



The sensitivity of stratospheric ozone changes through the 21st century to N₂O and CH₄

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Abstract. Through the 21st century, anthropogenic emissions of the greenhouse gases N₂O and CH₄ are projected to increase, thus increasing their atmospheric concentrations. Consequently, reactive nitrogen species produced from N₂O and reactive hydrogen species produced from CH₄ are expected to play an increasingly important role in determining stratospheric ozone concentrations. Eight chemistry-climate model simulations were performed to assess the sensitivity of stratospheric ozone to different emissions scenarios for N₂O and CH₄. Global-mean total column ozone increases through the 21st century in all eight simulations as a result of CO₂-induced stratospheric cooling and decreasing stratospheric halogen concentrations. Larger N₂O concentrations were associated with smaller ozone increases, due to reactive nitrogen-mediated ozone destruction. In the simulation with the largest N₂O increase, global-mean total column ozone increased by 4.3 DU through the 21st century, compared with 10.0 DU in the simulation with the smallest N₂O increase. In contrast, larger CH₄ concentrations were associated with larger ozone increases; global-mean total column ozone increased by 16.7 DU through the 21st century in the simulation with the largest CH₄ concentrations and by 4.4 DU in the simulation with the lowest CH₄ concentrations. CH₄ leads to ozone loss in the upper and lower stratosphere by increasing the rate of reactive hydrogen-mediated ozone loss cycles, however in the lower stratosphere and troposphere, CH₄ leads to ozone increases due to photochemical smog-type chemistry. In addition to this mechanism, total column ozone increases due to H₂O-induced cooling of the strato-

sphere, and slowing of the chlorine-catalyzed ozone loss cycles due to an increased rate of the CH₄ + Cl reaction. Stratospheric column ozone through the 21st century exhibits a near-linear response to changes in N₂O and CH₄ surface concentrations, which provides a simple parameterization for the ozone response to changes in these gases.

1 Introduction

Through the 21st century, decreasing concentrations of stratospheric chlorine and bromine, together with increasing concentrations of CO₂, are projected to lead to increased global-mean stratospheric ozone (Eyring et al., 2010). CO₂, the dominant anthropogenic greenhouse gas (GHG), elevates ozone by cooling the stratosphere, which slows the gas-phase ozone loss cycles (e.g. World Meteorological Organization, 1998; Rosenfield et al., 2002; IPCC/TEAP, 2005). Of the GHGs controlled under the Kyoto Protocol, those with the highest radiative forcing after CO₂ are N₂O and CH₄, both of which lead to changes in ozone via chemical processes. Although the roles of N₂O and CH₄ in ozone chemistry are qualitatively understood, the sensitivity of ozone to these gases has not been thoroughly investigated. It is the aim of this work to gain a quantitative understanding of the sensitivity of stratospheric ozone to N₂O and CH₄ through the use of a coupled chemistry-climate model.

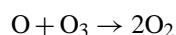
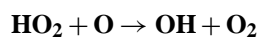
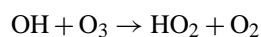
N_2O in the stratosphere affects ozone predominantly through NO_x -catalyzed ($\text{NO}_x = \text{NO} + \text{NO}_2$) ozone-loss cycles (Crutzen, 1970). However, increases in N_2O do not necessarily lead to increases in NO_x due changes in the chemical, dynamical and radiative environment of the stratosphere, as discussed in detail by Revell et al. (2012). For example, the sink for NO_x is temperature dependent, so CO_2 -induced cooling of the stratosphere decreases NO_x abundances by slowing the highly temperature-dependent Reaction (R1) (below). The subsequent increase in N leads to an increase in the rate of Reaction (R2), therefore decreasing NO_x abundances (Rosenfield and Douglass, 1998).



More recently, Plummer et al. (2010) found that nitrogen species induced large stratospheric ozone losses once the effects of CO_2 -induced stratospheric cooling were removed. In addition, increasing sea-surface temperatures (SSTs) are projected to strengthen the Brewer-Dobson circulation, resulting in a faster removal rate of reservoir nitrogen species from the stratosphere (Cook and Roscoe, 2012). As a consequence, NO_x abundances will be reduced.

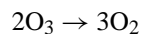
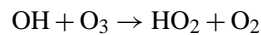
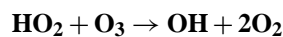
CH_4 weakens the ozone-depleting effectiveness of N_2O by producing reactive hydrogen species which: (1) slow NO_x -catalyzed ozone loss cycles in the upper stratosphere (Revell et al., 2012), and (2) remove NO_x from the middle stratosphere through reactions to form HNO_3 (Randeniya et al., 2002). Similarly, chlorine radicals produced by photolysis of ozone-depleting substances (ODSs), such as the CFCs, react with NO_x to form ClONO_2 , thus reducing NO_x abundances (Ravishankara et al., 2009). However, as the chlorine loading of the stratosphere decreases through the 21st century (owing to the success of the Montreal Protocol for Substances that Deplete the Ozone Layer and later amendments and adjustments), the effect of chlorine on NO_x will become less important. Furthermore, Ravishankara et al. (2009) have shown that N_2O is the dominant ODS currently emitted, and is expected to remain so through the remainder of the 21st century.

The oxidation of CH_4 produces HO_x radicals (here: $\text{HO}_x = \text{H} + \text{OH} + \text{HO}_2$) which catalyze ozone destruction cycles. In the upper stratosphere, the dominant HO_x -catalyzed ozone loss cycle is Cycle I (rate-determining step in bold):

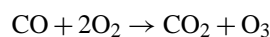
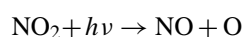
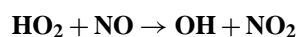
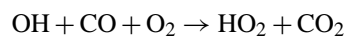


In the lower stratosphere, where the ratio of O_3 to O is much larger compared with in the upper stratosphere, the dominant

HO_x -catalyzed ozone loss cycle is Cycle II, which involves the reaction of HO_2 with O_3 in the rate-determining step:



HO_2 can also react with NO, leading to ozone production via Cycle III (so-called “photochemical smog chemistry”) (Johnston and Podolske, 1978; Nevison et al., 1999; Portmann and Solomon, 2007; Fleming et al., 2011). Cycle III occurs predominantly in the troposphere and very lower stratosphere, where the concentration of CO is sufficiently large.



Portmann and Solomon (2007) and Fleming et al. (2011) have shown that the predominant effect of increasing CH_4 is to increase total column ozone. This occurs via Cycle III in the lower atmosphere, and via H_2O -induced stratospheric cooling in the middle stratosphere, which slows the temperature-dependent gas-phase ozone loss cycles. Additionally, increasing CH_4 increases the reaction rate of Reaction (R3) (see below), which increases the rate of conversion of chlorine to the HCl reservoir and thereby slows the chlorine-catalyzed ozone loss cycles throughout the stratosphere. The removal of reactive chlorine by Reaction (R3) is less effective in polar regions where reaction with HCl is not important for chlorine deactivation (Douglass et al., 1995).



Oman et al. (2010) studied the effects of reactive nitrogen and hydrogen species on stratospheric ozone using two chemistry-climate model (CCM) simulations constrained by the IPCC SRES A1B and A2 emissions scenarios for GHGs, which portray intermediate (A1B) and large (A2) increases in CO_2 , N_2O and CH_4 (Nakicenovic and Swart, 2000). The evolution of upper stratospheric ozone in the two CCM simulations was similar, because although NO_x and HO_x species led to larger ozone losses in A2 compared with A1B, they were compensated by the effects of larger increases in CO_2 -induced stratospheric cooling.

Here an analysis of the chemical sensitivity of stratospheric ozone to N_2O and CH_4 through the 21st century is presented using the results from eight CCM simulations. Four simulations differed only in their N_2O concentrations, while the other four differed in their CH_4 concentrations. The same concentration scenario for CO_2 was used across all eight simulations.

Table 1. Summary of scenarios for the CCM simulations^a.

Simulation	N ₂ O scenario	CH ₄ scenario	ΔO ₃ (DU) ^b
N ₂ O-2.6	RCP 2.6	SRES A1B	10.0
N ₂ O-4.5	RCP 4.5	SRES A1B	7.6
N ₂ O-6.0	RCP 6.0	SRES A1B	4.9
N ₂ O-8.5	RCP 8.5	SRES A1B	4.3
CH ₄ -2.6	SRES A1B	RCP 2.6	4.4
CH ₄ -4.5	SRES A1B	RCP 4.5	5.2
CH ₄ -6.0	SRES A1B	RCP 6.0	9.1
CH ₄ -8.5	SRES A1B	RCP 8.5	16.7

^a All simulations used the IPCC SRES A1B scenario for CO₂ and adjusted A1 scenario for halocarbons.

^b Change in global-mean total column ozone through the 21st century (2090s decade minus the decade from 2015–2024), expressed in Dobson units.

2 Computational methods

2.1 The NIWA-SOCOL chemistry-climate model

The evolution of stratospheric ozone was simulated using the NIWA-SOCOL (National Institute of Water and Atmospheric Research – Solar Climate Ozone Links) CCM (SPARC CCMVal, 2010). NIWA-SOCOL is based on SOCOL v2.0 (Schranner et al., 2008), which consists of the MAECHAM4 global climate model (Manzini et al., 1997) coupled to a modified version of the MEZON chemistry transport model (Egorova et al., 2003). NIWA-SOCOL includes 41 chemical species, 140 gas-phase reactions, 46 photolysis reactions and 16 heterogeneous reactions. Chemical constituents are advected by a hybrid transport scheme (Zubov et al., 1999), and the chemical solver algorithm uses a Newton-Raphson iterative method. A 15-min time step is used for dynamical processes, while radiative and chemical calculations are performed every two hours. CCM simulations were performed for the period 2005–2100, with the first ten years discarded as spin-up.

The NIWA-SOCOL model attributes ozone loss to 15 catalytic cycles (listed by Revell et al., 2012), using a diagnostic approach similar to that employed by Lee et al. (2002). Odd-oxygen (O + O(¹D) + O₃) removal rates (molecules cm⁻³ s⁻¹) are calculated within the model based on the rate-limiting steps of the corresponding reaction cycles, recorded and accumulated as daily means in each model grid cell.

2.2 Concentrations scenarios

Eight GHG concentration scenarios were constructed, as described in Table 1, using combinations of the IPCC SRES A1B concentrations scenario for GHGs (Nakicenovic and Swart, 2000), and the four Representative Concentration Pathways (RCPs) 2.6, 4.5, 6.0 and 8.5, named according to the radiative forcings (in W m⁻²) reached by 2100. The RCPs were developed for the climate modelling community

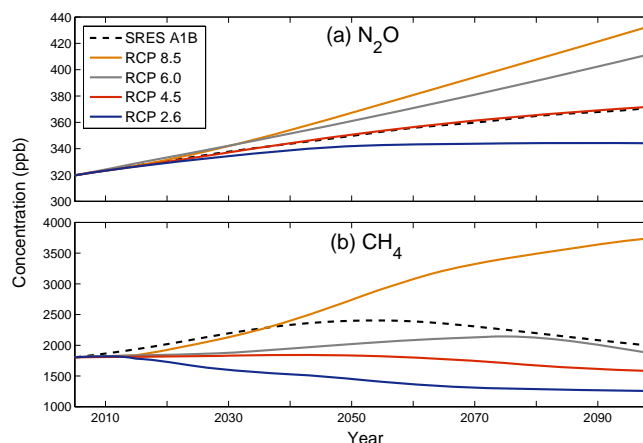


Fig. 1. (a) N₂O and (b) CH₄ surface concentrations used in the CCM simulations.

to provide possible concentration trajectories for the main climate change forcing agents. They do not include socio-economic, emission and climate projections (van Vuuren et al., 2011). Surface concentrations of N₂O and CH₄ for the individual scenarios are shown in Fig. 1. All simulations used the SRES A1B scenario for CO₂ and the adjusted A1 scenario for halocarbons (Daniel et al., 2007).

Sea-surface temperatures were prescribed under the SRES A1B scenario using output from the ECHAM5/MPIOM atmosphere-ocean general circulation model (AOGCM). To test whether they would have been different if they had been calculated from AOGCM simulations using the constructed GHG concentration scenarios (Table 1), SSTs for each of the eight scenarios were simulated using the simple climate model MAGICC6, which is designed to emulate AOGCMs (Meinshausen et al., 2011). Globally averaged annual-mean SSTs under the SRES A1B and the eight GHG concentrations scenarios are displayed in Fig. 2. SSTs exhibit a greater spread by 2100 in simulations employing different CH₄ scenarios, owing to the greater radiative forcing of CH₄ compared with N₂O. However, results do not significantly differ from the A1B simulation (at most, there is a difference of 0.5 K between the CH₄-8.5- and A1B-based SSTs in 2100). The conclusions drawn in this study are therefore not impacted by using A1B-based SSTs for all simulations.

3 Results and discussion

3.1 Ozone changes resulting from chemistry

Processes such as stratospheric cooling and the projected strengthening of the Brewer-Dobson circulation, as well as decreasing stratospheric halogen loading are expected to have a large impact on the evolution of stratospheric ozone through the 21st century (Bekki et al., 2011 and references therein). Because we use the same SST and CO₂

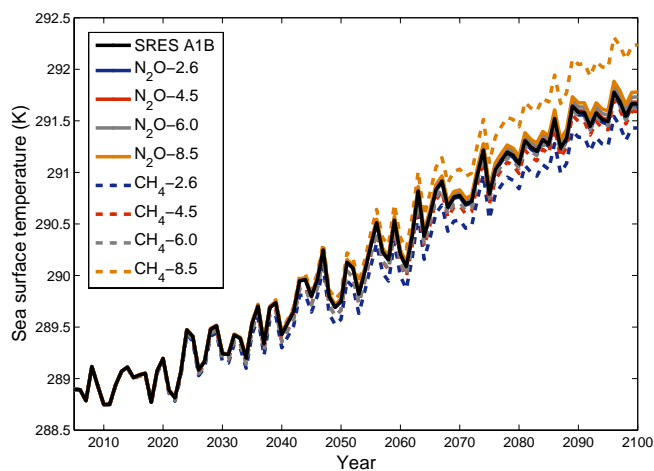


Fig. 2. Global-, annual-mean SSTs. The SRES A1B SSTs were used in all eight CCM simulations. The other SST series were calculated individually for each GHG concentration scenario using MAGICC6.

concentration scenarios for all of our simulations, the effects of stratospheric cooling and the strengthening of the Brewer-Dobson circulation on ozone (which are driven primarily by CO_2 and SST increase, respectively) are the same in all eight simulations. The different N_2O and CH_4 scenarios used allow us to examine the changes in ozone due to these greenhouse gases, which are mostly chemical changes.

In all eight CCM simulations performed for this study, global-mean total column ozone increases through the 21st century. The magnitude of the increase is listed as ΔO_3 in the rightmost column of Table 1. In general, this increase is caused by a combination of a slowing of the gas-phase ozone loss cycles due to stratospheric cooling (Rosenfield et al., 2002), and decreasing concentrations of stratospheric chlorine and bromine resulting from the phase-out of halogenated ODSs under the Montreal Protocol (Bekki et al., 2011). The simulations with larger N_2O surface concentrations lead to a smaller increase in ozone (4.3 DU in N_2O -8.5 compared with 10 DU in N_2O -2.6), while those with larger CH_4 surface concentrations lead to a larger increase in ozone (16.7 DU in CH_4 -8.5 compared with 4.4 DU in CH_4 -2.6).

To examine changes in chemically-induced ozone destruction, the differences in the rates of the nitrogen, hydrogen and chlorine cycles in the 2090s decade between the N_2O -8.5 and N_2O -2.6 simulations (a–c) and the CH_4 -8.5 and CH_4 -2.6 simulations (d–f) are shown in Fig. 3 as a function of pressure and latitude. The ozone-depleting nitrogen cycles speed up with increased N_2O throughout the upper and middle stratosphere, but remain largely unchanged in the lower stratosphere where concentrations of odd-oxygen are diminished (Fig. 3a). Figure 3b and c show that the hydrogen and chlorine cycles slow down throughout the upper and middle stratosphere through the 21st century. This is because enhanced ozone depletion due to NO_x means that the availabil-

ity of odd-oxygen to participate in reactions with hydrogen and chlorine species is reduced, as discussed by Revell et al. (2012).

Similarly, Fig. 3e shows that HO_x -induced ozone depletion (mostly due to Cycle I) speeds up with increased CH_4 in the upper stratosphere, where the nitrogen and chlorine cycles slow (Fig. 3d and f). HO_x -induced ozone destruction by Cycle II is important in the lower stratosphere, although we do not see the effects of it here as we show the absolute rather than fractional difference between simulations. As well as reduced availability of odd-oxygen, the chlorine cycles slow due to reduced availability of reactive chlorine, as determined by Reaction (R3). Although the effectiveness of Reaction (R3) is diminished in the 2090s decade due to reduced stratospheric chlorine loading, the larger CH_4 abundances in simulation CH_4 -8.5 relative to CH_4 -2.6 mean that Reaction (R3) is more effective with respect to chlorine deactivation in CH_4 -8.5.

Differences in NO_x between the N_2O -8.5 and N_2O -2.6 simulations for the 2090s decade are shown in Fig. 4 as abundances, and calculated as a percentage of NO_x in the N_2O -2.6 simulation. In absolute terms (Fig. 4a), NO_x species exhibit the greatest increase through the middle stratosphere, whereas the largest fractional increase is observed in the polar stratosphere (Fig. 4b). Similarly, Fig. 4c and d show changes in H_2O between the CH_4 -8.5 and CH_4 -2.6 simulations.

In all eight simulations presented here, ozone increases everywhere except for in the tropical lower stratosphere (not shown). Here, ozone decreases because the enhanced rate of tropical upwelling means there is less time for ozone to form in rising parcels of ozone-poor air from the troposphere to the stratosphere (Avallone and Prather, 1996). In Figs. 5 and 6, we examine the *difference* between 2090s ozone as a function of latitude and pressure.

Figure 5a shows the difference between 2090s ozone in the N_2O -8.5 and N_2O -2.6 simulations. Ozone is suppressed by as much as ~ 5 –10% in the middle stratosphere in the N_2O -8.5 simulation compared to the N_2O -2.6 simulation but is elevated by ~ 5 % in the tropical lower stratosphere (~ 100 –70 hPa). The smaller ozone increase in the N_2O -8.5 simulation is expected and is due to enhanced rates of the ozone-depleting nitrogen cycles (Fig. 3a). The larger ozone abundances in the troposphere and lower stratosphere in the N_2O -8.5 simulation (relative to the N_2O -2.6 simulation) are likely due to enhanced ozone production by Cycle III, as a result of increased N_2O and therefore NO_x abundances. This was also observed by Portmann and Solomon (2007), who studied the effects of N_2O on ozone.

The difference between 2090s total column ozone in the N_2O -8.5 and N_2O -2.6 simulations is shown in Fig. 5b as a function of latitude. Because the middle stratosphere dominates the ozone column, total column ozone is suppressed at all latitudes in the N_2O -8.5 simulation relative to the N_2O -2.6 simulation (but less so in the tropical stratosphere). The

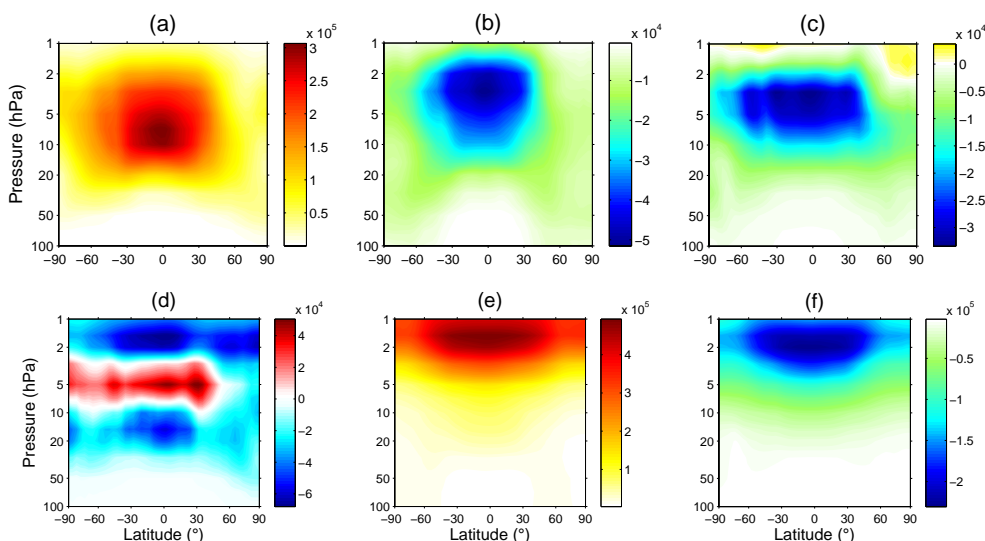


Fig. 3. (a) Contribution to ozone loss (molecules $\text{cm}^{-3} \text{s}^{-1}$) from the nitrogen cycles as a function of pressure and latitude in the 2090s decade in the N_2O -8.5 simulation, minus the same quantity for the N_2O -2.6 simulation. (b) Same as (a), but for the hydrogen cycles. (c) Same as (a), but for the chlorine cycles. (d) Contribution to ozone loss from the nitrogen cycles as a function of pressure and latitude in the 2090s decade in the CH_4 -8.5 simulation, minus the same quantity for the CH_4 -2.6 simulation. (e) Same as (d), but for the hydrogen cycles. (f) Same as (d), but for the chlorine cycles. Note the different orders of magnitude on the colour scales.

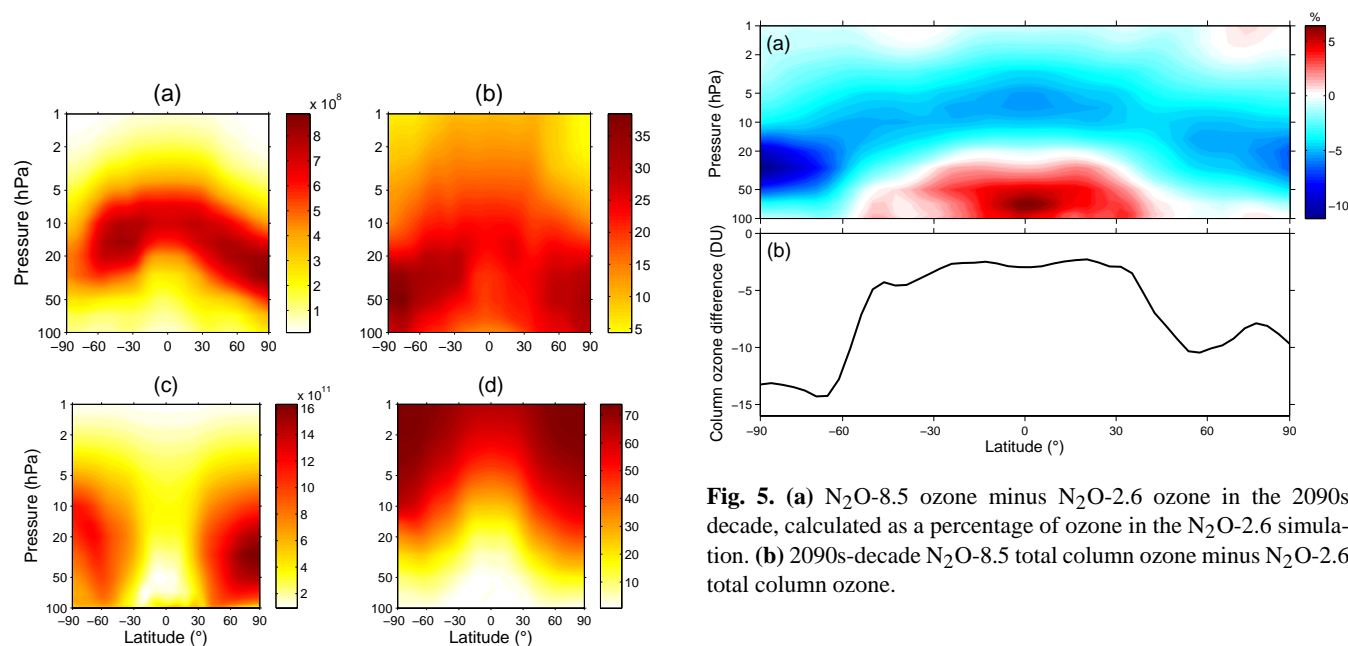


Fig. 4. (a) NO_x abundance (molecules cm^{-3}) in the 2090s decade for the N_2O -8.5 simulation, minus the same quantity for the N_2O -2.6 simulation. (b) The quantity in (a) expressed as a percentage of 2090s NO_x abundance for the N_2O -2.6 simulation. (c) Abundance of water vapour (molecules cm^{-3}) in the 2090s decade for the CH_4 -8.5 simulation, minus the same quantity for the CH_4 -2.6 simulation. (d) The quantity in (c) expressed as a percentage of 2090s water vapour abundance for the CH_4 -2.6 simulation.

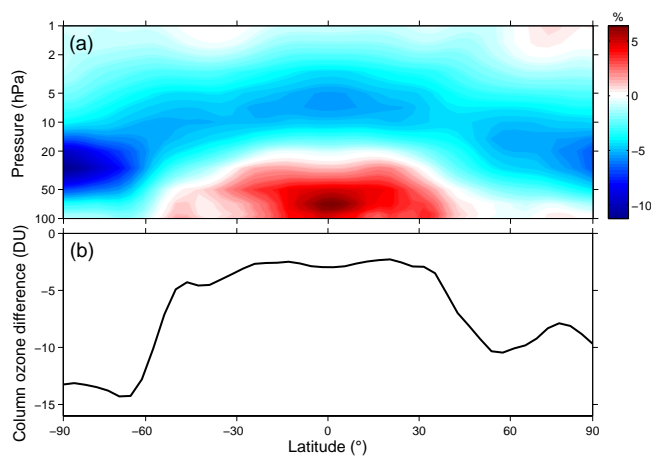


Fig. 5. (a) N_2O -8.5 ozone minus N_2O -2.6 ozone in the 2090s decade, calculated as a percentage of ozone in the N_2O -2.6 simulation. (b) 2090s-decade N_2O -8.5 total column ozone minus N_2O -2.6 total column ozone.

largest ozone decrease is seen at 50 hPa in the Antarctic stratosphere, which could be due to the large increase in NO_x in this region (Fig. 4b).

Figure 6 is similar to Fig. 5, but shows the differences between simulations CH_4 -8.5 and CH_4 -2.6. In simulation CH_4 -8.5, ozone increases of up to $\sim 15\%$ greater than those in the CH_4 -2.6 simulation are seen throughout the stratosphere, except for in the upper stratosphere where ozone is suppressed by more than 5% due to enhanced rates of the HO_x ozone loss cycles. Through the middle stratosphere, the rate

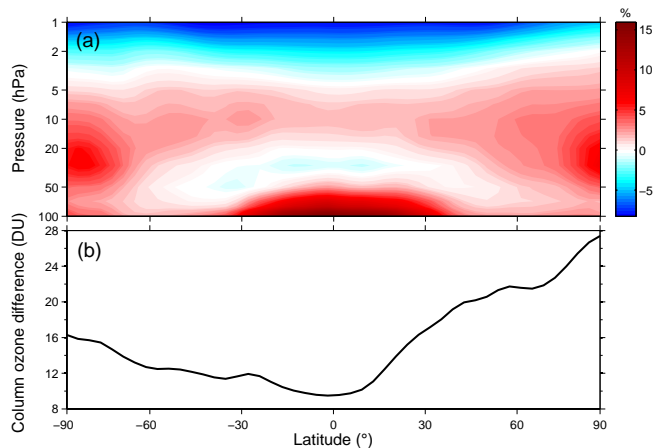


Fig. 6. (a) CH_4 -8.5 ozone minus CH_4 -2.6 ozone in the 2090s decade, calculated as a percentage of ozone in the CH_4 -2.6 simulation. (b) 2090s-decade CH_4 -8.5 total column ozone minus CH_4 -2.6 total column ozone.

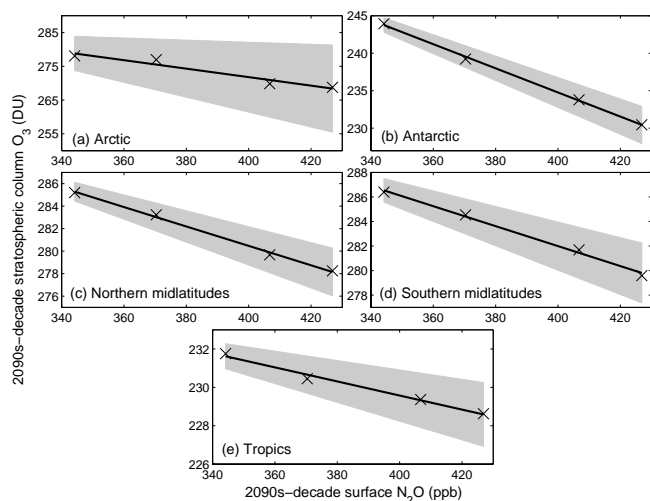


Fig. 7. (a) 2090s-mean Arctic (63 – 90° N) stratospheric column ozone (1 – 100 hPa) vs. 2090s-mean surface N_2O for the four N_2O simulations (crosses), fitted with a simple linear regression model (black line). The grey shaded region indicates the 95 % confidence interval for the slope and intercept of the regression model. (b–e) As for (a), but for: (b) the Antarctic (63 – 90° S); (c) northern midlatitudes (30 – 60° N); (d) southern midlatitudes (30 – 60° S); (e) the tropics (25° N– 25° S).

of Reaction (R3) increases in simulation CH_4 8.5 relative to CH_4 -2.6, thus decreasing the abundance of reactive chlorine and slowing the chlorine cycles (Fig. 3f). Additionally, increasing CH_4 leads to an increase in H_2O (Fig. 4c and d), which in turn cools the stratosphere and slows ozone depletion. H_2O increases noticeably in the Arctic polar stratosphere (Fig. 4c), where subsequent cooling could explain the relatively large ozone increase observed in Fig. 6b. This is in contrast to the findings of Kirk-Davidoff et al. (1999), Feck

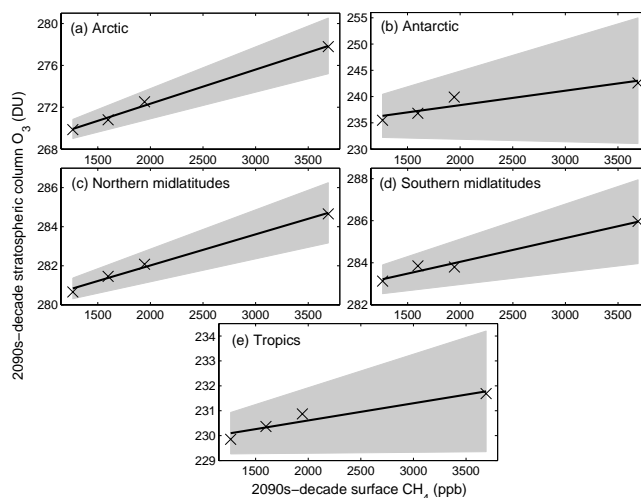


Fig. 8. Similar to Fig. 7, but for 2090s-mean stratospheric column ozone vs. 2090s-mean surface CH_4 for the four CH_4 simulations.

et al. (2008) and Vogel et al. (2011), who found that cooler temperatures resulting from increases in water vapour lead to enhanced heterogeneous chlorine chemistry and subsequent ozone loss. It is likely that because we focus on the 2090s decade in our analysis, when stratospheric chlorine levels are very low, heterogeneous chemistry is no longer of significance to polar ozone depletion.

CH_4 increases lead to an increase in HO_x abundances, which drive the rate of Cycle III. Therefore, in the troposphere and lower stratosphere, the relative increase in ozone between simulations CH_4 -8.5 and CH_4 -2.6 is likely due to enhanced ozone production by Cycle III. This mechanism was put forward by Portmann and Solomon (2007) and Fleming et al. (2011) to explain tropospheric and lower stratospheric ozone increases observed in simulations designed to isolate the impact of CH_4 on ozone. It should be noted that NIWA-SOCOL does not include oxidation of non-methane hydrocarbons in its tropospheric chemistry mechanism; therefore, ozone production by Cycle III is underestimated in the model simulations presented here.

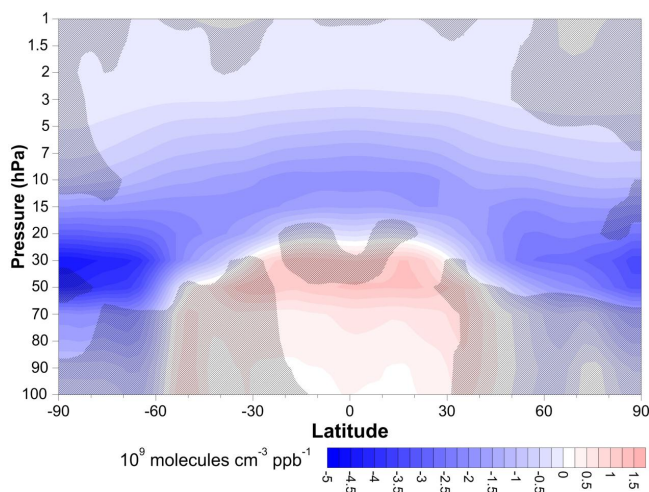
3.2 The sensitivity of ozone to N_2O and CH_4

To test whether there is a linear relationship between stratospheric ozone at the end of the 21st century, and the N_2O or CH_4 concentration at that time, linear fits to 2090s-mean stratospheric ozone columns (1 – 100 hPa) as a function of N_2O or CH_4 concentrations were calculated in five regions of the stratosphere (Figs. 7 and 8). The slopes for the linear fits in Figs. 7 and 8 are given in Table 2, along with the R^2 -values. The shaded regions in Figs. 7 and 8 represent the 95 % confidence interval calculated for the slope and intercept of the linear regression models.

As shown in Fig. 7 and Table 2, the slopes for the linear fits are negative in all regions of the stratosphere, and the

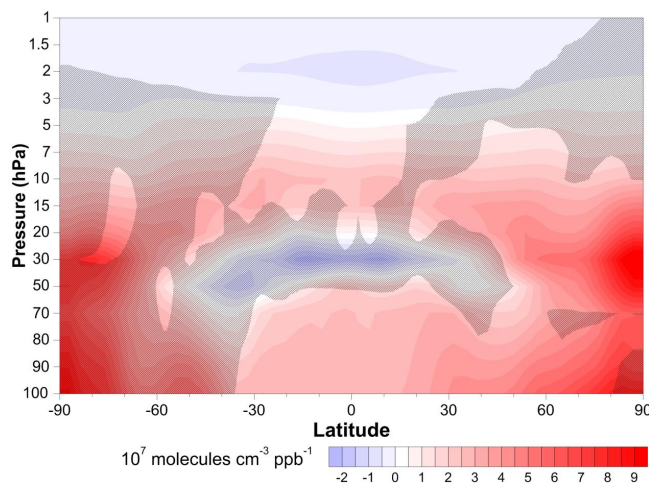
Table 2. Linear regression model slopes and R^2 -values.

	N ₂ O simulations		CH ₄ simulations	
	Slope (DU ppb ⁻¹)	R ² -value	Slope (DU ppb ⁻¹)	R ² -value
Arctic (63–90° N)	−10.4	0.942	7.9	0.995
Northern midlatitudes (30–60° N)	−7.1	0.996	3.9	0.993
Tropics (25° N–25° S)	−3	0.988	1.7	0.912
Southern midlatitudes (30–60° S)	−6.7	0.995	2.7	0.976
Antarctic (63–90° S)	−13.3	0.999	6.7	0.870

**Fig. 9.** Slopes from simple linear regression models fitted to 2090s-mean ozone vs. 2090s-mean surface N₂O for all latitudes and all pressure levels between 1–100 hPa, for the four N₂O simulations. Hatching indicates that the slope was not statistically significantly different from zero at the 95 % level of confidence.

R^2 -values exceed 0.94 everywhere. All fits are statistically significantly different from zero at the 95 % confidence level, indicating a strong linear relationship between stratospheric ozone abundance and N₂O concentrations. The linear fits between ozone and CH₄ in Fig. 8 all have positive slopes, and are statistically significantly different from zero at the 95 % confidence level in all regions of the stratosphere except for the Antarctic, where the R^2 -value is 0.87. Elsewhere, the R^2 -value exceeds 0.91. For both the N₂O and CH₄ simulations, sensitivities in the polar regions are enhanced compared with the tropics and midlatitudes. For the N₂O simulations, this is likely due to the change in NO_x loading, which shows the greatest relative increase in the polar stratosphere (Fig. 4b). For the CH₄ simulations, the likely cause is the large increase in water vapour observed in the polar regions (Fig. 4c), as discussed earlier.

Figures 9 and 10 show the slopes of linear fits to 2090s-ozone vs. N₂O or CH₄ surface concentrations as a function of pressure and latitude. Regions where the slope is not statistically significantly different from zero at the 95 % con-

**Fig. 10.** Similar to Fig. 9, but the slopes are from simple linear regression models fitted to 2090s-mean ozone vs. 2090s-mean surface CH₄ for the four CH₄ simulations.

fidence bounds are hatched. Figure 9 shows that in the polar regions, and throughout most of the middle stratosphere, ozone demonstrates a statistically significant negative linear relationship with N₂O. There is a positive correlation in the tropical lower stratosphere, where enhanced N₂O leads to ozone production. Figure 10 shows that ozone decreases linearly with increasing CH₄ in the upper stratosphere, and that this relationship is statistically significant at the 95 % confidence level. Statistically significant relationships between ozone and CH₄ are also found, for example, through much of the tropical, northern-midlatitude and Arctic stratosphere, where ozone increases with increasing CH₄.

These quasi-linear relationships between ozone and N₂O and CH₄ over the range of RCP scenarios tested here suggest that perturbations to either stratospheric column ozone (using the results presented in Figs. 7 and 8) or to vertically resolved ozone (using the results presented in Figs. 9 and 10) can be incorporated into simple models of stratospheric ozone to capture the changes in ozone resulting from changes in N₂O and CH₄ (noting that such parameterizations do not require a strict one way causality between N₂O and CH₄ changes and total column ozone response). However, the fits are based on

only four points and a single CO₂ and CH₄ scenario for the N₂O simulations and a single CO₂ and N₂O scenario for the CH₄ simulations; ozone may not exhibit this apparent linear sensitivity under different greenhouse gas scenarios.

4 Conclusions

Total column ozone increases through the 21st century in all of the eight CCM simulations presented here, due to decreased stratospheric chlorine loading and CO₂-induced cooling of the stratosphere. Larger increases are observed in simulations with low N₂O or high CH₄ concentrations. N₂O decreases stratospheric ozone abundance by increasing the rate of the ozone-depleting nitrogen cycles. Although mid- and lower-stratospheric ozone increase in response to increased CH₄, upper stratospheric ozone decreases due to an increase in the rate of the ozone-depleting hydrogen cycles. Furthermore, we have shown that at the end of the 21st century, stratospheric column ozone decreases linearly with increasing surface N₂O concentrations in all regions of the stratosphere. In contrast, stratospheric column ozone increases linearly with increasing CH₄ concentrations, however this relationship is not statistically significant at the 95 % confidence level in the Antarctic stratosphere. We have also shown the vertically-resolved relationship between ozone and N₂O and CH₄; ozone demonstrates a statistically significant negative linear relationship with N₂O in the polar and middle stratosphere, and with CH₄ in the upper stratosphere. Ozone increases are positively correlated with CH₄ increases in the middle and lower stratosphere, although this increase is not statistically significant at the 95 % confidence level through much of the southern midlatitude and polar stratosphere. Our conclusions are derived from simulations based on a single CO₂ concentration scenario, and ozone may not exhibit this linear sensitivity under different CO₂ scenarios; this will be the subject of future work.

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