

The effectiveness of N₂O in depleting stratospheric ozone

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Received 23 April 2012; revised 25 June 2012; accepted 4 July 2012; published 9 August 2012.

[1] Recently, it was shown that of the ozone-depleting substances currently emitted, N₂O emissions (the primary source of stratospheric NO_x) dominate, and are likely to do so throughout the 21st century. To investigate the links between N₂O and NO_x concentrations, and the effects of NO_x on ozone in a changing climate, the evolution of stratospheric ozone from 1960 to 2100 was simulated using the NIWA-SOCOL chemistry-climate model. The yield of NO_x from N₂O is reduced due to stratospheric cooling and a strengthening of the Brewer-Dobson circulation. After accounting for the reduced NO_x yield, additional weakening of the primary NO_x cycle is attributed to reduced availability of atomic oxygen, due to a) stratospheric cooling decreasing the atomic oxygen/ozone ratio, and b) enhanced rates of chlorine-catalyzed ozone loss cycles around 2000 and enhanced rates of HO_x-induced ozone depletion. Our results suggest that the effects of N₂O on ozone depend on both the radiative and chemical environment of the upper stratosphere, specifically CO₂-induced cooling of the stratosphere and elevated CH₄ emissions which enhance HO_x-induced ozone loss and remove the availability of atomic oxygen to participate in NO_x ozone loss cycles. **Citation:** Revell, L. E., G. E. Bodeker, D. Smale, R. Lehmann, P. E. Huck, B. E. Williamson, E. Rozanov, and H. Struthers (2012), The effectiveness of N₂O in depleting stratospheric ozone, *Geophys. Res. Lett.*, 39, L15806, doi:10.1029/2012GL052143.

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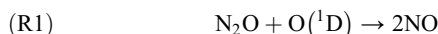
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0094-8276/12/2012GL052143

1. Introduction

[2] In the stratosphere, reaction of N₂O with O(¹D) leads to the production of NO:



NO subsequently undergoes various reactions to form stratospheric reservoir nitrogen (NO_y = N + NO + NO₂ + NO₃ + 2 × N₂O₅ + HNO₃ + HNO₄ + ClONO₂ + BrONO₂), and is one of the reactive nitrogen oxides (NO_x = NO + NO₂), participating in ozone-depleting catalytic cycles [Crutzen, 1970]. N₂O is the primary source of NO_x [McElroy and McConnell, 1971], and therefore an important ozone-depleting substance (ODS); indeed, of all the ODSs currently emitted, N₂O is projected to be the dominant contributor to ozone depletion through the 21st century [Ravishankara et al., 2009].

[3] The effect of NO_x on stratospheric ozone is moderated by dynamical, chemical and radiative processes. The principal dynamical process affecting NO_x is the Brewer-Dobson circulation (BDC), by which air is transported poleward and downward after entering the stratosphere in the tropics [Holton et al., 1995]. Throughout the 21st century, the BDC is projected to strengthen due to increasing sea-surface temperatures [Fomichev et al., 2007]. A strengthening BDC increases the rate at which air is transported through the stratosphere, and therefore decreases the time available for the production of NO by R1 [Cook and Roscoe, 2009; Plummer et al., 2010].

[4] Chemical factors influencing the effect of NO_x on ozone include the concentration of reservoir chlorine (Cl_y = Cl + 2 × Cl₂ + ClO + 2 × Cl₂O₂ + ClONO₂ + HCl + HOCl + BrCl). Since the reaction of NO₂ with ClO forms ClONO₂, when the concentration of reservoir chlorine is high, more ClONO₂ is formed and NO_x concentrations decrease [Ravishankara et al., 2009; Fleming et al., 2011].

[5] The radiative environment of the stratosphere is projected to change through the 21st century as increasing CO₂ concentrations cool the stratosphere. The concentration of NO_y decreases as the stratosphere cools because the NO_y sink is temperature-dependent [Rosenfield and Douglass, 1998]; this decreases the NO_y/N₂O and NO_x/N₂O ratios. Therefore, decreasing stratospheric temperatures are projected to slow ozone depletion by NO_x [Randeniya et al., 2002; Chipperfield and Feng, 2003].

[6] Chemistry-climate model (CCM) studies using the same boundary conditions as in this study observed the effect of CO₂-induced stratospheric cooling on N₂O [Oman et al., 2010; Plummer et al., 2010], and found that while N₂O remains an important gas for ozone depletion through the 21st century its effects are mitigated by stratospheric cooling. In a recent study, Fleming et al. [2011] removed the

effect of CO₂-induced stratospheric cooling by keeping all greenhouse gas concentrations (other than N₂O) constant. Without stratospheric cooling, the increase in N₂O concentrations lead to a decrease in global annual-mean total column ozone of ~6 DU between 1960 and 2100.

[7] Here, we use a CCM REF-B2 simulation of an evolving atmosphere to examine specifically the rate of the dominant ozone-depleting NO_x cycle, and how the rate of ozone loss by this cycle changes as the chemical, dynamical and radiative properties of the stratosphere change. This is an extension of the question posed by *Ravishankara et al.* [2009], and our results are complementary to their findings.

2. Computational Methods

[8] The NIWA-SOCOL (National Institute of Water and Atmospheric Research – Solar Climate Ozone Links) CCM is a modified version of the SOCOL model [*Schraner et al.*, 2008], in which ozone loss by catalytic cycles can be tracked (see below). NIWA-SOCOL was evaluated in the WMO SPARC CCMVal-2 activity [*Eyring et al.*, 2010], and compares favorably with other state-of-the-art CCMs. SOCOL comprises the MAECHAM4 global climate model [*Manzini et al.*, 1997] coupled with a modified version of the MEZON chemistry transport model [*Egorova et al.*, 2003]. MAECHAM4 is configured with a T30 spectral horizontal resolution and 39 vertical levels between Earth's surface and 0.01 hPa (~80 km). A hybrid transport scheme [*Zubov et al.*, 1999] is employed to advect the chemical constituents whilst the chemical solver algorithm uses a Newton-Raphson iterative method taking into account 41 chemical species, 140 gas-phase reactions, 46 photolysis reactions and 16 heterogeneous reactions. A 15-minute time step is used for dynamical processes while radiative and chemical calculations are performed every two hours. Boundary conditions, model parameters and model specifications are described by *Morgenstern et al.* [2010], however for this simulation the prescribed sea-surface temperatures were taken from ECHAM5/MPIOM output, thus removing the discontinuity in sea-surface temperature described by *Morgenstern et al.* [2010].

[9] The emissions scenario consists of the adjusted A1 scenario for halocarbons, which accounts for the accelerated phase-out of HCFCs [*Daniel et al.*, 2007], and the IPCC SRES A1B scenario for greenhouse gases [*Nakicenovic and Swart*, 2000]. Compared with other SRES scenarios, A1B portrays an intermediate increase in anthropogenic radiative forcing; CO₂ and N₂O emissions both increase throughout the 21st century and CH₄ emissions rise until the middle of the 21st century and then decrease.

[10] The method for attributing ozone removal to different catalytic cycles is similar to the diagnostic approach employed by *Lee et al.* [2002]. The 15 chemical cycles chosen here are appropriate for the chemical reaction set used in NIWA-SOCOL and form a general diagnostic set that can be used for a range of studies. Following the method of *Lee et al.* [2002], odd oxygen (O + O(¹D) + O₃) removal rates (molecules cm⁻³ s⁻¹) are calculated within the model using the rate-limiting steps of the corresponding reaction cycles. The total ozone change is logged in each grid cell at each time step, and decomposed into contributions from net chemical production and transport. Results for the 15 catalytic cycles

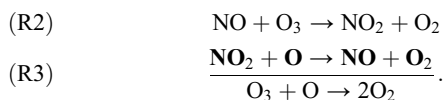
(detailed in the auxiliary material) are recorded and accumulated into monthly means within each model grid cell.¹

[11] Chemical box model calculations were performed using the AWI (Alfred Wegener Institute) model, which simulates 175 reactions among 48 chemical species in the stratosphere [*Lehmann*, 2004]. The model is based on modules for gas-phase chemistry [*Brasseur et al.* 1997], photolysis (TUV by *Madronich and Flocke* [1999]) and heterogeneous chemistry [*Carslaw et al.*, 1995]. Reaction rate constants were updated to the values given by *Sander et al.* [2006, 2009] and differential equations were generated and solved numerically by the kinetic pre-processor KPP [*Damian et al.*, 2002].

3. Results and Discussion

[12] Global annual-mean column ozone is projected to increase through the 21st century, due to stratospheric cooling [*Rosenfield et al.*, 2002] and the phase-out of halogenated ozone-depleting substances under the Montreal Protocol. NIWA-SOCOL simulates an increase in global annual-mean column ozone of 5.5 DU between 1960 and 2100, compared with the multi-model mean increase of 4 DU simulated by the CCMVal-2 models [*Bekki et al.*, 2011]. The ozone increase simulated by NIWA-SOCOL is larger than the multi-model mean owing to a larger-than-average reduction in Cl_y [*Eyring et al.*, 2010].

[13] Despite increasing global-mean column ozone, N₂O continues to play an important role in ozone depletion through the 21st century. Under the SRES A1B emissions scenario, N₂O emissions lead to a 27% increase in surface N₂O concentrations from 1960 to 2100. In a non-changing climate, we would expect a similar increase in NO_x, and also in the NO_x ozone loss cycles. Of these cycles, NIWA-SOCOL outputs show that R2 and R3 (see below), collectively termed 'cycle I,' account for >99% of NO_x-induced ozone depletion (rate-determining step in bold):



[14] Figure 1a shows the zonal-mean rate of cycle I averaged over the 2090s decade, relative to the 1960s decade. The strength of cycle I increases in the tropical upper stratosphere, although not as much as expected given the 27% increase in surface N₂O concentrations. Elsewhere, the rate of cycle I slows between 1960 and 2100.

[15] What causes the rate of cycle I to slow? Because NIWA-SOCOL simulates an evolving atmosphere, changes in stratospheric circulation, chemistry and temperature change the ratios NO_y/N₂O, NO_x/NO_y and NO₂/NO, all of which affect the concentration of NO₂ (required in R3, the rate-determining step of cycle I), and therefore the rate at which cycle I can proceed. These three ratios are plotted in Figures 1b–1d as global annual means, normalized to the 1960–1969 mean.

¹Auxiliary materials are available in the HTML. doi:10.1029/2012GL052143.

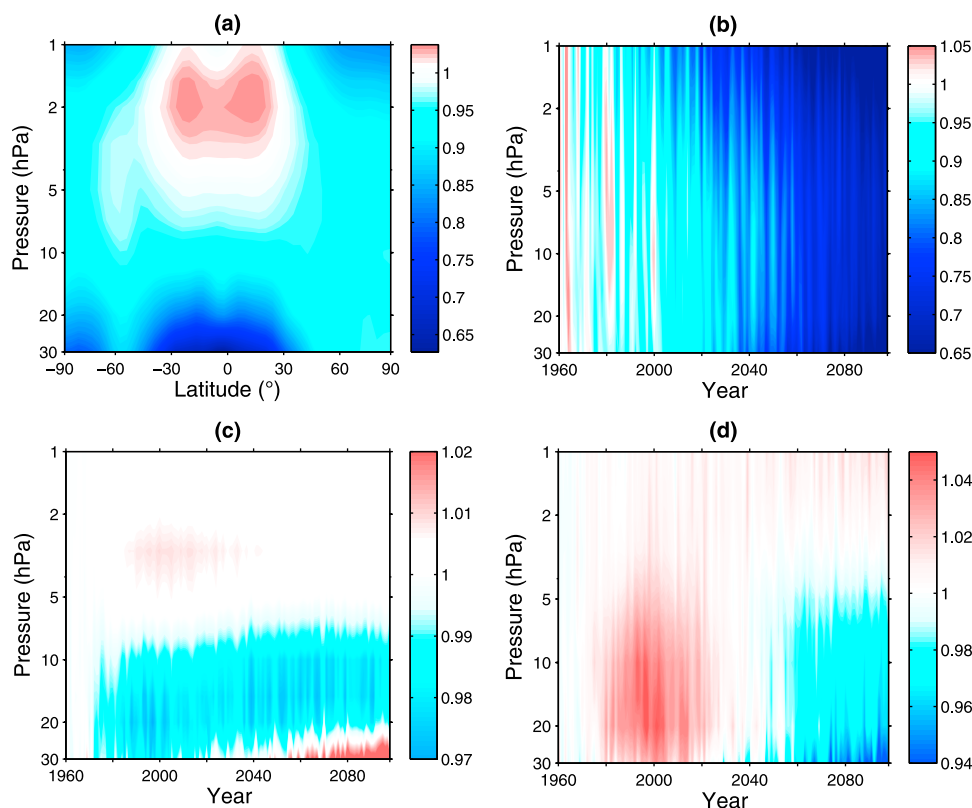


Figure 1. (a) 2090s zonal-mean rate of cycle I (molecules cm⁻³ s⁻¹) normalized to the 1960s mean, displayed as a function of pressure and latitude. (b) Global annual-mean ratio of NO_y/N₂O normalized to the 1960–1969 mean, displayed as a function of pressure and time. (c) Same as Figure 1b but for NO_x/NO_y. (d) Same as Figure 1b but for NO₂/NO.

[16] The NO_y/N₂O ratio decreases from 1960 to 2100 (Figure 1b), indicating that the strengthening BDC shortens the residence time of N₂O, leaving less time for it to undergo reaction to produce NO [Cook and Roscoe, 2009]. In addition, stratospheric cooling decreases NO_y [Rosenfield and Douglass, 1998], which contributes to the decrease in NO_y/N₂O. The NO_x/NO_y ratio decreases below ~7 hPa between 1960 and 2100 (Figure 1c) because stratospheric cooling and increasing concentrations of reactive hydrogen (HO_x = H + OH + HO₂) lead to an increase in the rate of R4:



Within the NO_x family, NO₂ and NO are in equilibrium throughout the stratosphere during daytime, and interconvert primarily by cycle I, NO₂ photolysis and R5 [Brasseur and Solomon, 2005]:



[17] Figure 1d shows that the NO₂/NO ratio increases from 1960 to ~2000, and then decreases through the 21st century. Chemical box model calculations show that the simulated increase in NO₂/NO between 1960 and 2000 is due to increased chlorine loading (as a result of halocarbon emissions) which increases the rate of R5. Conversely, between 2000 and 2100, the decreasing concentration of ClO slows R5, decreasing the NO₂/NO ratio. Additional decreases in the NO₂/NO ratio through the 21st century are

caused by CO₂-induced stratospheric cooling, which slows the temperature-dependent reaction R2.

[18] Through the 21st century, the NO_y/N₂O, NO_x/NO_y and NO₂/NO ratios decrease overall, which leads to smaller NO₂ concentrations than might be expected, given the increase in surface N₂O concentrations. Because NO₂ is required in the rate-determining step of cycle I (R3), smaller-than-expected NO₂ concentrations must be at least partially responsible for the slowing rate of cycle I observed through most of the stratosphere. To test whether they are entirely responsible, we divide the rate of cycle I by the NO₂ concentration.

[19] The rate of R3 is $k_3[\text{NO}_2][\text{O}]$, where k_3 is the (temperature-dependent) rate constant and [] denote concentrations. Dividing this rate by [NO₂] therefore allows examination of effects due to k_3 and [O]. This quantity (normalized to the 1960–1969 mean) is plotted in Figure 2a, which shows that R3/[NO₂] decreases throughout the stratosphere over the 21st century indicating that at least one of k_3 and [O] has decreased significantly over that period. However, k_3 has a negative activation energy [Sander et al., 2006] and will increase with stratospheric cooling. Consequently, the results displayed in Figure 2a cannot be explained by the behavior of k_3 and the reduction of R3/[NO₂] must be due to diminished [O].

[20] Stratospheric odd oxygen loss occurs via catalytic cycles commonly involving nitrogen, hydrogen, chlorine or bromine-containing species. Figure 2b shows the percentage contribution to global-mean ozone loss averaged over the period 1960–2100 from the 15 ozone loss cycles tracked in

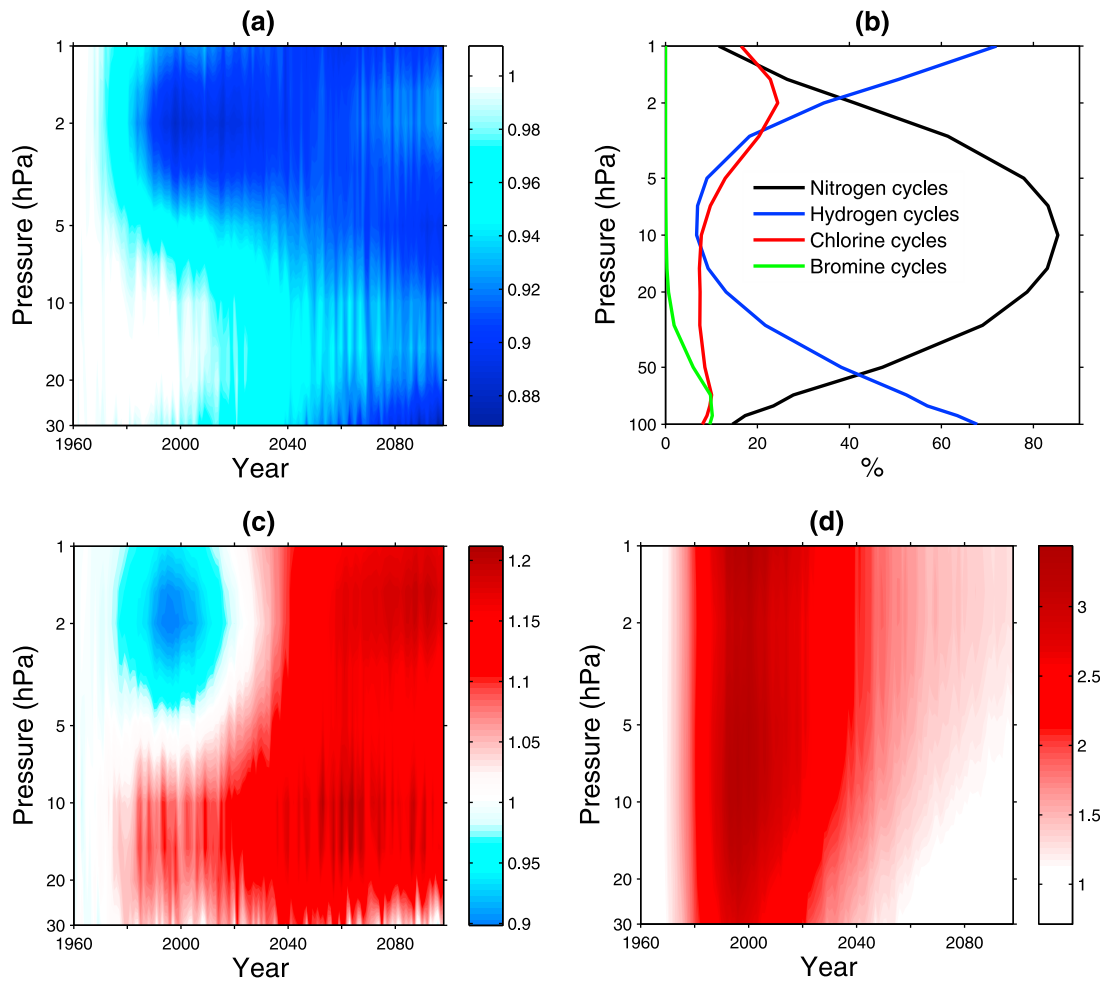
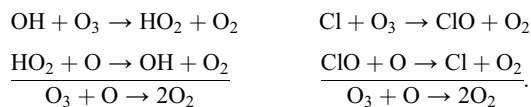


Figure 2. (a) The global annual-mean rate of cycle I (molecules cm⁻³ s⁻¹) divided by the global annual-mean abundance of NO₂ (molecules cm⁻³) and normalized to the 1960–1969 mean. (b) Percentage contributions to global-mean ozone loss from the 15 catalytic ozone loss cycles tracked by NIWA-SOCOL, averaged over 1960–2100. Cycles are shown in the auxiliary material and grouped as follows: Nitrogen cycles (I–III); hydrogen cycles (IV–VIII); chlorine cycles (IX–XIII); bromine cycles (XIV–XV). (c) The global annual-mean rate of the hydrogen cycles, normalized to the 1960–1969 mean. (d) Same as Figure 2c but for the chlorine cycles.

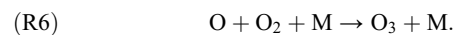
NIWA-SOCOL, grouped into nitrogen, hydrogen, chlorine and bromine families. The nitrogen cycles are dominant in the middle and upper stratosphere, and their combined rate maximizes at 10 hPa. Chlorine and hydrogen cycles are also important in the upper stratosphere while bromine cycle contributions maximize in the lower stratosphere. Of the five hydrogen cycles and five chlorine cycles tracked in NIWA-SOCOL, the dominant contributors to ozone loss from each family are:



[21] Increasing CH₄ emissions to mid-21st century lead to increased concentrations of HO_x [Wuebbles and Hayhoe, 2002] which enhances ozone loss due to the hydrogen cycles (Figure 2c). The projected decrease in stratospheric chlorine concentrations owing to the phase-out of halocarbons under the Montreal Protocol results in a slowing of

ozone loss due to the chlorine cycles (Figure 2d). Although these cycles are described as “ozone loss” cycles, they also lead to overall depletion of other odd oxygen species since the concentrations of O₃, O and O(¹D) are closely linked. Some cycles (such as the HO₂ + O and ClO + O cycles shown above) deplete O directly.

[22] Within the odd oxygen family, the O/O₃ ratio is projected to decrease over the 21st century because CO₂-induced stratospheric cooling increases the rate of [Jonsson *et al.*, 2004]:



[23] We hypothesize that, in addition to the effect of stratospheric cooling on O/O₃, the concentration of O decreases as a result of the hydrogen and chlorine cycles in the upper stratosphere, and that this decrease is partially responsible for the slowing rate of cycle I. To test the effects of HO_y (HO_y = 2 × H₂O + 2 × H₂ + 4 × CH₄ + 2 × CH₂O) and Cl_y (defined in Section 1) on upper stratospheric odd

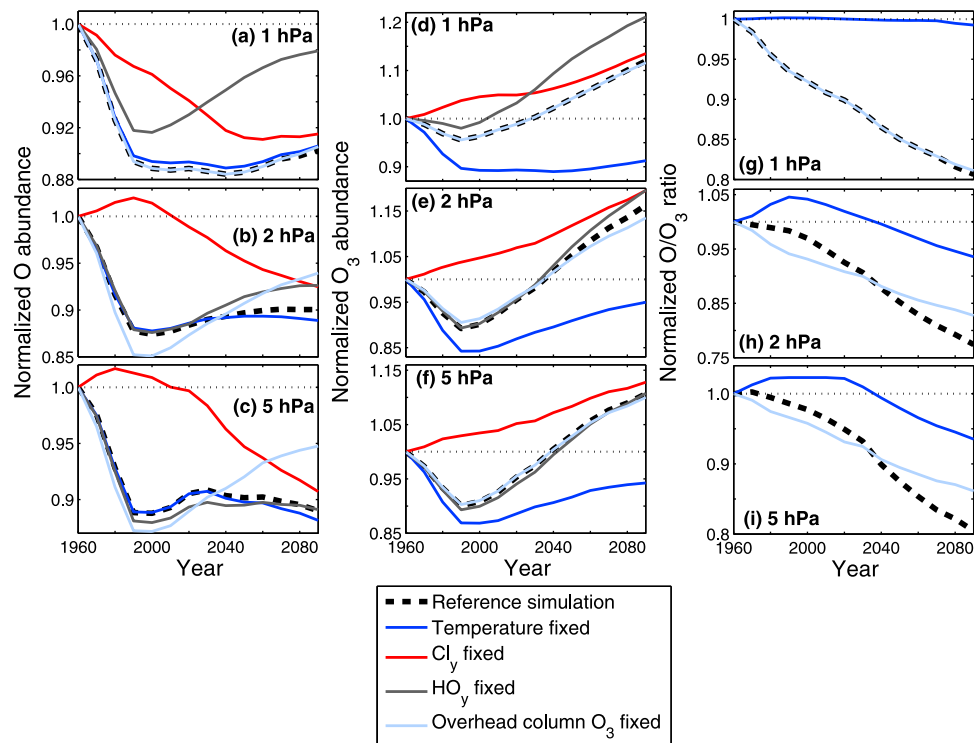


Figure 3. Box model simulations at 2°N showing normalized (to 1960) (a–c) local atomic oxygen abundances, (d–f) ozone abundances, and (g–i) the O/O₃ ratio at 1, 2 and 5 hPa. The reference simulation allowed all parameters to evolve, whilst the other four simulations kept one of temperature, Cl_y, HO_y and overhead column ozone fixed (all other parameters were allowed to evolve). The Cl_y and HO_y curves were omitted in Figures 3g–3i because they displayed no effect on O/O₃.

oxygen, we performed box model simulations for the upper stratosphere (between 1–5 hPa), where the odd oxygen lifetime is sufficiently short to warrant such an analysis.

[24] Five time-series box model simulations were performed at 2°N and at 1, 2 and 5 hPa. The first series constituted the ‘reference’ simulations, in which all parameters (temperature, overhead column ozone and chemical species concentrations) were allowed to vary from decade to decade. In the other four series one out of temperature, HO_y, Cl_y or overhead column ozone was fixed, and all others varied from decade to decade. Initial concentrations, overhead column ozone, and temperature for these runs were taken from outputs of the NIWA-SOCOL simulation. The box model simulations were run for 10 days each decade, and Figure 3 shows the simulated O, O₃ and O/O₃ ratio on the 10th day for the three pressure levels.

[25] Figures 3a–3f show that ozone and atomic oxygen abundances are strongly influenced by HO_y and Cl_y in the upper stratosphere, where the HO₂ + O and ClO + O cycles maximize. At 1 hPa, the increase of HO_y leads to ~8% less O by 2090 (Figure 3a, grey line minus dashed black line) meaning less O is available to participate in cycle I. Because CH₄ is a source of reactive hydrogen, the effectiveness of N₂O as an ODS is weakened by elevated CH₄ concentrations; however, this effect is slight given that the ozone abundance is small at 1 hPa. The effect of Cl_y on odd oxygen at 2 hPa is largest in 1990, when there is a 14% decrease in O (Figure 3b, red line minus dashed black line). Cl_y becomes less important for ozone depletion through the 21st century as its concentration decreases.

[26] Long-term cooling of the stratosphere decreases the O/O₃ ratio (Figures 3g–3i) and leads to ~20% more ozone by 2090 in the upper stratosphere at 1 and 2 hPa (Figures 3d and 3e, dashed black line minus blue line). Because the O/O₃ ratio decreases with stratospheric cooling, less atomic oxygen is available for cycle I for a constant O₃ mixing ratio. Partitioning between O and O₃ is also influenced by overhead column ozone at 2 and 5 hPa (Figures 3h and 3i), which moderates the local flux of ultraviolet radiation.

4. Conclusions

[27] Ravishankara *et al.* [2009] estimated the effects of increasing emissions of N₂O on ozone assuming constant stratospheric greenhouse gas concentrations. Here we have considered a complementary, but different, question: How, and to what extent, might various mechanisms associated with the stratospheric cooling effects of greenhouse gas increases (which are scenario dependent) mitigate the effects of N₂O on ozone? The results presented here indicate that while N₂O is an important gas for ozone depletion through the 21st century (in accordance with the findings of Ravishankara *et al.* [2009]), a number of factors mitigate its effectiveness in depleting ozone. CO₂-induced stratospheric cooling and the strengthening of the BDC decrease the yield of NO_x from N₂O by decreasing the NO_y/N₂O, NO_x/NO_y and NO₂/NO ratios. In addition, it has been shown that changes in the hydrogen and chlorine chemical cycles, whose rates are modulated by changes in emissions of CH₄ and chlorine-containing compounds, moderate the effectiveness of the NO₂

+ O cycle (the dominant NO_x cycle) by catalytically depleting odd oxygen, thereby reducing the availability of atomic oxygen for the NO₂ + O reaction.

[28] **Acknowledgments.** The Editor thanks two anonymous reviewers for their assistance in evaluating this paper.

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