

Linking anthropogenic climate change and stratospheric ozone depletion

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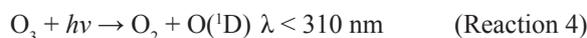
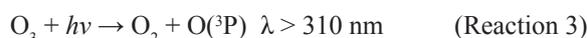
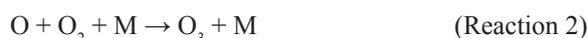
Global climate change and the Antarctic ozone hole are two well-known examples of how anthropogenic activities can alter the physical and chemical properties of the atmosphere, with significant consequences for life at Earth's surface. However, global climate change and stratospheric ozone depletion are not independent of one another. For example, common anthropogenic greenhouse gases such as carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O) participate indirectly in stratospheric ozone chemistry. Furthermore, the halogen-containing gases that lead to the formation of the Antarctic ozone hole are also greenhouse gases with large global-warming potentials. This article reviews the links between global climate change and ozone depletion; in particular the effects that CO₂, CH₄ and N₂O are expected to have on stratospheric ozone through the 21st century.

Stratospheric ozone

The region of the atmosphere approximately 10 – 50 km above Earth's surface is called the stratosphere, contains around 90% of atmospheric ozone, and is commonly referred to as “the ozone layer”. The remaining ~10% of atmospheric ozone is found in the troposphere (0 – 10 km above Earth's surface), and is produced as a result of human activities such as fossil fuel combustion and subsequent reactions between hydrocarbon and nitrogen oxide gases. Stratospheric ozone absorbs solar UV-B radiation (280–320 nm), which is harmful to terrestrial organisms in that it can cause skin cancer, eye disease and DNA damage. While stratospheric ozone is beneficial to life on Earth's surface, tropospheric ozone is detrimental: it is an air pollutant and contributes (for example) towards respiratory problems in humans.¹ More information about the composition and properties of the atmosphere is given in textbooks.^{2–4}

Stratospheric ozone is produced and destroyed in a series of reactions known as the Chapman cycle, first proposed by Sidney Chapman in 1930.⁵ The cycle begins with photolysis of molecular oxygen (by absorption of a solar photon of energy $h\nu$) to produce two oxygen atoms (Reaction 1). Atomic oxygen then undergoes a three-body reaction with O₂ (Reaction 2), in what is the dominant ozone production process in the stratosphere. (The molecule M, which is nearly always O₂ or N₂, is unaffected during the reaction, but carries away excess kinetic energy that would otherwise cause the ozone to fragment back to O and O₂). Ozone can be photolysed by Reaction 3, producing atomic oxygen either in its ground state (O(³P), referred to hereafter as O), or in an energetic metastable excited state (O(¹D)), depending on the wavelength of the incident photon (Reaction 4). Although it is short-lived, O(¹D) is highly reactive and is present in sufficient con-

centration to play a crucial role in the chemistry of the upper stratosphere. It is deactivated to ground state atomic oxygen via molecular collisions (Reaction 5). Finally, in the last step of the Chapman cycle, atomic oxygen and ozone react to produce O₂ (Reaction 6).



Reactions 2 and 6 are strongly temperature-dependent, and are central to changes in ozone abundances anticipated through the 21st century, as will be discussed later.

Halocarbons, the Antarctic ozone hole and Montreal Protocol

By the 1970s, a class of compounds called halocarbons was in widespread use in industry for applications such as refrigerants and aerosol propellants. Halocarbon applications took advantage of the compounds' low toxicity and low reactivity. However, because of their low reactivity, it was theorized that they would survive for long enough to pass up to the stratosphere where they could undergo UV photolysis, thus releasing chlorine and bromine atoms and leading to accelerated ozone destruction.⁶

In 1985, ozone measurements indicating a substantial decrease in average amounts of ozone in the Antarctic atmosphere in October were published.⁷ This phenomenon, now commonly referred to as “the ozone hole,” is caused by chlorine- and bromine-catalysed chemical cycles.^{8–10} The processes leading to the formation of the ozone hole are not reviewed here, but overviews are available.^{3,11}

In response to widespread concern about the impacts of halocarbons on the ozone layer, a protocol was designed to phase-out chlorine- and bromine-containing ozone-depleting substances. Called the Montreal Protocol for Substances that Deplete the Ozone Layer, it was signed in 1987 and has now been ratified by all United Nations member countries. Subsequent amendments and adjustments to the protocol mean that concentrations of stratospheric chlorine and bromine are now decreasing.¹¹

As well as benefitting the ozone layer, the Montreal Protocol has had a substantially beneficial impact on Earth's climate, since most ozone-depleting substances are also

greenhouse gases with large global-warming potentials.¹² A greenhouse gas's global-warming potential is measured as the global-mean radiative forcing¹³ resulting from a 1 kg emission of that gas, relative to the radiative forcing resulting from a 1 kg emission of CO₂, and integrated over a 100-year time period. The 100-year global-warming potentials for CO₂, CH₄ and N₂O are 1, 25 and 298, respectively. In contrast, common halocarbons such as CFC-11, CFC-12 and halon-1301 have huge 100-year global warming potentials — 4750, 10900 and 7140, respectively.¹⁴

21st century ozone and CO₂

Owing in part to the phase-out of halocarbons under the Montreal Protocol, stratospheric ozone abundances are projected to increase through the 21st century, as shown in Fig. 1.¹⁵ The lines in Fig. 1 represent results from different chemistry-climate models. Briefly, chemistry-climate models consist of a general circulation model (that describes the way in which the atmosphere circulates and contributes to changes in climate) coupled to an atmospheric chemistry model; they are currently the best tool available for simulating the long-term evolution of the global atmosphere.¹⁶ It is apparent from Fig. 1 that total column ozone¹⁷ is projected to increase to greater amounts than those observed in 1960, prior to abundances of stratospheric chlorine and bromine becoming elevated. This is primarily due to the influence of increasing CO₂ concentrations cooling the stratosphere, as will now be discussed.

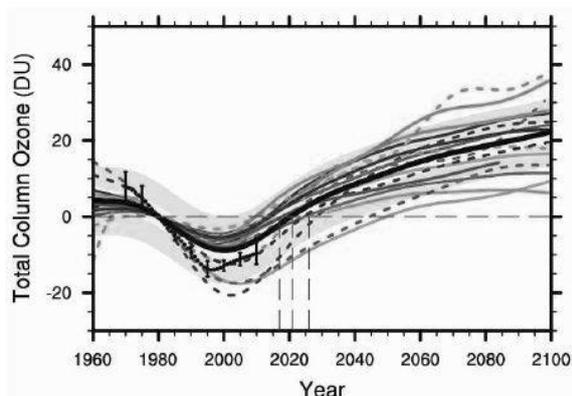


Fig. 1. Chemistry-climate model projections of annual-mean total column ozone at northern midlatitudes (35-60°N). The various traces represent projections from different chemistry-climate models (Eyring, Fahey & Waugh, reference 16), and the thick black line shows the multi-model mean. The series of dots with error bars between 1970 and 2010 are observations, calculated from ground-based and satellite ozone measurements. All traces have been adjusted to the 1980 baseline (reproduced from ref.15).

Although increasing greenhouse gas concentrations lead to warming of the troposphere, they lead to cooling of the stratosphere. This is because greenhouse gases in the stratosphere emit heat to space, and the cooling effect exceeds the absorption of infrared radiation in the stratosphere. The absorption of infrared radiation in the stratosphere is decreasing because increasing amounts of greenhouse gases in the troposphere trap infrared radiation lower down in the stratosphere. The net effect is cool-

ing.¹⁸ Because key reactions in the Chapman cycle are temperature-dependent, a cooling stratosphere is projected to lead to increased ozone abundances.^{19,20} The rate of Reaction 2 actually increases with decreasing temperature, thus producing more ozone. Concurrently, Reaction 6 slows with decreasing temperature, and therefore ozone loss by this reaction diminishes.

Chemistry-climate models project that stratospheric ozone will increase in all regions of the atmosphere through the 21st century, with the exception of in the tropical lower stratosphere.¹⁵ Here, ozone is affected by changes in stratospheric circulation. The overall meridional (north-south) circulation is called the Brewer-Dobson circulation. This is the process by which air from the tropical troposphere ascends into the stratosphere, is subsequently transported towards the poles and descends in middle and polar latitudes.²¹ It is by this mechanism that chlorine compounds, historically produced from halocarbons (which were predominantly emitted in the Northern Hemisphere), were transported to the Antarctic stratosphere and thus led to the development of the Antarctic ozone hole.^{7,9,22}

It is thought that increasing sea-surface temperatures (attributed to global warming) through the 21st century will lead to a strengthening of the Brewer-Dobson circulation.^{23,24} A strengthening Brewer-Dobson circulation would result in enhanced transport of gases to polar latitudes, and would shorten the residence times of chemical constituents in the stratosphere, which would affect the lifetimes of long-lived greenhouse gases.²⁵ Going back to the case of projected decreases in tropical lower stratospheric ozone through the 21st century, the effect of a strengthening Brewer-Dobson circulation is that less time would be available for ozone to form in rising parcels of air.²⁶

Greenhouse gases (predominantly CO₂) lead to cooling of the stratosphere and warming sea-surface temperatures. Stratospheric cooling affects ozone through changes in the reaction rates of the Chapman cycle; while increasing sea-surface temperatures are thought to lead to strengthening of the Brewer-Dobson circulation, which has implications for ozone abundances. Following CO₂, the two most important anthropogenic greenhouse gases controlled by the Kyoto Protocol are CH₄ and N₂O. While the effects of CO₂ on ozone are somewhat indirect, CH₄ and N₂O affect ozone directly via chemical processes. The chemistry of these gases in relation to ozone depletion will be discussed in the following sections.

The effect of CH₄ on stratospheric ozone

The concentration of atmospheric CH₄ has increased from 700 ppb to around 1800 ppb since pre-industrial times.^{4,27} CH₄ is produced by methanogenic bacteria which grow in low-oxygen environments and cause the fermentation of cellulose and other organic material in (for example) wetlands, and in the rumina of cows and sheep. As well as agriculture, other anthropogenic sources include landfills and biomass burning.²⁸

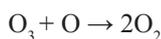
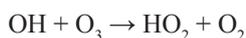
In the stratosphere, CH₄ undergoes oxidation with ener-

getic oxygen atoms to produce an OH radical (Reaction 7).

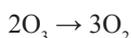
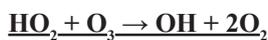
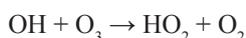


OH is highly reactive and rapidly interconverts to H atoms and HO₂ radicals.³ Collectively, H, OH and HO₂ are referred to as the HO_x family, and participate in catalytic cycles (such as cycles I and II shown below; rate-determining steps are in bold), which lead to loss of odd-oxygen (O + O(¹D) + O₃) species:

Cycle I:



Cycle II:



Cycle I is the dominant HO_x-induced mechanism for ozone loss in the upper stratosphere, where UV radiation is more intense and abundances of O are large. In the lower atmosphere where there is the greatest concentration of O₃ relative to O, cycle II is the dominant HO_x-induced ozone loss process.

The main process for removal of HO_x radicals is formation of water vapour via Reaction 8:



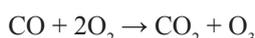
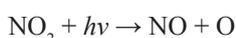
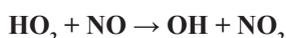
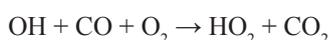
Water vapour cools the stratosphere, which, in turn, increases ozone abundances. Therefore, CH₄ can have both a positive (via increase of water) and negative (owing to cycles I and II) effect on ozone abundances.

Chemistry-climate model studies have shown that the overall effect of increasing CH₄ is to increase total column ozone.^{29,30} As well as the cooling effect achieved from the production of water vapour, two further pathways serve to increase ozone abundances. Firstly, CH₄ decreases Cl abundances via Reaction 9, thus slowing chlorine-catalyzed ozone loss cycles.



Secondly, HO_x radicals lead to production of tropospheric ozone via cycle III.^{31,32}

Cycle III:



My research colleagues and I have investigated whether the relationship between CH₄ and ozone (and N₂O and ozone), is linear or otherwise.³³ Figure 2a shows that stratospheric column ozone increases as the CH₄ concentration increases. Stratospheric column ozone decreases as N₂O concentrations increase, shown in Fig. 2b. Furthermore, there is a quasi-linear relationship between the CH₄ and N₂O concentrations and the stratospheric column ozone abundance.

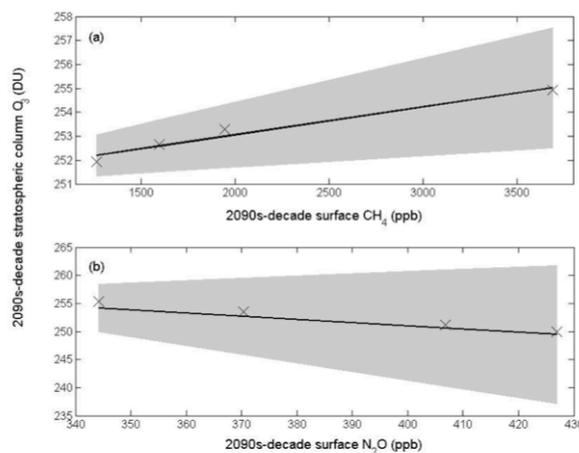


Fig. 2. (a) Global-mean stratospheric (1-100 hPa) column ozone (Dobson units) in the 2090s decade vs. global-mean CH₄ surface concentration in the 2090s decade. The crosses represent results from four chemistry-climate model simulations, where the only parameter changing between each simulation was the CH₄ concentration scenario. A simple linear regression model was fitted (represented by the black line), and the grey shaded region indicates the 95% confidence interval for the slope and intercept of the regression model. (b) As for (a), but for these simulations the same CH₄ concentration scenario was used, and a different N₂O concentration scenario was applied (both parts of the diagram are adapted from ref. 33).

The effect of N₂O on stratospheric ozone

N₂O is produced from microbial activity in tropical soils and the oceans, and as a result of anthropogenic activities such as agriculture – particularly the use of nitrogen-based fertilizers. The concentration of N₂O in Earth's atmosphere has increased from 276 ppb to 322 ppb since pre-industrial times, and is projected to continue increasing through the 21st century.²⁷

N₂O is sufficiently stable to migrate to the stratosphere, where around 90% of it is destroyed via photolysis (Reaction 10):



The rest is destroyed by oxidation (Reactions 11, 12);³



Reaction 12 is an extremely significant pathway for stratospheric ozone, since it produces NO and is the major source of stratospheric nitrogen oxides (NO_x = NO + NO₂). NO_x radicals participate in a number of ozone-depleting catalytic cycles, of which cycle IV dominates.³⁴ The projected rate of the ozone-depleting NO_x cycles through the 21st century, as simulated by a chemistry-climate

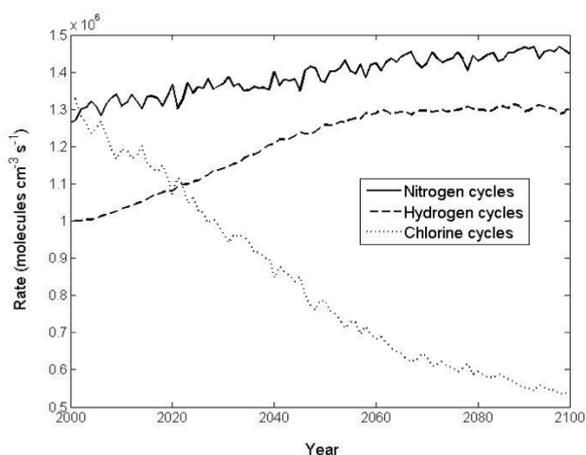
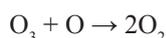
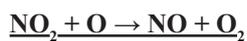
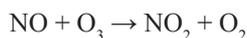


Fig. 3. Global-mean rates of the ozone-depleting NO_x , HO_x and chlorine cycles at 2 hPa (~ 40 km) in the 21st century, as simulated by a chemistry-climate model (adapted from the results presented in ref. 36).

mate model, is shown in Fig. 3, together with the rates of the ozone-depleting HO_x and chlorine cycles.

Cycle IV:



Although chlorofluorocarbon production has been phased out under the Montreal Protocol, chlorofluorocarbons are still the dominant ozone-depleting substance owing to their long stratospheric lifetime. However, of the ozone-depleting substances currently emitted, N_2O emissions dominate.³⁵ The effect of N_2O on stratospheric ozone through the 21st century is moderated by a number of factors, such as interference from other greenhouse gases and climate change effects; for example stratospheric cooling and the increasing strength of the Brewer-Dobson circulation. A strengthening Brewer-Dobson circulation shortens the lifetimes of some chemical constituents, as discussed earlier. This means that nitrogen species are projected to be removed from the atmosphere at a faster rate, therefore slowing the NO_x -induced ozone loss cycles.²⁵

As the stratosphere cools, the dominant ozone-depleting NO_x cycle, cycle IV, is projected to slow for two reasons:³⁶

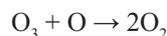
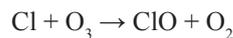
1. The first step of cycle IV is highly temperature-dependent and is projected to slow as the stratosphere cools. Therefore, the ratio of NO_2/NO decreases and less NO_2 is available for the rate-determining step of cycle IV.
2. Because Reaction 2 of the Chapman cycle is highly temperature-dependent and is projected to speed up as the stratosphere cools, the ratio of O/O_3 decreases and less O is available for the rate-determining step of cycle IV.

NO_x species react with chlorine species, leading to a slowing of NO_x chemistry, for example by Reaction 13:³⁵



ClO also reacts with O in catalytic cycle V, which is analogous to cycles I and IV:

Cycle V:



ClO and HO_2 compete with NO_2 for O in the upper stratosphere, and therefore slow the $\text{NO}_2 + \text{O}$ reaction (Cycle IV).³⁶ Ozone-depleting chlorine chemistry will be of decreasing importance through the 21st century following the phase-out of halocarbon emissions, as shown in Fig. 3. However, if CH_4 emissions continue to increase through the 21st century, then so will the rate of HO_x -induced ozone loss in the upper stratosphere (also shown in Fig. 3).

There are numerous ways in which the effects of N_2O and CH_4 on ozone are altered by the chemical and physical environment of the stratosphere, as discussed above. The key message here is that the entire physical and chemical environment of the stratosphere must be taken into account when assessing the effect of a single species. And, despite the many factors discussed above that are projected to ameliorate the effect of N_2O on ozone, the conclusions of Ravishankara *et al.* do not change,³⁵ of all the substances currently emitted, N_2O is the most important substance for ozone depletion this century.

Could widespread biofuels production and consumption have an impact on stratospheric ozone?

Concerns were first raised in 2008 over potential detrimental effects to the climate if the production and consumption of first-generation biofuels (those produced from vegetable oil, sugar or starch) were to become widespread.³⁷ Biofuels are often considered carbon-neutral, because plants remove CO_2 from the air by photosynthesis, and CO_2 is released when the biomass is burnt. However nitrogen-based fertilizers are applied to the crops used to produce biofuels, and therefore any CO_2 reduction achieved (by using biofuels in place of fossil fuels) could be countered by a subsequent increase in N_2O emissions.³⁷ Furthermore, as mentioned earlier, while the 100-year global warming potential for CO_2 is 1, for N_2O it is 298.¹⁴

As well as offsetting climate change mitigation measures, an increase in N_2O emissions from increased biofuels consumption could potentially be damaging to the ozone layer. Using a chemistry-climate model, my research colleagues and I simulated the evolution of the stratosphere through the 21st century under a “biofuels” scenario, in which N_2O emissions increased and CO_2 emissions decreased.³⁸ As shown in Fig. 1, ozone abundances are generally expected to increase through the 21st century. However under the biofuels scenario ozone decreased slightly between 2000-2100, for the following reasons:

1. A smaller growth in CO_2 emissions was used in the biofuels scenario compared with the control scenario,

to represent reduced fossil fuel burning. As a result, the stratosphere cooled less through the 21st century, and so temperature-dependent Chapman chemistry was not altered to favour increased ozone abundances.

- The biofuels scenario used a large growth in N₂O emissions compared with the control scenario, to represent increased application of nitrogen-based fertilizer. This resulted in enhanced NO_x-induced ozone loss in the stratosphere.

The effects of biofuels are crop-dependent,³⁷ and second-generation biofuels show promise in transitioning the regions where they are grown from net sources to net sinks for greenhouse gases.³⁹ In terms of climate policy, the conclusions drawn from our work suggest that if future attempts are made to mitigate CO₂ emissions, then N₂O emissions must also be addressed,³⁸ the combination of reduced stratospheric cooling and increased NO_x-induced ozone depletion could be damaging to the ozone layer.

Summary

This article has discussed the effects that the three dominant anthropogenic greenhouse gases have on stratospheric ozone. CO₂ predominantly affects ozone by cooling the stratosphere, which changes temperature-dependent reaction rates and is projected to lead to an overall increase in ozone abundances. CH₄ leads to ozone destruction in the upper atmosphere (through the production of HO_x radicals), but, overall, leads to an increase in the ozone abundance. Despite this, it hardly needs to be said that CO₂ and CH₄ should not be viewed as policy alternatives for protecting the ozone layer owing to their harmful effect on other areas of the climate system. Now that the halocarbons have been phased out, N₂O is the most important substance for ozone depletion in the 21st century, although its impact on ozone is moderated by other greenhouse gases; shown, for example, by the study on potential impacts of biofuels on the ozone layer.

CO₂, CH₄ and N₂O will play important roles in determining stratospheric ozone abundances this century; however the model projections discussed here are based (and can only be based) on current knowledge. Unprecedented changes in the atmosphere have occurred in the past as a consequence of anthropogenic activities (for example, the Antarctic ozone hole), and could well occur in the future. It is vital that we understand the effects of human activities on atmospheric processes and composition, and their consequences for the rest of the Earth system.

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