Stratospheric ozone depletion from future nitrous oxide increases

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Abstract

We have investigated the impact of assumed nitrous oxide (N\textsubscript{2}O) increases on stratospheric chemistry and dynamics by a series of idealized simulations. In a future cooler stratosphere the net yield of NO\textsubscript{y} from a changed N\textsubscript{2}O is known to decrease, but NO\textsubscript{y} can still be significantly increased by the increase of N\textsubscript{2}O. Results with a coupled chemistry-climate model (CCM) show that increases in N\textsubscript{2}O of 50 %/100 % between 2001 and 2050 result in more ozone destruction, causing a reduction in ozone mixing ratios of maximally 6 %/10 % in the middle stratosphere at around 10 hPa. This enhanced destruction could cause an ozone decline in the second half of this century in the middle stratosphere. However, the total ozone column still shows an increase in future decades, though the increase of 50 %/100 % in N\textsubscript{2}O caused a 2 %/6 % decrease in TCO compared with the reference simulation. N\textsubscript{2}O increases have significant effects on ozone trends at 20–10 hPa in the tropics and at northern high latitude, but have no significant effect on ozone trends in the Antarctic stratosphere. The ozone depletion potential for N\textsubscript{2}O in a future climate depends both on stratospheric temperature changes and tropospheric N\textsubscript{2}O changes, which have reversed effects on ozone in the middle and upper stratosphere. A 50 % CO\textsubscript{2} increase in conjunction with a 50 % N\textsubscript{2}O increase cause significant ozone depletion in the middle stratosphere and lead to an increase of ozone in the upper stratosphere. Based on the multiple linear regression analysis and a series of sensitivity simulations, we find that the chemical effect of N\textsubscript{2}O increases dominates the ozone changes in the stratosphere while the dynamical and radiative effects of N\textsubscript{2}O increases are insignificant on average. However, the dynamical effect of N\textsubscript{2}O increases may cause large local changes in ozone mixing ratios, particularly, in the Southern Hemisphere lower stratosphere.
1 Introduction

Stratospheric ozone destruction involves complex chemical reactions and a range of chemical species. The catalytic destruction by reactive chlorine and bromine has accounted for a large part of the ozone loss in the stratosphere over the past few decades (WMO, 2007). However, the stratospheric chlorine and bromine loading is now decreasing due to reductions of emissions of anthropogenic chlorofluorocarbons (CFCs) and other halogen-containing chemicals mandated by the Montreal Protocol. Therefore, the effects of other ozone-depleting substances (ODSs) have become a subject of renewed concern in recent years (Wuebbles and Hayhoe, 2002; Chipperfield, 2003; Dentener et al., 2005; Stenke and Grewe, 2005; Ravishankara et al., 2009; Tian et al., 2009). Among these other chemical species, nitrous oxide has been recognized as an important substance affecting stratospheric ozone, and the effect of N₂O on ozone depletion has been discussed in a number of studies (e.g. Crutzen, 1976; Crutzen and Ehhalt, 1977; Kinnison et al., 1988; Randeniya et al., 2002; Chipperfield, 2003). Crutzen and Ehhalt (1977) first pointed out that the increasing use of fixed nitrogen as fertilizer might result in a reduction of the Earth’s ozone layer of a few percent at the beginning of the 21st century. Portmann and Solomon (2007) found that increasing N₂O could lead to 2–4% decline of total column ozone (TCO) by the end of this century under the IPCC A2 scenario. Ravishankara et al. (2009) re-opened the debate on the importance of nitrous oxide for ozone depletion when they argued that N₂O is now the single most important anthropogenic ODSs compared with those regulated by the Montreal Protocol and its amendments.

On the other hand, since the loss of ozone is inversely related to local temperature changes throughout most of the stratosphere, increases in other GHGs such as CO₂ in the future climate also have a large impact on chemical processes in the stratosphere. The effect of N₂O on the ozone layer is not only related to N₂O emission changes but is also modulated by the radiative cooling caused by other GHG emission changes (Rosenfield et al., 2002; Chipperfield, 2009; Wuebbles, 2009; Dameris, 2010). The ef-
Efficiency of $\text{N}_2\text{O}$ for global ozone depletion is expected to decrease in the stratosphere due to projected increases in $\text{CO}_2$ (Rosenfield and Douglass, 1998). Some other studies argued that $\text{CO}_2$-induced cooling could cause stratospheric ozone to recover to values greater than 1980 levels during this century (Chipperfield, 2009; Wuebbles, 2009) and lead to a so-called “super recovery”. Fleming et al. (2011) further carried out a comprehensive study of long-term stratospheric effects of some source gases including $\text{N}_2\text{O}$ and $\text{CO}_2$ through series of two-dimensional (2-D) chemistry-climate model simulations. They predicted that in the latter half of the 21st century $\text{CO}_2$, $\text{N}_2\text{O}$, and $\text{CH}_4$ loading will all have significant impacts on global total ozone while the effect of $\text{CO}_2$ loading on global total ozone has twice the magnitude of the effect of $\text{N}_2\text{O}$.

Although previous studies have investigated the impact of $\text{N}_2\text{O}$ on ozone depletion, the relative importance of the radiative and chemical effect of $\text{N}_2\text{O}$ remains unclear and the net effect of increased $\text{N}_2\text{O}$ on the ozone layer in the changing climate is still under debate. Previous studies have mostly been based on mechanistic analysis, with the main focus being the chemical effect of $\text{N}_2\text{O}$ (Ravishankara et al., 2009), or have used relatively simple two-dimensional chemical-dynamical models (e.g. Portmann and Solomon, 2007; Chipperfield, 2009; Fleming et al., 2011) to diagnose the effect of $\text{N}_2\text{O}$ changes on the ozone layer. In this study, we re-examine the effect of $\text{N}_2\text{O}$ increases on ozone using a fully coupled 3-D chemistry-climate model (CCM). We attempt to clarify quantitatively the radiative and chemical effects of $\text{N}_2\text{O}$ increases on the ozone layer and to diagnose the ozone changes in a changing climate when $\text{CO}_2$ and $\text{N}_2\text{O}$ are both increasing. The details of the model and numerical experiments are given in Sect. 2. The effect of $\text{N}_2\text{O}$ increases on ozone depletion under different scenarios is addressed in Sect. 3. In Sect. 4, we analyze contributions of various factors associated with $\text{N}_2\text{O}$ increases in modulating ozone depletion. Conclusions and a discussion are presented in Sect. 5.
2 Models and numerical experiments

We have used a fully coupled chemistry-climate model, the Whole Atmosphere Community Climate Model 3 (WACCM3) to investigate the chemical and thermal-dynamical responses to a linear future increase in N$_2$O. WACCM3 has 66 vertical levels from the ground to $4.5 \times 10^{-6}$ hPa (approximately 145 km geometric altitude) with detailed interactive chemistry (Garcia et al., 2007) and a finite volume dynamical core (Lin, 2004). For this study simulations were carried out at $4^\circ \times 5^\circ$ horizontal resolution. The WACCM3 chemistry module is derived from the three-dimensional (3-D) chemical transport Model for Ozone and Related chemical Tracers (MOZART) (Brasseur and Hitchman, 1988; Hauglustaine et al., 1998; Horowitz et al., 2003). More details of WACCM3 model can be found in Garcia et al. (2007).

Four long-term WACCM simulations were performed in this study and detailed configurations of those simulations are listed in Table 1. The surface volume mixing ratios (vmrs) of GHGs in the control run (E0) are taken from IPCC A1b scenario. In runs E1 and E2, the surface vmrs of N$_2$O were increased linearly with time from 2001 to 2050 at a rate of 1 % yr$^{-1}$ in run E1 and 2 % yr$^{-1}$ in run E2. More specifically, N$_2$O values in E1 are increased by 1 % in 2001, 2 % in 2002, and 50 % in 2050. It should be pointed out that the percentage increases of N$_2$O in each year are based on N$_2$O values of A1B scenario. For instance, in year 2050, N$_2$O value of A1B scenario is 344 ppbv in run E0, therefore, it is 517 ppbv in run E1 and 688 ppbv in run E2. This increasing approach makes the N$_2$O variation in our simulations close to A1B scenario during the first half of the simulations with small additional increases in each year compared to A1B scenario, but far off A1B scenario with much larger N$_2$O increases during the later half of the simulations for the purpose of amplifying response signals of the atmosphere. In run E3, both N$_2$O and CO$_2$ are increased linearly with time from 2001 and increased by 50 % in 2050 with an increasing rate of 1 % yr$^{-1}$. The sea surface temperature (SST) and sea ice fields used in four runs are the same (HadGEM1) and derived from the SST and sea ice fields prepared for the Chemistry-Climate Model Validation activity 2
(CCMVal-2) REF2 simulations (Eyring et al., 2008; Morgenstern et al., 2010) for the period 2001 to 2050.

To separate the radiative and chemical effects of increasing N₂O on stratospheric ozone, 4 extra WACCM time-slice simulations were performed. In the first simulation (S0), GHG loadings were based on the IPCC A1b scenario and fixed at the year 2050 in both the chemistry and radiation scheme. In simulations S1 and S2, N₂O mixing ratios were increased by 50 % relative to that in simulation S0 in the model's chemistry and radiation schemes, respectively. In the last simulation S3, N₂O was increased by 50 % relative to that in simulation S0 in both the chemistry and radiation schemes. All of these sensitivity simulations used 12 month SST and sea ice climatology derived from observed monthly mean values for the time period from 1996 to 2000 (Rayner et al., 2003).

3 Results

3.1 Ozone responses to N₂O changes in a CCM

Figure 1 shows percentage changes of ozone mixing ratio and total column ozone (TCO) caused by N₂O increases. These ozone changes are calculated from the climatology of the final 10 yr (2041–2050) of the four WACCM runs listed in Table 1. It is apparent from Fig. 1 that the ozone changes have large spatial and temporal variations. In the middle and upper stratosphere, a decrease of 6–10 % ozone occurs when N₂O increases by 50 %/100 % (Fig. 1a and b).

In the middle and upper stratosphere, N₂O decomposes by photolysis or by reactions with O(¹D):

\[ \text{N}_2\text{O} + h\nu \rightarrow \text{N}_2 + \text{O} \quad \text{(R1)} \]
\[ \text{N}_2\text{O} + \text{O(¹D)} \rightarrow \text{N}_2 + \text{O}_2 \quad \text{(R2)} \]
\[ \text{N}_2\text{O} + \text{O(¹D)} \rightarrow 2\text{NO} \quad \text{(R3)} \]
Only the minor channel of Reaction (R3) leads to NO\(_y\) (= NO\(_x\) + NO\(_3\) + HNO\(_3\) + HONO\(_2\) + ClONO\(_2\) + 2N\(_2\)O\(_5\) + BrONO\(_2\) +...) production. NO\(_y\) is removed from the stratosphere by transport to the troposphere and washout or by local photochemical loss at high altitudes via:

\[
N + NO \rightarrow N_2 + O \quad k_4 = 2.1 \times 10^{-11} \exp(\frac{+100}{T}) \quad (R4)
\]

The abundance of N is determined by photolysis of NO and by the reaction:

\[
N + O_2 \rightarrow NO + O_2 \quad k_5 = 1.5 \times 10^{-11} \exp(-\frac{3600}{T}) \quad (R5)
\]

Because of the temperature dependence of the reactions controlling the chemical loss of NO\(_y\), NO\(_y\) tends to decrease in a future cooler stratosphere as Reaction (R4) speeds up while Reaction (R5) slows down (Rosenfield and Douglass, 1998). Without significant stratospheric cooling, N\(_2\)O increases in the atmosphere will cause NO\(_y\) and NO\(_x\) increases in the stratosphere. Figure 2 shows the time series of global mean NO\(_x\) and NO\(_y\) fields from the four experiments and corresponding changes in global mean column NO\(_x\) and NO\(_y\) in runs E1, E2 and E3 relative to that in control run E0. Note that a 100% increase in N\(_2\)O by the end of 2050 causes an increase in the global mean column NO\(_y\) and NO\(_x\) by 12 \times 10^{15} \text{molecules cm}^{-2} \text{ and } 4 \times 10^{15} \text{molecules cm}^{-2}, \text{ respectively. However, when CO}_2 \text{ is also increased by 50% in conjunction with a 50% N}_2\text{O increase at the end of 2050 in run E3, which implies a cooler stratosphere than that in run E1 in which only N}_2\text{O is increased by 50% at the end of 2050, the NO}_y \text{ and NO}_x \text{ increases are smaller than those in run E1 (Fig. 1a and c). Even though the yield of NO}_x \text{ from N}_2\text{O decreases in a cooler stratosphere, the efficiency of ozone loss due to NO}_y \text{ increases so that N}_2\text{O increases in run E3 still causes an increase in ozone loss due to the increasing NO}_y \text{ in an atmosphere with decreasing halogens. These results imply that the ozone depletion potential for N}_2\text{O in a future climate will actually depend both on stratospheric temperature changes and tropospheric N}_2\text{O changes, which have reversed effects on ozone in the middle and upper stratosphere. Figure 1 clearly indicates that the destruction of ozone associated with N}_2\text{O increases in run E3}
is reduced relative to that in runs E1, particularly in the middle and upper stratosphere, consistent with previous findings that CO$_2$-induced cooling tends to increase ozone in the future (e.g. Haigh and Pyle, 1982; Shepherd, 2008; Chipperfield, 2009; Wuebbles, 2009; Oman et al., 2010a) by slowing down the gas-phase chemical reactions associated with ozone.

In the lower stratosphere, increased N$_2$O could reduce the efficiency of Cl$_y$ and Br$_y$ for ozone destruction by tying up more of these halogens in the ClONO$_2$ and BrONO$_2$ reservoir species, consequently, N$_2$O increases lead to more ozone. Meanwhile, projected decreases in Cl$_y$ and Br$_y$ tend to tie up less NO$_y$ in ClONO$_2$ and BrONO$_2$, and increase the efficiency of N$_2$O in ozone destruction processes (e.g. Ravishankara et al., 2009; Daniel et al., 2010), but Fig. 1 suggests that this effect is outweighed by the effect of N$_2$O increases. On the other hand, in the lower stratosphere/upper troposphere UV radiation is enhanced due to the ozone decreases in the middle and upper stratosphere, resulting in more ozone production through the so-called “self-healing” effect. A notable feature in Fig. 1 is that this ozone increase in the lower stratosphere/upper troposphere can be seen mostly at Southern Hemisphere mid-latitudes. Ravishankara et al. (2009) pointed out that the “self-healing” effect is most significant at tropical latitudes. As will be discussed later, this significant ozone increase in the Southern Hemisphere is partly caused by the enhanced vertical transport of ozone from the upper atmosphere to the lower stratosphere/upper troposphere, which may not be well simulated in 2-D models. Below 100 hPa in the troposphere, N$_2$O increases result in more ozone with a maximum 10% increase at southern high latitudes when N$_2$O is increased by 100% from 2001 to 2050 (Fig. 1b).

Due to significant ozone decreases in the middle and upper stratosphere caused by increased N$_2$O, the TCO in the two WACCM simulations (E1 and E2) decreases compared with control run E0 (Fig. 1d and e), particularly at high latitudes. A 50% increase in N$_2$O causes a maximum 6% decrease in TCO (Fig. 1d). When N$_2$O is increased by 100% in run E2, TCO changes become larger with a maximum decrease of 10% at high latitudes. The combined effect of N$_2$O and CO$_2$ increases results in
a slight TCO decrease (1–2 %) in the Northern Hemisphere but an increase (2–6 %) in the Southern Hemisphere (Fig. 1f), due to the offsetting impact of CO₂-induced cooling.

Figure 3a–c shows modeled ozone trends as a function of latitude and pressure from 2000 to 2050 under different assumed N₂O changes. Also shown are the time series of TCO averaged over different latitude bands, i.e., 90° N–70° N, 22° S–22° N, and 70° S–90° S. Consistent with results in previous studies (e.g. Tian and Chipperfield, 2005; Austin and Wilson, 2006; Newman et al., 2006; Eyring et al., 2007; WMO, 2007), the global ozone will generally recover in the next half century under the IPCC A1b GHGs scenario with a maximum increasing trend of 0.3 ppmv/10 yr at 10–1 hPa (Fig. 3a). However, if N₂O is further increased by 50 % relative to the IPCC A1b projection, the ozone in the middle stratosphere at around 20 hPa decreases with a maximum trend of −0.2 ppmv/10 yr, although the ozone in the upper stratosphere still increases (Fig. 3b). Note that a steadily declining trend in ozone in the tropical lower stratosphere was also simulated in previous simulations (Oman et al., 2010a; SPARC-CCMVal, 2010; Eyring et al., 2010a), but there is no significant ozone trend in the tropical lower stratosphere in our simulations through 2050. A possible reason is that the upwelling in our 50 yr simulations has not significantly increased in the lower stratosphere/upper troposphere (Table 3) though we used an increased GHG scenario and time varying SSTs. As in Fig. 1, CO₂ increases tend to offset the effect of N₂O on ozone trends in the middle stratosphere (Fig. 3c). When N₂O and CO₂ are both increased by 50 %, the declining trend of ozone in the middle stratosphere becomes less significant. It is worth noting that the effect of increased N₂O on long-term trends of ozone mixing ratios at about 20–10 hPa have evident spatial variations. Ozone mixing ratios decrease most significantly in the tropics with a trend up to −0.1 ppmv/10 yr when N₂O is increased by 50 %. N₂O increases have no significant effect on ozone trends in the Antarctic stratosphere but tend to slow down the ozone recovery in the Arctic stratosphere. Previous studies also found that ozone evolution over Antarctic shows small sensitivity to changes in GHGs (Eyring et al., 2010a). Similar features can be noted in the TCO time series shown in Fig. 3d–f. Figure 3 also indicates that the higher N₂O corresponds to a less
significant increasing trend of ozone, implying that increased N₂O overall tends to delay the recovery of ozone.

To understand the hemispheric asymmetry of ozone trends in the middle stratosphere exhibited in Fig. 3, Fig. 4 shows the time series of ozone mixing ratios averaged over different latitude bands between 20–10 hPa. Also shown are the corresponding time series of the reactive chlorine (ClOₓ, ClOₓ = Cl + ClO + 2Cl₂O₂). Generally, in all simulations ClOₓ tends to decrease in response to the decreasing chlorine loading due to the Montreal Protocol and its amendments, which is imposed in the model through specified surface halocarbon mixing ratios. However, the relative rates of ClOₓ decline between experiments are different. In the Arctic stratosphere ClOₓ tends to increase with increased N₂O in the first half of the simulations and then reverses in the second half. In the Antarctic middle stratosphere, N₂O increases have no significant effect on ClOₓ, which shows an evident decreasing trend with marginal differences between the four experiments. Accordingly, the ozone time series in the Antarctic middle stratosphere show persistent increasing trends in all four experiments.

A further examination of the model chemical fields reveals that NOₓ concentrations in the Antarctic stratosphere are lower than those in the Arctic stratosphere (not shown), and the differences become larger when the additional N₂O increases from 50 % to 100 %. As discussed below (see Fig. 6), in the Arctic higher odd nitrogen values from increased N₂O lead to more PSC occurrence which results in more ozone loss. Meanwhile in the Antarctic PSC occurrence does not change from our model simulations. Those effects of N₂O increases on ozone between 20–10 hPa are evident in Fig. 1a, c which show that ozone concentrations in the Arctic stratosphere tend to decrease when N₂O is increased, but in the Antarctic stratosphere, ozone still exhibits an increasing trend.

3.2 Thermal-dynamical feedbacks associated with N₂O increases

The effect of N₂O increases on ozone in the tropical stratosphere is not only related to chemical processes. Austin et al. (2010a) pointed out that the strengthened Brewer–
Dobson (BD) circulation in the future climate could lead to ozone decreases in the tropical lower stratosphere as a result of intensified upward transport of ozone-poor air from below. Table 3 lists the tropical (25° N–25° S) upwelling ($w^*$) at 70–20 hPa averaged over the last 10 yr of the 4 WACCM experiments, and its change ($\delta w^*$) relative to the first 10 yr of simulations. It is apparent that the tropical upwelling increases with increased GHGs. However, one can see that relative changes of $w^*$ between the first and last decade of the simulations do not vary simply with GHG loading. In the experiment with both N$_2$O and CO$_2$ increases (run E3), $\delta w^*$ is not even the largest. This is consistent with the result in Xie et al. (2008) who showed that without SST increases associated with GHGs increases, the change in the tropical upwelling is not significant. Note that there is only very small value for $\delta w^*$ in our reference run (E0), which is a possible reason for the small ozone declining trend in the tropical lower stratosphere. It is known that the tropical upwelling is increasing in a warming climate. It is interesting that the trend in the tropical upwelling in our reference run is insignificant. A careful examination of the trends of the SSTs used in our simulation reveals that the SST trends are relatively weak compared with those of CCSM3 SST data which are widely used in CCM simulations in previous studies (SPARC-CCMVal, 2010). This may be the possible reason for the short of significant increases in the tropical upwelling in our reference run (E0).

As a greenhouse gas, N$_2$O increases can directly warm the troposphere and can also influence stratospheric temperature, by the direct radiative effect and by the indirect radiative effect associated with ozone feedbacks. Figure 5 shows the modeled temperature changes caused by different N$_2$O increases. A 50% increase of N$_2$O causes a 1 K cooling in the northern middle stratosphere and a 2 K cooling above 1 hPa at southern high latitudes (Fig. 5a). A 100% increase in N$_2$O causes a cooling in most regions of the stratosphere, with a maximum 3 K cooling in the tropical middle stratosphere (Fig. 5b). By comparing Figs. 3 and 5, we can see that the impact of N$_2$O on stratospheric temperatures is mainly caused by N$_2$O-induced ozone changes, rather than the direct radiative effect of N$_2$O. As expected, the cooling of the stratosphere...
becomes much larger when CO$_2$ is also increased by 50% together with a 50% N$_2$O increase (Fig. 5c). Also shown in Fig. 5 are the water vapor changes between the WACCM runs. Stratospheric water vapor depends on tropopause temperatures and production from CH$_4$ oxidation. As temperature changes in the upper troposphere and lower stratosphere (UTLS) region (Fig. 5a–c), a general decrease of water vapor on the order of 0.05 ppmv is simulated in the upper stratosphere and a significant increase of 0.15 ppmv can be noted in the mid-latitude lower stratosphere in the SH if N$_2$O is increased by 50%. When N$_2$O is increased by 100%, water vapor increases in the atmosphere due to warming of the tropopause, as is evident in Fig. 5b. Due to the significant cooling of the stratosphere caused by CO$_2$ and N$_2$O increases, the stratospheric water vapor decreases in run E3 (Fig. 5f).

Stratospheric methane and water vapor are closely related through chemical oxidation and dynamical transport processes. Figure 5g, h, j show the CH$_4$ changes caused by N$_2$O and CO$_2$ increases. Throughout the stratosphere, water vapor changes are anti-correlated with methane changes. More CH$_4$, which is shown as a round 0.05–0.07 ppmv in the middle to upper stratosphere (10 hPa to 1 hPa) and maximises in the tropics, is transported to the middle and upper stratosphere as a result of an enhanced BD circulation in response to N$_2$O and CO$_2$ increases. Compared with CH$_4$ increases in E1, in which N$_2$O is increased by 50% (Fig. 5g), the CH$_4$ increases seem to be smaller in magnitude when N$_2$O increased by 100% in run E2 (Fig. 5h). This is partly caused by transport differences in the tropical lower stratosphere between runs E1 and E2, since the BD circulation in E2 is stronger than that in E1. Also, a more significant decrease of CH$_4$ can be found in E2 in the lower stratosphere compared with in E1. CH$_4$ is oxidized by reactions involving OH, O($^1$D) and Cl radicals (e.g. Röckmann et al., 2004), which are perturbed by the GHG increases. The non-linear responses of CH$_4$ to N$_2$O increases indicate that the changes in CH$_4$ are due to the competing effects of transport and chemistry.

As polar stratospheric clouds (PSCs) are closely related to ozone loss in the polar stratosphere (e.g. Rex et al., 2004; Chipperfield et al., 2005; Austin et al., 2010b), it
is useful to examine the effect of N$_2$O increases on the occurrence of PSCs. Figure 6 shows the vertical distribution of the modeled change in the PSC surface area in the Antarctic and Arctic. The modeled PSC area is enlarged by 1–2 × 10$^6$ km$^2$ in the Arctic between 200 and 20 hPa, when N$_2$O is increased by 50–100 %. In the Antarctic lower stratosphere, however, N$_2$O increases cause no significant changes in the moddled PSC area. An exception occurs in the Antarctic mid-stratosphere at about 10 hPa, at the upper limit of PSC occurrence, where additional cooling can cause more PSCs. Figure 6 suggests that the N$_2$O increases have a different impact on the modeled PSC area in the Arctic and Antarctic stratosphere. In the Arctic stratosphere, temperatures are close to the threshold for widespread PSC formation and the cooling caused by N$_2$O increases can result in more PSCs. In the Antarctic lower stratosphere, temperatures in winter and spring are essentially always low enough for PSC formation, therefore, a small cooling caused by N$_2$O increases has no significant impact on PSC formation. This difference in the change in modeled PSC area between the Arctic and Antarctic makes a significant contribution to the hemispheric asymmetry of ozone destruction discussed in Fig. 3. However, previous studies (SPARC-CCMVal, 2010) showed that the potential for chlorine activation (PACl) in the Arctic simulated by WACCM is overall larger than expected, though it performs well for polar ozone depletion processes. This may lead to an overestimate for the ozone depleting effects of N$_2$O increases in the Arctic. Also noticeable is that compared to run E1, the impact of an additional 50 % N$_2$O increase (run E2) causes a larger increase in PSC area in the Arctic than an additional 50 % CO$_2$ increase. Here the increased NO$_y$ from N$_2$O promotes the formation of nitric acid trihydrate.

4 Contributions to ozone depletion from different factors due to N$_2$O changes

The attribution of ozone variations to dynamical, radiative, and chemical effects resulting from changes in GHGs and ODSs is an important problem in stratospheric climate. Multiple linear regression (MLR) is typically used to estimate statistical model parame-
ters (e.g. WMO, 2007; Shepherd, 2008; Stolarski et al., 2010; Oman et al., 2010b). For a given location and time, an ozone change ($\Delta O_3$) can be expressed as follows:

$$\Delta O_3(t) = \sum_j c_j \Delta X_j(t) + \epsilon(t)$$

where the variables $X_j$ are the factors that can affect ozone, the coefficients $c_j$ are the sensitivity of ozone to the factor $X_j$, and $\epsilon$ is the error in the fit. Here, $\Delta O_3$ and $\Delta X_j$ are the changes in ozone and other quantities between different model experiments with respect to the control experiment (E0) (i.e., $\Delta O_3 = O_{3,E1} - O_{3,E0}$, where $O_{3,E1}$ and $O_{3,E0}$ represent modeled ozone data from runs E0 and E1, respectively).

We select NO$_x$, ClO$_x$, as well as temperature ($T$) as proxies to represent the direct chemical effect, indirect chemical effect and radiative effect result from N$_2$O increases, respectively. Reactive hydrogen (HO$_x$) and transport parameters are not included, since their effects are relatively small (not shown). The MLR analysis described above is performed on the modeled data from the control run E0 and run E1, in which N$_2$O is increased by 50% by 2050. Ozone changes ($\Delta O_3$) caused by the selected regression factors are examined over different latitude bands (i.e., $90^\circ$N–$70^\circ$N, $22^\circ$N–$15^\circ$S, and $70^\circ$S–$90^\circ$S) on all the model levels from surface to 1 hPa, and the results are shown in Fig. 7.

The contributions of different factors to ozone changes are strongly latitude and altitude dependent. In the Arctic, NO$_x$ and temperature changes cause ozone decreases in the lower and middle stratosphere. NO$_x$ changes, which represent the direct chemical effect of N$_2$O increases, contribute over 80% or even higher to the 0.5 ppmv ozone decrease from 70 to 10 hPa (Fig. 7a). Figure 7a also shows that in the upper stratosphere, ClO$_x$ changes result in more ozone. In the tropics (Fig. 7b) both temperature and ClO$_x$ changes tend to result in more ozone in the mid-upper stratosphere. NO$_x$ changes lead to large ozone depletion (about 150% of total ozone changes) which are partly offset (about 50%) by the $T$ and ClO$_x$ contributions. NO$_x$ changes in the lower stratosphere cause more ozone on the order of 0.2 ppmv, while ClO$_x$ and $T$ have no
significant effects on ozone there. The contribution of NO\textsubscript{x} to ozone changes, which peaks at 10–3 hPa, is consistent with earlier studies (Oman et al., 2010b; Eyring et al., 2010b). In the Antarctic (Fig. 7c) the ozone changes caused by NO\textsubscript{x} changes are still negative but relatively small compared to those in the tropical and Arctic stratosphere. In contrast to those in the Arctic stratosphere, ozone changes associated with ClO\textsubscript{x} are negative in the Antarctic stratosphere. Note also that temperature has a more significant contribution on ozone changes than NO\textsubscript{x} in the Antarctic stratosphere. Similar features can be obtained when MLR analysis is performed on the modeled data from control run E0 and run E2 in which N\textsubscript{2}O is increased by 100 % by 2050 (not shown).

This multiple regression analysis suggests that the direct chemical effect (indicated by NO\textsubscript{x}) of N\textsubscript{2}O on ozone changes contributes to the largest part of ozone changes in the lower stratosphere, while the indirect chemical effect (indicated by ClO\textsubscript{x}) of N\textsubscript{2}O, which is associated with enhanced chlorine-catalyzed ozone destruction, is more important in the upper stratosphere. The effect of temperature changes (indicated as T) is more pronounced in the tropical upper stratosphere but relatively less significant in the polar stratosphere. It should be pointed out that some non-linear or interdependent effects of N\textsubscript{2}O increase on ozone, such as ozone depletion associated with PSCs, may not be well separated by the MLR analysis. Nevertheless, it provides us with some useful information on the contributions of different processes associated with N\textsubscript{2}O increases to ozone changes.

We now discuss the results of the WACCM sensitivity runs which applied N\textsubscript{2}O increases separately to the model’s radiation and chemistry schemes. The changes in ozone and temperature caused by chemical and radiative effects of N\textsubscript{2}O increases are shown in Fig. 8. Ozone decreases up to 10 % (1 ppmv) (Fig. 8a) when the 50 % N\textsubscript{2}O increase is applied to the chemistry routine, while the same increase of N\textsubscript{2}O in the radiation scheme causes no more than 1 % (0.1 ppmv) ozone decrease (Fig. 8b). When N\textsubscript{2}O is increased in both the chemistry and radiation schemes, the ozone changes show no significant differences from those caused by the chemical effect of a 50 % N\textsubscript{2}O alone (not shown). It is clear that the chemical effect contributes most to the ozone changes.
caused by N$_2$O increase, which is consistent with the MLR analysis. The ozone depletion causes significant subsequent stratospheric cooling, with a maximum of $-1.7$ K in the middle stratosphere (around 10 hPa) in the tropics (Fig. 8c). The direct radiative effect of N$_2$O is much smaller (below 1 K) than the indirect radiative effects (Fig. 8c and d) without a clear pattern in the spatial distribution.

Another factor which should also be considered is the dynamical effect of increasing N$_2$O. As shown in Table 3, the increase in N$_2$O is likely to strengthen the BD circulation. Meanwhile, this strengthened circulation influences the distribution and also contributes to the variability of O$_3$. Figure 9 shows the vertical ozone flux in the reference experiment E0 (Fig. 9a) as well as the corresponding changes in E1 relative to that in control run E0 (Fig. 9b). For a given grid cell $A[lat_i, lev_k]$ located at the latitude of $lat_i$ and the pressure levels of $lev_k$, the vertical ozone flux is defined as the incoming ozone at the lower level $lev_{k-1}$ ($O_3[lat_i, lev_{k-1}] \times w^*[lat_i, lev_{k-1}]$) minus the ozone coming out at higher level $lev_{k+1}$ ($O_3[lat_i, lev_{k+1}] \times w^*[lat_i, lev_{k+1}]$). Consistent with the overall picture of the BD circulation, the ozone in the tropical lower stratosphere is transported to the upper stratosphere and ozone in the mid-latitude upper stratosphere is transported downward to the lower stratosphere (Fig. 9a). It is evident from Fig. 9b that the strengthened BD circulation caused by the increased N$_2$O leads to a net decrease of ozone in the tropical lower stratosphere and a net ozone increase at around 100 hPa at southern mid-to-high latitudes. The large ozone increases around 100 hPa at southern mid-latitudes exhibited in Fig. 1a–c may be mainly caused by this transport effect. The MLR analysis with $w^*$ as an additional regression factor suggests that the dynamic effect of a N$_2$O increase on ozone changes is much less significant than its chemical and radiative effects in most of the areas (not shown). The result here implies that the dynamical effect of increasing N$_2$O on ozone is small on average, but may have a significant contribution to local ozone changes in the mid-latitude stratosphere.
5 Discussion and conclusions

The distribution of ozone changes resulting from N₂O increases in a 3-D CCM shown as function of latitude and altitude and the chemical mechanism was discussed by examining various chemical species related to ozone destruction. Subsequent climate changes induced by these N₂O increases, such as changes in stratospheric temperatures and water vapor, BD circulation and area of PSCs, were also examined, helping us to understand the N₂O and ozone interactions with climate changes. A series of sensitivity simulations and MLR were performed to detect the dominant factors controlling the ozone changes caused by N₂O increases.

The CCM results suggest that N₂O increases by 50%/100% between 2001 and 2050 result in more ozone destruction, reducing in ozone mixing ratios of maximally 6%/10% in the middle stratosphere at around 10 hPa. However, the total ozone column still shows an increase in future decades. The increase of N₂O also results in significant temperature and H₂O changes, which are seen in a slight cooling in the stratosphere and an evident increase of stratospheric H₂O. In a future cooler stratosphere the net yield of NOₓ is known to decrease, and our simulations indicate that the ozone-depleting impact of N₂O becomes smaller due to the cooling and fewer halogens in the stratosphere. The ozone depletion potential for N₂O in a future climate depends on whether the stratospheric cooling effect is larger than the effect of tropospheric N₂O changes. The increase of N₂O has only a small influence on chemical processes associated with Antarctic ozone destruction. However, increased emissions of N₂O are likely to delay recovery of the ozone in the Arctic stratosphere.

The depletion of ozone caused by nitrous oxide involves complex dynamical, chemical and radiative processes. The analyses based on a series of sensitivity simulations and MLR suggests that N₂O increases cause ozone changes mainly through chemical processes. The direct chemical effect of N₂O increases (via NOₓ chemistry) contributes the majority of ozone changes in the lower and middle stratosphere, while the indirect chemical effect of N₂O increases (via halogen chemistry) is simulated as the dominant...
factor in ozone depletion in the upper stratosphere. The direct radiative effect of \( \text{N}_2\text{O} \) increases on ozone is very small, but the indirect radiative effect associated with ozone changes is evident and coupled with chemical and dynamical processes. The dynamical effect of increasing \( \text{N}_2\text{O} \) is also small on average, but can cause large local ozone changes in the mid-latitude stratosphere. The ozone depleting effect of \( \text{N}_2\text{O} \) increases can be significantly reduced in the middle stratosphere when \( \text{CO}_2 \) is also increased, implying that the depletion of ozone caused by \( \text{N}_2\text{O} \) increases depends strongly on stratospheric temperature changes.

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References


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Table 1. The configurations of four CCM transient simulations.

<table>
<thead>
<tr>
<th>Experiments</th>
<th>GHGs Scenario</th>
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<tbody>
<tr>
<td>E0</td>
<td>IPCC A1B scenario</td>
</tr>
<tr>
<td>E1</td>
<td>Linear 50 % increase in N₂O surface vmr from 2001–2050</td>
</tr>
<tr>
<td>E2</td>
<td>As E1 but with 100 % increase in N₂O 2001–2050</td>
</tr>
<tr>
<td>E3</td>
<td>As E1 with additional 50 % linear increase in CO₂ vmr from 2001–2050</td>
</tr>
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**Table 2.** The configurations of four CCM sensitive simulations.

<table>
<thead>
<tr>
<th>Simulations</th>
<th>GHGs Settings</th>
</tr>
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<tbody>
<tr>
<td>S0</td>
<td>Fix N\textsubscript{2}O as 2050 climatology in IPCC A1B scenario</td>
</tr>
<tr>
<td>S1</td>
<td>Increase N\textsubscript{2}O by 50 % on S0 only in chemistry</td>
</tr>
<tr>
<td>S2</td>
<td>Increase N\textsubscript{2}O by 50 % on S0 only in radiation</td>
</tr>
<tr>
<td>S3</td>
<td>Increase N\textsubscript{2}O by 50 % on S0 interactively</td>
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</tbody>
</table>
Table 3. The tropical (25° N–25° S) upwelling ($w^*$) averaged between 70–20 hPa over the last 10 yr of the four simulations and changes in $w^*$ ($\Delta w^*$) relative to the first 10 yr of the corresponding simulations.

<table>
<thead>
<tr>
<th>Experiments</th>
<th>$w^*$ ($10^{-3}$ m s$^{-1}$)</th>
<th>$\Delta w^*$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E0</td>
<td>0.029</td>
<td>5.5</td>
</tr>
<tr>
<td>E1</td>
<td>0.032</td>
<td>28.4</td>
</tr>
<tr>
<td>E2</td>
<td>0.037</td>
<td>37.3</td>
</tr>
<tr>
<td>E3</td>
<td>0.033</td>
<td>21.9</td>
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Fig. 1. Latitude-pressure cross sections of differences (%) in zonal mean ozone mixing ratios (2041–2050) between WACCM experiments (a) E1 and E0, (b) E2 and E0, and (c) E3 and E0. Time-latitude cross sections of differences (%) in zonal mean total column ozone climatology (2041–2050) between experiments (d) E1 and E0, and (e) E2 and E0, (f) E3 and E0. The contour interval is 2% for percentage ozone changes. The grey colors represent significance levels for the mean state differences between different experiments by the Student’s T test.
Fig. 2. Time series of global mean (a) column NO$_y$ (molecules cm$^{-2}$) and (b) column NO$_x$ (molecules cm$^{-2}$) in E0 (black line), E1 (blue line), E2 (green line) and E3 (red line). Difference in (c) column NO$_y$ and (d) column NO$_x$ between E1 and E0 (blue line), E2 and E0 (green line), E3 and E0 (red line).
Fig. 3. (a, b, c) Latitude-pressure cross sections of the long-term (2001–2050) trends of zonal mean ozone mixing ratios (ppmv yr$^{-1}$) in WACCM experiments E0, E1 and E3. The contour interval is 0.005 ppmv yr$^{-1}$. Grey colors represent statistic significance levels of the trends. (d, e, f) Time series of total column ozone (DU) in different regions (Arctic, Tropics, Antarctic) in experiments E0 (black line), E1 (blue dashed line), E2 (green dashed-dotted line) and E3 (red dashed-dotted line).
Fig. 4. Time series of mean (a, b, c) ozone and (d, e, f) Clx (Clx = Cl + ClO + 2 Cl2O2) between 20–10 hPa averaged over (a) Arctic (60° N–90° N), (b) Tropics (22° N–22° S) and (c) Antarctic (60° S–90° S) in E0 (black line), E1 (blue line), E2 (green line) and E3 (red line).
Fig. 5. Latitude-pressure cross sections of differences in (a, b, c) zonal mean temperature, (d, e, f) H₂O and (g, h, i) CH₄ climatology (2041–2050) between WACCM experiments. The contour intervals are 1 K for temperature, 0.01 ppmv for CH₄ and 0.05 ppmv for H₂O in the stratosphere where H₂O mixing ratios low. Grey colors represent statistical significance levels for the mean state differences between different experiments by the Student’s T test.
Fig. 6. Profiles of differences in annual mean PSCs area ($\times 10^6$ km$^2$) between WACCM experiments E1 and E0 (blue dashed line), E2 and E0 (green dashed dotted line), and E3 and E0 (red dashed dotted line) in (a) Antarctic and (b) Arctic.
Fig. 7. Results of multiple regressions for spatially-averaged ozone change ($\Delta O_3 = O_3 (E1) - O_3 (E0)$) with spatially-averaged NO$_x$, ClO$_x$ and $T$ change. The averaging domains are 90° N–70° N, 22° N–22° S, and 70° S–90° S. The black thick line shows the changes of $\Delta O_3$ from 2001 to 2050 ($d\Delta O_3$), calculated by a simple linear regression of $\Delta O_3$ with year ($\Delta O_3 = a_0 + a_1 \times \text{year}$, $d\Delta O_3 = a_1 \times 50$). The blue dashed line, green dashed-dotted line and red dashed double point line show the NO$_x$, EESC and $T$ contributions to $\Delta O_3$ (i.e. $d\Delta O_{3,NO_x} = \Delta NO_x \times \text{Coefs}_{NO_x}$), respectively.

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Fig. 8. Latitude-pressure cross sections of zonal mean ozone differences (%) between WACCM sensitivity experiments (a) S1 and S0, and (b) S2 and S0, and temperature differences (K) between sensitivity experiments (c) S1 and S0, and (d) S2 and S0. The contour interval for ozone is 2% and for temperature is 0.5 K. Grey colors represent statistical significance levels for the mean state differences between different simulations by the Student’s T test.
Fig. 9. Vertical ozone fluxes associated with the BD circulation (w*) calculated from (a) reference experiment (E0) and (b) the differences between E1 and E0 (for more details of the definition of ozone flux see text). The contour intervals are $0.3 \times 10^3\, \text{kg s}^{-1}$ and $0.1 \times 10^3\, \text{kg s}^{-1}$ in (a) and (b), respectively. Grey colors (b) represent the statistical significance levels for the mean state differences between different experiments by the Student's T test.