

## Impact of future nitrous oxide and carbon dioxide emissions on the stratospheric ozone layer

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## LETTER

## Impact of future nitrous oxide and carbon dioxide emissions on the stratospheric ozone layer

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## Abstract

The atmospheric levels of human-produced chlorocarbons and bromocarbons are projected to make only small contributions to ozone depletion by 2100. Increases in carbon dioxide (CO<sub>2</sub>) and nitrous oxide (N<sub>2</sub>O) will become increasingly important in determining the future of the ozone layer. N<sub>2</sub>O increases lead to increased production of nitrogen oxides (NO<sub>x</sub>), contributing to ozone depletion. CO<sub>2</sub> increases cool the stratosphere and affect ozone levels in several ways. Cooling decreases the rate of many photochemical reactions, thus slowing ozone loss rates. Cooling also increases the chemical destruction of nitrogen oxides, thereby moderating the effect of increased N<sub>2</sub>O on ozone depletion. The stratospheric ozone level projected for the end of this century therefore depends on future emissions of both CO<sub>2</sub> and N<sub>2</sub>O. We use a two-dimensional chemical transport model to explore a wide range of values for the boundary conditions for CO<sub>2</sub> and N<sub>2</sub>O, and find that all of the current scenarios for growth of greenhouse gases project the global average ozone to be larger in 2100 than in 1960.

## 1. Introduction

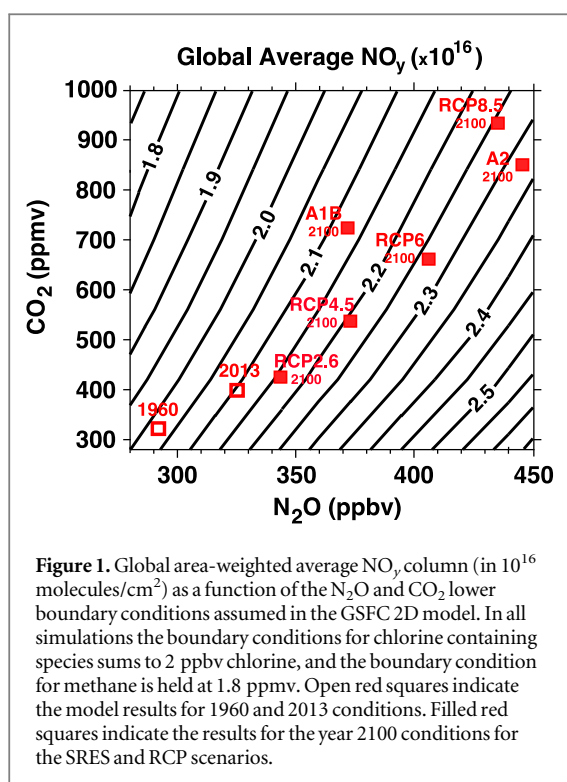
Anthropogenic ozone-depleting chlorocarbons and bromocarbons are declining due to cessation of their production as a result of the Montreal Protocol and its amendments (Andersen and Sarma 2002). By the year 2100 the role of chlorine and bromine in determining the amount of ozone in the stratosphere will be small, and factors including other trace gases will control the ozone concentration.

One factor that will impact future ozone is the concentration of nitrous oxide (N<sub>2</sub>O). Reaction of N<sub>2</sub>O with excited atomic oxygen (O<sup>1</sup>D) is the primary natural source of nitrogen oxides (NO<sub>x</sub> = NO + NO<sub>2</sub>) to the stratosphere (McElroy and McConnell 1971). As NO<sub>x</sub> make the largest contribution to stratospheric ozone loss, even for elevated chlorine levels (e.g., figure 9.2 of Holloway and Wayne 2010), an increase in N<sub>2</sub>O could decrease stratospheric ozone. In fact, Ravishankara *et al* (2009) have shown that N<sub>2</sub>O is the dominant ozone depleting substance (ODS) currently emitted, and is expected to remain so through the remainder of the 21st century. Kanter *et al* (2013) have suggested that the ozone impact of N<sub>2</sub>O could be used

as a basis for international regulations to control its future emissions to the atmosphere.

Another important factor that will impact future ozone levels is the concentration of carbon dioxide (CO<sub>2</sub>). CO<sub>2</sub> cools the stratosphere, slowing temperature-dependent ozone loss processes, resulting in rising ozone levels (Brasseur and Hitchman 1988). Model calculations indicate that past and future increases in CO<sub>2</sub> should speed-up the Brewer–Dobson circulation (e.g., Butchart *et al* 2006), which would decrease ozone in the tropics and increase ozone in middle and high latitudes (e.g., Austin and Wilson 2006, Shepherd 2008, Li *et al* 2009). The combination of cooling and the speed-up of the Brewer–Dobson circulation can lead to a ‘super-recovery’ of ozone at middle and high latitudes to amounts greater than observed in the pre-CFC era (pre-1960).

Cooling also affects ozone loss through its impact on the amount of nitrogen oxides. The NO<sub>x</sub> loss reaction (N + NO → N<sub>2</sub> + O) competes with the reaction of N atoms with O<sub>2</sub> to form NO. The N + O<sub>2</sub> reaction is strongly temperature dependent (Sander *et al* 2010). Cooler temperatures favor the loss reaction, thus reducing the effectiveness of N<sub>2</sub>O in producing NO<sub>x</sub>.



This feedback between temperature and  $\text{NO}_x$  concentrations affects the impact of increased  $\text{N}_2\text{O}$  on stratospheric ozone. For example, Rosenfield and Douglass (1998) explored the relationship between  $\text{NO}_x$  and stratospheric cooling, noting that for fixed  $\text{N}_2\text{O}$  boundary conditions the upper stratospheric  $\text{NO}_x$  decreased by 15% for doubled  $\text{CO}_2$ .

In recent years, several studies have examined the interactions of changing  $\text{CO}_2$  and  $\text{N}_2\text{O}$  on ozone using two-dimensional (Fleming *et al* 2011, Portmann *et al* 2012) or three-dimensional (Oman *et al* 2010, Plummer *et al* 2010, Revell *et al* 2012a, 2012b, Wang *et al* 2014) models. These model studies have shown that  $\text{CO}_2$ -induced stratospheric cooling and strengthening of the meridional circulation reduces the yield of  $\text{NO}_x$  from  $\text{N}_2\text{O}$ , and mitigate the effectiveness of  $\text{N}_2\text{O}$  in depleting ozone. Further, for the GHG scenarios considered, changes in  $\text{NO}_x$  have only a small effect on the future evolution of ozone (e.g., Oman *et al* 2010, Plummer *et al* 2010).

The above studies have focused primarily on ozone changes for a single scenario for future GHG concentrations or have examined only a limited range of  $\text{N}_2\text{O}$  and  $\text{CO}_2$  boundary conditions. Here we examine the coupled impacts of changes in  $\text{N}_2\text{O}$  and  $\text{CO}_2$  on stratospheric  $\text{NO}_x$  and ozone for a wide range of future boundary conditions, encompassing the range of values in the year 2100 from the Intergovernmental Panel on Climate Change (IPCC) scenarios. For all of the current scenarios for growth of  $\text{N}_2\text{O}$  and  $\text{CO}_2$ , the model indicates larger global average column ozone in 2100 than in 1960.

## 2. Model and simulations

We examine the output from steady-state simulations of stratospheric composition obtained using the two-dimensional Goddard Space Flight Center coupled chemistry–radiation–dynamics model (GSFC2D). Fleming *et al* (2011) describe in detail this model and its performance compared with the three-dimensional Goddard Earth Observing System Chemistry Climate Model (GEOSCCM) (Pawson *et al* 2008). Briefly, we used the model with a 2 km vertical resolution and  $10^\circ$  latitude resolution. Many of the components of the GSFC2D model are the same as those in GEOSCCM. These include: the infrared (IR) radiative transfer scheme (Chou *et al* 2001); the photolytic calculations (Anderson and Lloyd 1990, Jackman *et al* 1996); and the microphysical model for polar stratospheric cloud formation (Consideine *et al* 1994).

The dynamics in GSFC2D are coupled to chemistry through the IR heating and UV absorption. Mixing and momentum deposition are computed using a linearized parameterization. The lower boundary condition for the dynamics is solved for planetary zonal wave numbers 1–4 (see Fleming *et al* 2011 for details). The model includes mixing under the assumption that horizontal eddy mixing is directed along the zonal mean isentropes, and projects the  $K_{yy}$  mixing rates onto isentropic surfaces. The model also includes parameterized gravity wave breaking that is interactive with the mean flow (Appendix A of Fleming *et al* 2011).

Fleming *et al* (2011) show that the time-dependent ozone responses from GSFC2D and GEOSCCM models are similar for the reference simulation of ODSs and greenhouse gases used in the second phase of the SPARC validation activity for chemistry climate models (CCMVal-2) (SPARC CCMVal 2010). Additional simulations with GSFC2D (Fleming *et al* 2011) exploit its computational efficiency while separating the contributions of the ODSs and other time-varying source gases to ozone response. GSFC2D also produced results consistent with the GEOSCCM in ‘world avoided’ simulations with unabated increases in anthropogenic chlorocarbons and bromocarbons (Newman *et al* 2009) demonstrating that the responses of both models to large perturbations are consistent. Here we again exploit the computational efficiency of GSFC2D, this time focusing on the relative and combined effects of  $\text{N}_2\text{O}$  and  $\text{CO}_2$  on both the radiation and chemistry of the stratosphere.

We examine the sensitivity of both the global amount of total reactive nitrogen ( $\text{NO}_x$  plus reservoir gases

$$\text{NO}_y = \text{N} + \text{NO}_x + \text{HNO}_3 + \text{ClONO}_2 + \text{BrONO}_2)$$

and ozone ( $\text{O}_3$ ) by running the GSFC2D model to a steady state for three values of the lower boundary condition for  $\text{N}_2\text{O}$  (280, 360 and 440 ppbv) for each of five values of the lower boundary condition for  $\text{CO}_2$  (280, 420, 560, 700 and 840 ppmv). The units for the boundary conditions are parts per

billion by volume (1 ppbv =  $10^{-9}$  moles/mole) and parts per million by volume (1 ppmv =  $10^{-6}$  moles/mole). For each of these simulations, CFC boundary conditions are set to achieve 2 ppbv of  $\text{Cl}_y$  in the upper stratosphere. This is approximately the amount experienced in 1980 and expected to be reached in 2050. The  $\text{CH}_4$  boundary condition is also set at a fixed value (1.8 ppmv) in all simulations.

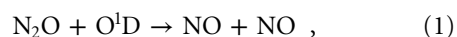
### 3. Reactive nitrogen ( $\text{NO}_y$ )

We first examine how  $\text{NO}_y$  varies with  $\text{N}_2\text{O}$  and  $\text{CO}_2$  boundary conditions. We focus on the globally average total column  $\text{NO}_y$  ('global  $\text{NO}_y$ ' for short), as a simple metric for the  $\text{NO}_y$ . Figure 1 presents the global  $\text{NO}_y$  from the GSFC2D simulations as a function of the  $\text{N}_2\text{O}$  and  $\text{CO}_2$  boundary conditions.

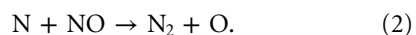
Figure 1 shows that the global-average  $\text{NO}_y$  increases with increasing  $\text{N}_2\text{O}$  and fixed  $\text{CO}_2$ . The increase in global  $\text{NO}_y$  is with a near linear function of lower boundary  $\text{N}_2\text{O}$ , but the relative rate of increase of  $\text{NO}_y$  is less than that of  $\text{N}_2\text{O}$ . For example, there is a 60% increase in  $\text{N}_2\text{O}$  for the range shown in figure 1 (280–450 ppbv) but the increase in  $\text{NO}_y$  is only around 32% (e.g., 2.0–2.65 ppbv when  $\text{CO}_2 = 300$  ppmv). This difference in relative increase is because  $\text{N}_2\text{O}$  is not the only source of atmospheric  $\text{NO}_y$ . Galactic cosmic rays, lightning, and pollution are also sources of  $\text{NO}_y$ . These are included in GSFC2D and contribute about a 1/3 of the global  $\text{NO}_y$  in the model at 320 ppbv  $\text{N}_2\text{O}$ .

For increasing  $\text{CO}_2$  with fixed  $\text{N}_2\text{O}$  boundary conditions global  $\text{NO}_y$  decreases as shown in figure 1. This occurs primarily because increasing  $\text{CO}_2$  cools the stratosphere, altering the rate of chemical reactions of the production and loss of  $\text{NO}_y$ . Increasing  $\text{CO}_2$  also speeds up the mean meridional circulation (so called 'Brewer–Dobson circulation') in the model, but this has less net impact on  $\text{NO}_y$ . The acceleration of the Brewer–Dobson circulation pushes  $\text{N}_2\text{O}$  upward in the tropics, raising the altitude at which  $\text{N}_2\text{O}$  reacts with  $\text{O}(^1\text{D})$  to produce  $\text{NO}_y$  and also pushing more  $\text{NO}_y$  upward into the destruction region (Rosenfield and Douglass 1998).

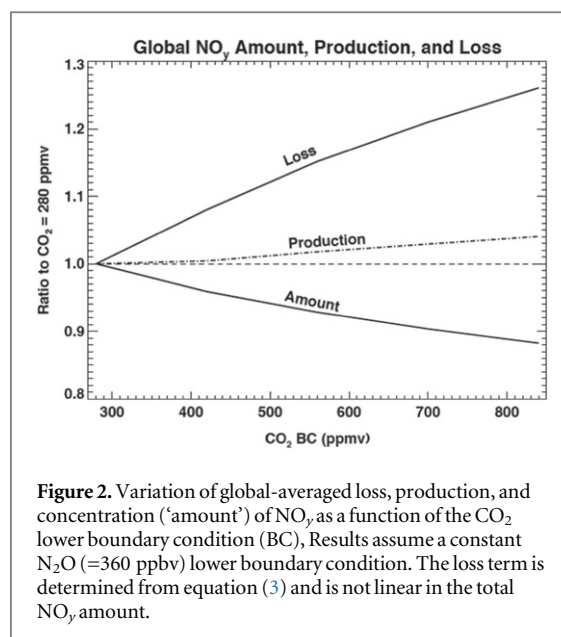
To better understand the impact of increases in  $\text{CO}_2$  on  $\text{NO}_y$ , we examine the production and loss of  $\text{NO}_y$ .  $\text{NO}_y$  is produced mainly from  $\text{N}_2\text{O}$  via the reaction



while the  $\text{NO}_y$  loss rate is controlled by the reaction



The N atoms participating in reaction (2) are generated by the photolysis of NO to form N + O. The N atoms have two possible paths; they can react with NO as in reaction (2) to reform  $\text{N}_2$  or they can react with  $\text{O}_2$  to reform NO with no net loss of  $\text{NO}_y$ . Presuming

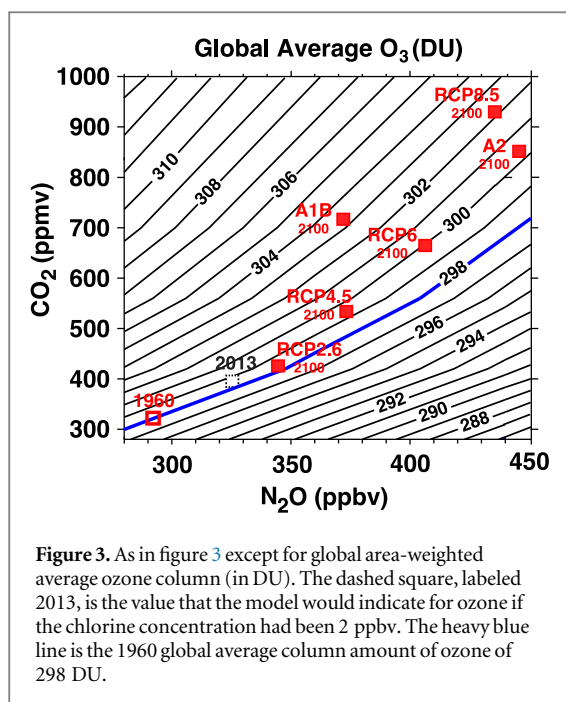


steady state for nitrogen atoms, the following expression is obtained for  $\text{NO}_y$  loss:

$$\begin{aligned} \text{Loss} &= 2k_{\text{N,NO}}[\text{N}][\text{NO}] \\ &\approx \frac{2k_{\text{N,NO}}J_{\text{NO}}[\text{NO}]^2}{k_{\text{N,NO}}[\text{NO}] + k_{\text{N,O}_2}[\text{O}_2]}, \end{aligned} \quad (3)$$

where square brackets indicate concentrations in molecules/cm<sup>3</sup>,  $k_{\text{N,NO}}$  is the rate coefficient for the reaction of N with NO,  $k_{\text{N,O}_2}$  is the rate coefficient for the reaction of N with  $\text{O}_2$ , and  $J_{\text{NO}}$  is the photolysis rate of NO. As the temperature decreases due to the addition of  $\text{CO}_2$  and other GHGs the rate coefficient  $k_{\text{N,O}_2}$  decreases, reducing the denominator in equation (3) and increasing the total loss rate for  $\text{NO}_y$ . Although  $J_{\text{NO}}$  values are shown to vary widely among the CCMs that participated in CCMVal-2, differences in  $J_{\text{NO}}$  would affect the magnitude of the loss of  $\text{NO}_y$  in a given CCM but not the sensitivity of loss to cooling. The relative magnitude of the two terms in the denominator is a function of both the temperature and the amount of NO. At 10 parts per billion by volume (ppbv) of NO and 240 K the N +  $\text{O}_2$  term is about 4 times larger than the N + NO term. Thus the change in rate of the N +  $\text{O}_2$  reaction caused by cooling almost linearly translates into a change in the loss rate for  $\text{NO}_y$ . Another way of thinking of this result is that a decrease in temperature favors the reaction branch of N + NO, leading to increased  $\text{NO}_y$  loss due to this reaction.

To illustrate this, figure 2 shows the variation of the globally-averaged production, loss, and concentration of  $\text{NO}_y$  for  $\text{CO}_2$  increasing from 300 to 850 ppmv (with  $\text{N}_2\text{O}$  boundary condition fixed at 360 ppmv). As  $\text{CO}_2$  increases there is a moderate change in the  $\text{NO}_y$  production but a large increase in its loss, leading to a reduction in the overall  $\text{NO}_y$  concentration.

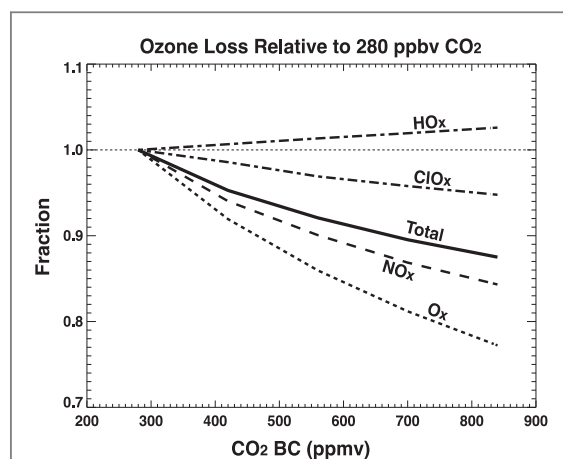


**Figure 3.** As in figure 3 except for global area-weighted average ozone column (in DU). The dashed square, labeled 2013, is the value that the model would indicate for ozone if the chlorine concentration had been 2 ppbv. The heavy blue line is the 1960 global average column amount of ozone of 298 DU.

As increasing  $N_2O$  causes global  $NO_y$  to increase but increasing  $CO_2$  affects global  $NO_y$  in the opposite sense, the change in global  $NO_y$  when both  $N_2O$  and  $CO_2$  increase depends on their relative increases. As shown in figure 1, for larger increases in  $CO_2$  relative to  $N_2O$  there is a decrease in global-average  $NO_y$ , whereas there is an increase in global-average  $NO_y$  if the relative increase in  $N_2O$  is larger.

We now consider the changes in  $NO_y$  for changes in  $N_2O$  and  $CO_2$  corresponding to the different Special Report on Emissions Scenarios (SRES) (IPCC 2000) or Representative Concentration Pathways (RCPs) (Moss *et al* 2010, Meinshausen *et al* 2011). The red squares in figure 3 show the increases in  $CO_2$  and  $N_2O$  following different future scenarios. The open red square in figure 1 is placed at the observed  $N_2O$  and  $CO_2$  values in 1960, while the filled red squares are placed at the  $N_2O$  and  $CO_2$  values projected for the year 2100 for the SRES A1B and A2 scenarios, and the RCP2.6, RCP4.5, RCP6.0, and RCP8.5 Pathways.

GSFC2D simulates an increase of around  $0.1 \times 10^{16}$  molecules/cm<sup>2</sup> in global  $NO_y$  between 1960 and 2100 for the A1B scenario (figure 1), which has been considered in many previous modeling studies. This corresponds to around a 5% increase in global  $NO_y$ , which is much less than the 25% increase in the  $N_2O$  boundary condition. This small increase in global  $NO_y$  for the A1B scenario is consistent with simulations by the three-dimensional CCMs that participated in CCMVal-2. The average change in globally integrated  $NO_y$  between 1960 and 2100 for the A1B scenario is  $-2\% \pm 5\%$  for the 14 CCMs in CCMVal-2. The change in global-average  $NO_y$  is the net effect of the positive and negative regions integrated over the globe (e.g., Oman *et al* 2010), and models with a slightly different balance of  $NO_y$  production and loss



**Figure 4.** Fraction of globally-averaged ozone loss due to each catalytic loss cycle as a function of the  $CO_2$  boundary condition (BC) in the model simulation. The loss fraction for each cycle has been normalized to its value at 280 ppbv of  $CO_2$ . The total is indicated by the heavy black line, showing a decrease to about 88% of its 280 ppbv value when the  $CO_2$  boundary condition reaches 840 ppbv. The fractions for the  $O_x$  and  $NO_x$  cycles decrease more rapidly than the total because these are the most temperature-sensitive cycles. The fractions for the  $ClO_x$  and  $HO_x$  cycle decrease less (small increase for  $HO_x$ ) because these are the least temperature-sensitive cycles.

will get a slightly different answer. The change is small for all models.

For the other IPCC scenarios there are somewhat larger increases in  $NO_y$ , but in all cases the percentage increases in global  $NO_y$  are much smaller than would be obtained for constant  $CO_2$ . The impact of climate (temperature and circulation) change is seen clearly for scenarios with similar  $N_2O$  and larger increases in  $CO_2$ , i.e., compare RCP4.5 and A1B, A2 with RCP8.5.

#### 4. Ozone ( $O_3$ )

We now consider the change in global column amount of ozone from the suite of GSFC2D simulations. Figure 3 shows the global average  $O_3$  as a function of  $N_2O$  and  $CO_2$ . As for global-average  $NO_y$ , the sign of the change in ozone differs between increasing  $N_2O$  and increasing  $CO_2$ . Global column amount of ozone decreases with increasing  $N_2O$  and fixed  $CO_2$ , but increases with increasing  $CO_2$  and fixed  $N_2O$ . When the increase in  $CO_2$  is large and the  $N_2O$  increase is small there is an increase in total ozone, whereas if there is a large  $N_2O$  increase and small  $CO_2$  change then there can be a decrease in ozone.

It is important to note that changes in  $O_3$  shown in figure 3 are due not only to changes in  $NO_x$  chemistry but also to changes in other ozone loss cycles. In particular, as the stratosphere cools (due to increased  $CO_2$ ) there is a decrease in the ozone loss via each of the loss cycles. In particular, the  $O_x$  and  $NO_x$  cycles are strongly temperature dependent while the  $ClO_x$  and  $HO_x$  cycles are significantly less temperature dependent (see e.g. Stolarski *et al* (2012)). Figure 4 illustrates

the dependence of the contributions of the catalytic cycles as a function of the CO<sub>2</sub> concentration. The importance of the NO<sub>x</sub> cycle thus decreases relative to the other cycles as the temperature cools due to CO<sub>2</sub> increases.

As in figure 1, the open red symbol in figure 3 shows the observed values of N<sub>2</sub>O and CO<sub>2</sub> in 1960, while the values of N<sub>2</sub>O and CO<sub>2</sub> from various scenarios for the year 2100 are indicated by the filled red squares. The simulation using the 1960 concentrations of N<sub>2</sub>O and CO<sub>2</sub> (291 and 316 respectively) yielded a global average ozone column of 298 DU as indicated by the open red box and the heavy blue line. For all of the scenarios the global-average ozone in 2100 is greater than that in 1960. The largest increase (5 DU) occurs for A1B, whereas there is only a very small increase for RCP2.6. This 'super-recovery' of column ozone occurs primarily in the mid and high latitudes with little change in the tropics (e.g., Li *et al* 2009).

Caution is required interpreting the results shown in figure 3 as they are from a single model and are for steady state calculations. However, these results are consistent with the 1960 to 2100 transient simulations from GSFC2D and other models. First, the 5.1 DU increase in global ozone from 1960 to 2100 in the GSFC2D model transient A1B simulation (Fleming *et al* 2011) is consistent with the steady-state calculation shown in figure 3. The global ozone difference from 3D CCMs is also of similar magnitude; the multi-model mean increase in ozone for the A1B scenario is  $4 \pm 2$  DU for the 17 CCMs in CCMVal-2 (Eyring *et al* 2010a, 2010b). Furthermore, sensitivity studies from a small subset of CCMs show a similar dependence of global ozone on N<sub>2</sub>O and CO<sub>2</sub>. For example, the changes in ozone for simulations of the different RCPs vary from slight decrease in global ozone for RCP2.6 to a ~6 DU increase for RCP8.5 (Eyring *et al* 2007), compared to slight increase to ~4 DU increase in figure 3. Revell *et al* (2012b) performed a series of transient simulations with N<sub>2</sub>O following the different RCP scenarios but CO<sub>2</sub> and CH<sub>4</sub> following the A1B scenario, and show 2100 global ozone for RCP2.6 (N<sub>2</sub>O = 344 ppbv) to be 6.7 DU larger than in RCP8.5 (N<sub>2</sub>O = 435 ppbv). Again, this difference is similar to that in figure 3 (for N<sub>2</sub>O increasing from 340 to 445 ppbv with CO<sub>2</sub> ~ 700 ppmv). Note that the results for RCP2.6 and RCP8.5 shown in figures 2 and 3 are not directly comparable to the results obtained by other models because our boundary condition for CH<sub>4</sub> is constant (1.8 ppmv). Our results are designed to show the model response for the N<sub>2</sub>O/CO<sub>2</sub> relationship without the complicating factor of changes in CH<sub>4</sub>. We have run simulations for varying levels of CH<sub>4</sub> and find that global ozone increases by 3–4 DU per ppm of CH<sub>4</sub>. The exact amount depends on the amounts of CO<sub>2</sub> and N<sub>2</sub>O. For RCP8.5, the CH<sub>4</sub> mixing ratio reaches about 3.5 ppmv by 2100. This results in an extra 6–7 DU of total ozone above the amount shown in figure 3. For RCP2.6, the CH<sub>4</sub>

mixing ratio in 2100 is reduced to about 1.2 ppmv resulting in a decrease of 2–3 DU in the deduced total ozone from our model simulations.

## 5. Conclusions

We performed a series of steady-state simulations with the GSFC2D model to examine the potential future control of the ozone layer, focusing on the year 2100 when the concentrations of chlorine and bromine species will have declined due to the continued implementation of the Montreal Protocol. These simulations show that global-average NO<sub>y</sub> and O<sub>3</sub> respond oppositely to increasing N<sub>2</sub>O and increasing CO<sub>2</sub>. Global NO<sub>y</sub> increases and ozone decreases with increasing N<sub>2</sub>O and fixed CO<sub>2</sub>, whereas NO<sub>y</sub> decreases and ozone increases with increasing CO<sub>2</sub> and fixed N<sub>2</sub>O. Thus, the responses of NO<sub>y</sub> and ozone to increases in N<sub>2</sub>O are coupled to increases in CO<sub>2</sub> and climate change.

These simulations indicate that for all of the GHG scenarios considered in recent IPCC assessments there will only be a small change in global NO<sub>y</sub> and O<sub>3</sub> for conditions in the year 2100 compared to the year 1960. The GSFC2D models shows small increases in global NO<sub>y</sub> for all IPCC scenarios, with the percentage change significantly smaller than the increase in the N<sub>2</sub>O mixing ratio imposed at the lower boundary of the model. This occurs because the total amount of NO<sub>x</sub> available for catalytic ozone loss depends on the amounts of both N<sub>2</sub>O and CO<sub>2</sub> assumed at the lower boundary of the model.

For all scenarios, we also simulate a small increase (~0–5 DU) in global O<sub>3</sub> in 2100 compared to that in 1960 for constant CH<sub>4</sub>. This increase occurs mainly because of the projected increases in CO<sub>2</sub> and despite projected increases in N<sub>2</sub>O. Taking CH<sub>4</sub> variation into account, we obtain a slight decrease (~2 DU) in global O<sub>3</sub> in 2100 for the RCP2.6 scenario because of the projected decrease in CH<sub>4</sub> in this scenario.

Although N<sub>2</sub>O will likely be the most important anthropogenic ODS by the end of the 21st century (Ravishankara *et al* 2009) and decreases in global ozone are to be expected for an N<sub>2</sub>O increase at constant CO<sub>2</sub>, the simulations presented here suggest that increases in N<sub>2</sub>O will only lead to large reductions in global O<sub>3</sub> in the unlikely situation where CO<sub>2</sub> concentrations are held constant while N<sub>2</sub>O concentrations continue to grow rapidly.

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