations and OH concentrations on regional scales. An overarching issue is that most of these models are based on measured data from a limited number of locations, such as in Europe, Japan, North America, and over the Pacific. The troposphere still remains largely under-sampled with respect to OH measurements from the tropics (rain forests) or very large cities such as those in East Asia, key areas for the understanding of how climate change and air quality will influence each other in the near future.⁵⁴

Global numerical models of OH in the atmosphere have advanced significantly. Three dimensional models that include the important known atmospheric chemistry processes⁵⁵ are now being augmented with models that include atmospheric transport.⁵⁶ Such models will be useful in assessing the impacts of climate change on OH concentrations. One such study has been carried out for the United States, which predicts an increase in OH of between 10 and 15%, and significant increases in ozone in the eastern states.⁵⁷

Observed changes in tropospheric ozone. Hydroxyl radicals (OH) are believed to be one of the major reactive intermediates in the atmosphere. As stated earlier, the process of the production of hydroxyl radicals couples stratospheric ozone depletion directly to tropospheric chemistry. The chemistry of hydroxyl radicals with organic compounds can be simply summarized in two generalized reactions:



or



The distinction between the two routes (4) and (5) is the amount of nitric oxide (NO) in the atmosphere, with the first route occurring at low NO concentrations found in remote (clean) environments.

Estimates have been made of the impact of stratospheric ozone depletion on tropospheric chemistry, using ground-level ozone as the primary indicator. There are two competing processes. A decrease in stratospheric ozone will decrease the amount of ozone transported from the stratosphere to the troposphere (as discussed earlier). Secondly, the reduction in stratospheric ozone will lead to enhanced UV-B radiation, leading to a change in ozone due to the photolytically driven OH reactions shown above.

Two different chemical transport models have been used, with Isaksen *et al.*⁵⁸ calculating the impact of a uniform 10% decrease in ozone column, and Fusco and Logan¹⁴ using the measured stratospheric ozone amounts from 1979 and 1993. The results from Isaksen *et al.*⁵⁸ are shown in **Figure 3** for both the ozone amount (left hand panels) and the change in ground-level ozone

(right hand panels). While the details of the models are quite different, the broad conclusions they draw are similar. In clean Southern Hemispheric air, the ground-level ozone amount is predicted to decrease with decreased stratospheric ozone (Equation (4)). In the northern hemisphere, a slight increase in ozone amounts is predicted with decreasing stratospheric ozone (Equation (5)). This difference between the hemispheres is caused by the concentration of NO_x from air pollution. Some features of the modeled results differ, and the swap between ozone removal and production would be expected at lower nitrogen oxide concentrations (e.g.⁵⁹), however, the changes estimated by the models indicate that the magnitude of the induced change in tropospheric ozone is small in comparison with the impacts of air pollution.^{14, 60}

The impact of likely future changes in atmospheric composition has been assessed using eleven different atmospheric climate models, and they predicted that tropospheric ozone will increase globally by 10 to 30 ppbv from 2000 to 2100.⁶¹ These models have ignored the impact of changes in atmospheric circulation, and so this increase is driven by the increase in anthropogenic emissions of gases like NO/NO₂ and hydrocarbons. Stratospheric ozone recovery is predicted to increase tropospheric ozone by a further 3 ppbv.⁶¹

Other relevant photolytic processes. Ketones such as acetone ((CH₃)₂CO), are present in the atmosphere either due to direct release at the ground or as a product of the decomposition of a range of organic compounds. They are important atmospheric trace gases,⁶² playing a key role in the formation and transport of pollutants. For example, acetone can decompose via direct photolysis or via OH, which can be abbreviated as follows:



The product CH₃COONO₂ (PAN) is a well known urban pollutant but is also stable at upper troposphere temperatures, and has been recognized as a means of long-range transport of pollutants, such as reactive nitrogen.⁶³

A reassessment of the direct photolysis reaction for acetone⁶⁴ and for some other ketones⁶⁵ has significantly decreased estimates of their overall photolytic sensitivity (quantum yield) in the UV-B region. The changes increase the relative importance of the UV-B region, but decreases the calculated rate of photolysis by 80 – 90%.⁶⁶ This indicates that acetone will be quite widely distributed in the upper troposphere in both hemispheres and hence available for reaction to produce PAN. Consequently, the reaction with OH is now understood to be the dominant loss mechanism for acetone. When included in calculations of the global atmosphere, these changes improve the agreement between the theoretical estimates and observations.⁶⁶

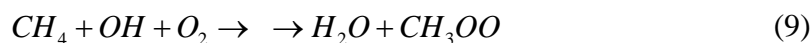
The photolysis rate for formaldehyde, one of the key products of the atmospheric decomposition of organic molecules, has been investigated. There are two different routes for decay, and the rate of both routes will depend on stratospheric ozone. Methods for deriving the photolysis rate from irradiance have been proposed,³² although to date such estimates have not been widely used.

Antarctic atmosphere. Surface ozone at the South Pole is of particular interest as it lies underneath the region of greatest stratospheric ozone depletion. An analysis of measurement records has shown that, during November – December, there was a decrease in ground-level

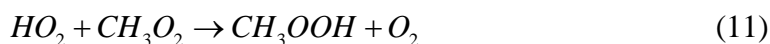
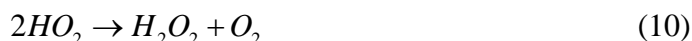
ozone over the period 1970 – 1990.⁶⁷ Since 1990, there has been a detectable increase in surface ozone (up to 20%).⁶⁸

Photolysis of ozone and NO in the Antarctic

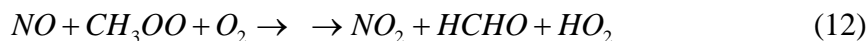
The importance of photolysis was elegantly demonstrated by measurements of a second peroxide, methylhydroperoxide (CH₃OOH). In this clean environment, the following two reactions represent a significant fraction of the OH reactions:



It should be noted that there are other reactions which produce these radicals. HO₂ can then react to form H₂O₂ or other peroxides:



Additional NO can permit the following reactions to become significant:



The NO removes methylperoxide and produces HO₂ (Reaction (13)). So, when UV was enhanced the increased H₂O₂ was accompanied by a 20% decrease in CH₃OOH.

In the clean Antarctic atmosphere, the NO concentrations would be expected to be low enough that enhanced radical chemistry should result in a decrease in ozone (reaction (4)), as observed in the period before 1990. The change after 1990 is attributed to the impact of additional UV radiation on the snowpack, enhancing nitrogen oxide release.⁶⁸ The extra NO produced then alters the atmospheric reactions so that additional UV radiation enhances ozone production. This effect is most noticeable during November when the largest absolute increase in UV radiation is experienced.

Measurements made on the West Antarctic Ice Sheet in 2000 – 2002 showed strong evidence of a negative correlation between stratospheric ozone and ground-level hydrogen peroxide (H₂O₂). A 70% increase in surface H₂O₂ concentration under conditions of low stratospheric ozone (less than 220DU compared to around 320 DU) has been observed.⁶⁹ The increase in hydrogen peroxide was explained by an enhanced photolysis of ozone and NO production (see box).

If the impact of UV radiation on NO was not included in a theoretical model, it failed to capture the magnitude of the observed H₂O₂ changes.⁶⁹ These changes imply that the

atmospheric boundary layer in Antarctica has become more oxidizing due to stratospheric ozone depletion. The ecological impact of this has not been studied.

Impact of air pollution on photolysis by UV-B radiation. The transmission of UV-B radiation to the Earth's surface is increased by removal of stratospheric ozone. The reduction in UV-B radiation by aerosols, and primarily carbon black from combustion has been found to be significant.³⁹ A global chemical transport model⁷⁰ has been used to estimate the impact of aerosols on tropospheric chemistry. Calculations of the impact of aerosols indicate that they typically cause a 1 – 5% reduction in radiation driving O(¹D) formation (UV-B radiation) in general (see **Figure 4**). However, there are regions, notably in Africa, Europe and Asia where impacts of the order of 30% or more are predicted due to increased aerosol release. The net effects on ozone concentrations are more modest (< 5%) and are somewhat smaller than the direct effect of reactions on the aerosol surface.

Fluorinated substances

Volatile halogenated substances have an important role in ozone depletion and global warming. Since several of these substances are used as refrigerants, there is a potential for interaction between their use, their effects on ozone, and climate change. A number of highly fluorinated compounds (PFCs) undergo degradation and transformation in the atmosphere and several of these have relevance to interactions between global warming and stratospheric ozone depletion. The ultimate degradation products are perfluorinated acids with varying chain lengths, depending on the starting material. The mechanisms of the atmospheric transport and breakdown of long- and short-chain hydrochlorofluorocarbons (HCFCs) have been well-characterized^{71, 72} and the results indicate that they are not likely to form the short-chain perfluorocarboxylic acids (PFCAs), such as trifluoroacetic acid (TFA). Perfluorinated aldehydes formed during the atmospheric oxidation of HFCs, HCFCs, and fluorinated alcohols are transported in the atmosphere dissolved in cloud water and react and are subsequently transported to the surface in precipitation. This mechanism has been identified as an additional source of longer chain PFCAs (such as of perfluorooctanoic acid), from the breakdown of fluorotelomer alcohols and possibly explains the presence of perfluorooctanoic acid in remote regions such as the Arctic.⁷² These longer chain acids and their parent materials are very resistant to breakdown and have been observed to become more concentrated up the food chain in mammals and birds,^{73, 74} where they may have harmful effects.⁷⁵

In contrast to the longer chain PFCs discussed above, several of the HCFCs and HFCs can break down into trifluoroacetic acid (TFA **Figure 5**). These are halothane, isoflurane, HCFC 123, HCFC-124, HFC-134a, and HFC-143a. Observations in both hemispheres (Mace Head, Ireland and Cape Grim, Tasmania) between 1998 and 2002 showed that the concentration of HFC-134a had increased rapidly (3 picomol mol⁻¹ year⁻¹) equivalent to 12% year⁻¹ based on measured concentrations of approximately 25 picomol mol⁻¹ year⁻¹ measured in the troposphere at Mace Head, Ireland in 2002.⁷⁶ This increase is in agreement with the known usage and atmospheric loss processes. As HFC-134a is a potent greenhouse gas, this increasing concentration has implications for climate change⁷⁷ as well as the production of TFA.

The final environmental sink for TFA is in the oceans and landlocked lakes. Concentrations of TFA in rainwater range from <0.5 to 350 ng L⁻¹, depending on location and distance from anthropogenic activity.⁷⁸ The predominant source of TFA in non-oceanic surface waters is likely anthropogenic as concentrations in surface water samples >2 000 years-old obtained from

groundwater and ice cores in Greenland were not detectable ($< 2 \text{ ng L}^{-1}$).⁷⁹ There are probably natural sources of TFA in seawater; relatively large concentrations have occasionally been detected in close proximity to undersea volcanic vents.⁸⁰ Concentrations up to 350 ng L^{-1} in flowing surface waters have been reported from several locations.⁸¹⁻⁸³ However, in landlocked lakes, they may be as large as $40\,000 \text{ ng L}^{-1}$.⁸¹ Reports of TFA concentrations in oceans are generally less than or equal to 200 ng L^{-1} .^{180, 81, 83} and much of this appears to have pre-industrial natural origins.⁸⁴ Based on historical production⁸⁵ of HFCs and HCFCs that are potential sources of TFA as well as projections of future uses,⁷⁷ an estimate of total production was made (Table 1). A worst-case estimate of TFA release from complete conversion of HFCs and HCFCs to TFA produced a total of 22×10^6 tonnes of TFA. After dilution and complete mixing in the volume of the oceans ($1.34 \times 10^{21} \text{ L}$), the increase in concentration above the nominal base level of 200 ng L^{-1} reported by Frank *et al.*⁸⁴ would be small (0.016 ng L^{-1}). Even if mixing were slow, concentrations in receiving zones would be less than those in flowing fresh waters or less than double the nominal base concentration. Even considering other sources of TFA, the added inputs from anthropogenic activity will be insignificant.

Table 1. Historical and projected production of HFCs and HCFCs in tonnes

	HCFC-124	HFC-134a	HFC-143a
Total production as of 2003 ^a	32 253	1 172 891	39 615
Estimated annual production in 2015 ^b	1 000	446 000	72 000
Estimated total production by 2020/2040 ^c	93 681	19 402 446	3 351 615

^a From⁸⁵. ^b From⁷⁷. ^c Phaseout projected for 2020 in developed countries and 2040 in developing countries, half of the total use attributed to developed countries and half to developing countries.

TFA is a strong acid (dissociation constant, $\text{pK}_a = 0.3$) and is completely ionised at normal environmental pHs and is present in the environment as a salt form. It is also highly stable under normal environmental conditions. Its stability in the environment is a direct result of the great strength of the C-F bond and the lack of functional groups on the molecule that are susceptible to chemical or biological degradation (**Figure 5**).

Laboratory and microcosm studies with TFA and related substances^{82, 86, 87} have suggested no additional environmental hazards from current environmental loadings in fresh or salt water. The smallest effect concentrations (EC50s) for TFA in sensitive species such as aquatic plants ranged from 0.222×10^6 to $10 \times 10^6 \text{ ng L}^{-1}$.⁸⁷ Estimates of more sensitive responses (assay endpoints) suggested a toxic benchmark concentration⁸⁸ of $0.046 \times 10^6 \text{ ng L}^{-1}$,⁸² which is much greater than current⁸² or projected concentrations in fresh and saltwater environments. The projected future increased loadings to the oceans from fresh water due to climate change and continued use of HCFCs and HFCs, are judged to present negligible risks for aquatic organisms and humans.

There is evidence that the perfluoropolyethers, substances which are proposed as chloro-hydrofluorocarbon (CHFC) substitutes, have great stability to chemical degradation in the

atmosphere as well as very large global warming potential.⁸⁹ Perfluoropolyethers (PFPEs) are commonly used industrial heat transfer fluids that may be released to the atmosphere. In smog chamber studies on a distilled fraction of a commercial mixture containing perfluoropolymethylisopropyl ethers (PFPMIEs, **Figure 6**), reactivity of PFPMIE with Cl was less than $2 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, while reactivity with OH was less than $6.8 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, indicating low reactivity in the troposphere. Using half-life data from perfluorinated alkanes, a lower limit for the total atmospheric lifetime of PFPMIE was calculated to be 800 years. PFPMIE was shown to have instantaneous radiative forcing of $0.65 \text{ W m}^{-2} \text{ ppb}^{-1}$.⁸⁹ This corresponds to a global warming potential (GWP) on a 100 year time-frame of 9000 relative to carbon dioxide (GWP of one) and 1.95 relative to CFC-11, a value exceeded by only a few hydrofluoro ethers.⁸⁹ PFPMIE has a longer atmospheric lifetime than CFC-11, and hence, the GWP of PFPMIE increases with the time horizon. For example, the GWP of PFPMIE over a 500 year horizon was estimated at 6.89 relative CFC-11.⁸⁹ These substances have been suggested as substitutes for CHFCs⁹⁰ but, as they are very persistent in the atmosphere, they may be important contributors to global warming. It is not known whether these substances will contribute significantly to global warming and its interaction with ozone depletion but they should be considered for further evaluation.

Conclusions, uncertainties and data needs

Research has now uncovered a distinct signature in air quality due to changes in stratospheric ozone. This is most noticeable in the Antarctic, where the change in stratospheric ozone is the largest and there are relatively few sources of atmospheric contamination. Elsewhere, changes in stratospheric ozone have apparent impacts on air quality, in particular ground level ozone concentrations, which depend on the composition of the atmosphere at that location. These conclusions are in agreement with current understanding of the chemistry of the atmosphere. Calibration and verification data for models are frequently taken from less polluted areas in temperate regions. Additional spatial and temporal measurements of air pollutants, OH, and ozone from other regions such the tropics, forested areas, and highly polluted areas would allow models of interactions between UV-B radiation, climate change, and air quality to be improved.

The decomposition products of CFC's and their replacements do not appear to have a significant environmental impact at this time. Trifluoroacetic acid is very persistent in water, but unlikely to be found at concentrations which present a significant environmental risk. Some other highly fluorinated compounds do have significant global warming potentials and long environmental lifetimes, so their climate impact will need to be considered carefully.

Future impacts of variations in stratospheric ozone on air quality will depend heavily on the magnitude of other changes to the atmosphere, driven by effects such as climate change and increasing industrialization. The projected increase in ground level ozone due to human activities is likely to be somewhat enhanced by recovering stratospheric ozone in the next century.

Our understanding of the atmosphere and the changes that are occurring within it are focused on relatively small regions of the globe. In particular little is known about the tropics, partially because of a lack of measurement but also because of the complexity of the environment. This lack will need to be redressed.

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Figure legends

Figure 1 Production rate of O(¹D) as a function of wavelength with a solar zenith angle of 60°

Figure 2 Two commonly used measures of the “intensity” of solar radiation from the sun. Both have units of W·m⁻²

Figure 3 Illustration of modeled ground level ozone and the change in ground level ozone resulting from changes in stratospheric ozone. The left hand panels show the modeled monthly average amount of ozone in January and July. The right hand panel shows the changes calculated using a 10% decrease in total ozone column. Figure adapted from Isaksen *et al.*⁵⁸

Figure 4 Calculated change in ground-level ozone concentration due to the effect of aerosols on (UV-B) photolysis. From Tie *et al.*⁷⁰.

Figure 5 Formation of trifluoroacetic acid (TFA) from an HFC

Figure 6 Structure of a perfluoropolymethylisopropyl ether

Graphical abstract text

Risks to humans and the environment from substances, such as TFA, produced by atmospheric degradation of hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) are considered minimal.