On the Changing Role of the Stratosphere on the Tropospheric Ozone Budget: 1979–2010

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Abstract We study the evolution of tropospheric ozone over the period 1979–2010 using a chemistry-climate model employing a stratosphere-troposphere chemistry scheme. By running with specified dynamics, the key feedback of composition on meteorology is suppressed, isolating the chemical response. By using historical forcings and emissions, interactions between processes are realistically represented. We use the model to assess how the ozone responds over time and to investigate model responses and trends. We find that the chlorofluorocarbon (CFC)-driven decrease in stratospheric ozone plays a significant role in the tropospheric ozone burden. Over the period 1979–1994, the decline in transport of ozone from the stratosphere, partially offsets an emissions-driven increase in tropospheric ozone production. From 1994–2010, despite a leveling off in emissions, increased stratosphere-troposphere transport of ozone drives a small increase in the tropospheric ozone burden. These results have implications for the impact of future stratospheric ozone recovery on air quality and radiative forcing.

Plain Language Summary We use a modeling approach to study the effect of stratospheric ozone depletion on the composition of the troposphere. We focus on the period 1979–2010 and use a chemistry-climate model employing historical emissions, climate forcing, and meteorology. Our model has a good description of both stratospheric and tropospheric ozone chemistry and allows us to calculate the effect of exchange between stratosphere and troposphere. We show that stratospheric ozone depletion over the period 1979–2010 has a critical effect on tropospheric composition – with less ozone in the lower stratosphere, there is less transport to the troposphere, and this offsets an emissions-driven increase in ozone production in the troposphere. Such combined studies are important to quantify the future effects of stratospheric ozone recovery on the evolution of tropospheric composition.

1. Introduction

The changes in tropospheric ozone since the preindustrial era are estimated to have resulted in an increase in radiative forcing of 0.4 W m\(^{-2}\) (Myhre et al., 2013; Stevenson et al., 2006), making tropospheric ozone the third most important anthropogenic greenhouse gas. Unlike the major greenhouse gases, carbon dioxide (CO\(_2\)) and methane (CH\(_4\)), ozone is not emitted directly, but is the result of the oxidation of volatile organic compounds (VOCs) in the presence of NO\(_x\) (Monks et al., 2015). The tropospheric ozone abundance is controlled by a balance of sources, including photochemical production (P\(_{O_3}\)) and downward transport of ozone-rich air from the stratosphere (S\(_{O_3}\)), and sinks, principally physical losses at the surface (deposition, D\(_{O_3}\)), and chemical loss throughout the free troposphere (L\(_{O_3}\)).

Ozone has important impacts on vegetation and human health. In addition, ozone is important since it indirectly affects the lifetime of other greenhouse gases, particularly methane, through its role in the formation of the hydroxyl radical (OH) (Voulgarakis et al., 2013). OH and ozone also have an impact on aerosol radiative forcing, a major source of uncertainty in the climate system, as secondary aerosols such as sulfate, nitrate, and secondary organic aerosol are mediated by tropospheric oxidants and play a major role in the aerosol budget and burden (Karset et al., 2018). Therefore, ozone is linked throughout the Earth system, as changes in ozone can have knock on impacts on emissions of ozone precursors through feedbacks induced by changes in temperature and the hydrological cycle (driven by the changes in aerosols and clouds and radiative forcing), which themselves will modify ozone.
Measurements of ozone on a global scale are challenging, making modeling of atmospheric composition, and accurate model treatment of ozone production and loss, critical to our understanding of this important species. The International Global Atmospheric Chemistry (IGAC) Chemistry Climate Model Initiative (Eyring et al., 2013; Morgenstern et al., 2017) provided a mechanism to coordinate multimodel simulations of the historic evolution of ozone in the troposphere and stratosphere and their future evolution out to the end of the 21st century. Results from CCMI indicate that global mean stratospheric ozone is projected to return to 1980s levels between 2045–2059 (Dhomse et al., 2018), but that the timing of this return depends on the extent of greenhouse gas emissions. As a result of increased greenhouse gas abundances, tropical total column ozone is likely to decrease by the end of the century (Eyring et al., 2013; Keeble et al., 2018; Oman et al., 2010). Revell et al. (2018) highlight a large spread in the CCMI models tropospheric ozone columns, with a bias compared to OMI-MLS data for the year 2005 of ±14 Dobson Units (~50%). They go on to explore the causes of bias in tropospheric ozone in the SOCOL model through performing an extensive series of sensitivity studies highlighting a large sensitivity of the SOCOL model tropospheric column ozone to emissions of ozone precursors in the year 2000. Ahalos, Polvani, et al. (2019) focus on the role of changes in the stratospheric in

In this study we aim to understand how the budget of tropospheric ozone has evolved over the recent historical period. Our focus is 1979–2010, and our assessment is based on the results from an updated run from the CCMI nudged dynamics refC1SD simulation (Morgenstern et al., 2017). Our aim is to quantify the impact of changes in emissions of ozone precursors (and so the chemical source of tropospheric ozone) relative to the change in influx of ozone from the stratosphere over this time period. Our paper is arranged with a description of the model and simulation set up (section 2), a summary of the results of our analysis, and a discussion of their impacts on our understanding (section 3). We finish with some conclusions on how future observations may enable improved understanding of the role of stratospheric ozone trends on the troposphere.

2. Method

Here we assess recent changes to the tropospheric ozone budget using version 7.3 of the Met Office Unified Model, based on the science version HadGEM3-A configuration (Hewitt et al., 2011) coupled with the United Kingdom Chemistry and Aerosol scheme, hereafter UKCA-StratTrop. The simulation follows the experimental design of the IGAC/Stratosphere-troposphere Processes And their Role in Climate (SPARC) Chemistry-Climate Model Initiative (CCMI) refC1SD experiment. This simulation spans 1979–2010, with emissions taken from MACCity (Granier et al., 2011) and uses prescribed sea surface temperatures and sea ice from HadISST (Rayner et al., 2003). Horizontal wind components (u and v) and potential temperature (θ) are nudged (following (Telford et al., 2008)) to ERA-Interim Reanalysis data (Dee et al., 2011). The meteorological reanalysis includes dynamical effects of stratospheric ozone depletion and increased
**Table 1**

| Chemical O3 production/Tg per year | Chemical destruction/Tg per year |
|-----------------------------------|----------------------------------|
| P1: HO2 + NO                   | 3,185                            |
| P2: CH3O2 + NO                 | 1,092                            |
| P3: RO2 + NO                   | 345                              |
| P4: OH + RCO2H                 | 18.9                             |
| P5: OH + RONO2                 | 7.8                              |
| P6: OH + PAN                   | 45.9                             |
| P7: RONO2 + hv                 | 1.8                              |
| P8: JO2                       | 55.0                             |
| STE                            | 451                              |

Note. All quantities are given in units of Tg(O3) per year for UKCA-StratTrop integrations for year 2000.

For the monthly mean data, the tropopause height was diagnosed using the World Meteorological Organization (WMO) thermal tropopause, and a mask applied to the reaction fluxes. For this study we calculate ozone production and loss terms using sums of reaction fluxes, similar to the methods used by Tilmes et al. (2016). Ozone production is calculated as the reaction flux through the rate-determining reactions, namely HO2 + NO, the sum of the various RO2 + NO reactions involving peroxy radicals derived from methane, ethane, propane, and isoprene, and the release of peroxy radicals from organic nitrate photolysis, the reactions of OH with carboxylic acid (RCO2H), organic nitrates, and peroxyacetyl nitrate (PAN). Ozone chemical destruction is derived from O1D + H2O, HO2 + O3, OH + O3, ozonolysis of alkenes, as well as indirect terms including loss of the Ox reservoirs, N2O5, and reaction of NO3 with VOCs. Dry deposition of O3 and NOx species, as well as wet deposition of NOy, are also included as ozone loss.

From Table 1, it can be seen that the residual STE of ozone, calculated from the budget as \( \text{STE} = L_{O3} + D_{O3} - P_{O3} \), agrees with the diagnosed online STE of ozone to within 2%. When making budget calculations, the table shows that it is important to include the contribution from photolysis of molecular oxygen in the upper tropical troposphere, which is of the order of 10% of this residual contribution, with its inclusion closing the budget to within 2%, consistent with the findings of (Prather, 2009). The model terms compare well with (Tilmes et al., 2016) for similar CCMI refC1SD experiments of \( P_{O3} = 4693 \), \( L_{O3} = 4256 \), and \( D_{O3} = 871 \) Tg yr\(^{-1} \) and slightly lower but within the range of the ACCMIP mean values of 4937 ± 656, 4442 ± 570 and 996 ± 203 Tg yr\(^{-1} \) (Young et al., 2018). The residual STT of 441 Tg yr\(^{-1} \) is within the ACCMIP range of 535 ± 161 Tg yr\(^{-1} \) (Young et al., 2013).

In order to assess the role of recent changes to the stratospheric ozone burden on the tropospheric ozone budget, a second integration (fODS_LBC) was performed in which the lower boundary condition of all halogenated ozone-depleting substances (ODS) was kept constant at 1979 values, but all other forcings and emissions were allowed to evolve as in the HIST experiment. Comparing fODS_LBC with the HIST simulations allows us to quantify the impacts of stratospheric ozone decreases arising from the emission of halogenated ODS on tropospheric ozone. Both simulations were nudged to the same meteorology, as this isolates the chemical effects of halogenated ODS, and keeps the mass flux between the troposphere and stratosphere constant between the two experiments, ensuring that any changes to STE are the result of stratospheric ozone burden changes.
3. Results and Discussion

3.1. Model Performance for Year 2000

Figure S1 shows a comparison of the tropospheric ozone column with OMI-MLS data, generated by applying a tropospheric mask generated from a 125-ppbv ozonopause (Gaudel et al., 2018). The UKCA-StratTrop model accurately captures the observed seasonality, albeit with a slightly late onset of ozone in the NH and a slightly early onset in the SH. The spatial structure compares well with the satellite observations, with the largest differences occurring in the boreal summer in the extratropics. The area weighted mean TCO in UKCA-StratTrop is 28.4 DU versus the OMI mean of 35.2 DU. The mean ozone value is significantly closer to the OMI/MLS mean than the configuration of the models employing UKCA used in the CCMI refC1 integrations, analyzed in (Revell et al., 2018), which, in contrast to the scheme used here, used a reduced complexity tropospheric chemistry scheme that does not treat NMVOC. In that configuration, UM-UKCA showed the lowest tropospheric ozone burden of the various models, with a low bias with respect to OMI/MLS of 14.1 DU for 2005 (Figure 6 of Revell et al., 2018). For these experiments, the model bias is around 7 DU low, highlighting the importance of the chemical scheme and the role of NMVOC in tropospheric ozone production. It should be noted that the exact value of the bias also depends strongly on tropopause definition, with a lower bias generally observed when using the WMO tropopause definition. The tropospheric O_3 burden averaged from 60°S to 60°N (using 125-ppbv ozonopause) is 295 Tg for year 2000, which compares well with observational estimates of between 280 Tg and 320 Tg (Gaudel et al., 2018), over the same latitude range. The model whole troposphere burden for year 2000 is 320 Tg, which is in agreement with estimates from Young et al. (2013) of 337 ± 23 Tg. Methane is forced by a lower boundary condition that follows CCMI historical concentrations at the surface, from which we derive a tropospheric CH_4 burden of 5,000 Tg and a lifetime with respect to oxidation by tropospheric OH of 9.0 years, in good agreement with the ACCMIP mean CH_4 lifetime of 9.3 ± 0.9 years (Voulgarakis et al., 2013). The airmass-weighted tropospheric mean OH is 10.610^5 cm^{-3} which agrees well with ACCMIP MMM of (11.7 ± 1.0) 10^5 cm^{-3} (Naik et al., 2013).

3.2. Evolution of Tropospheric Ozone Burden and Budget 1979–2005

Figure 1 shows the evolution of the stratospheric and tropospheric burden for both the HIST and fODS_LBC integrations. It can be seen that in HIST there is a strong decrease in modeled stratospheric ozone over the period 1980–1995 as a result of the increased CFC concentrations in the stratosphere and accompanying ozone destruction via chlorine species. Stratospheric chlorine reaches a maximum in 1997 (Maeder et al., 2010), and in the mid 1990s the decline in stratospheric ozone burden ceases, and signs of recovery emerge over the next 10 years. Over this period, the trend in tropospheric ozone burden follows the behavior in stratospheric ozone although less strongly and with a greater effect of interannual variability. In the fODS_LBC experiment, significantly less ozone depletion is calculated, although there is some decline as the stratospheric chlorine loading adjusts to the imposed 1979 constant lower boundary condition. This adjustment requires a period of around 5 years for the chlorine to be transported to high latitudes by the Brewer-Dobson circulation (Butchart, 2014). In the HIST experiment, the trend in tropospheric ozone burden follows a different behavior is calculated, with no significant trend from 1980–1993, and a positive trend thereafter.

Piecewise linear regression was used to determine the linear trends in burdens and fluxes, and these are shown in Figure 1. To fit the trends, least squares regression was used, with initial parameters determined by latin hypercube sampling, optimizing using root mean square error. We find inflection points in the stratospheric burden at 1995 (±1 year) for the HIST run, and 1993 ± 1 at for fODS_LBC. For the troposphere, these inflection points are 1992 ± 3 for the HIST run, and 1992 ± 2 for fODS_LBC.

4. Discussion

The MACCity emission data (Granier et al., 2011) used for these simulations describe an increase in emissions of tropospheric ozone precursors over the period 1979–2009 that leads to enhanced chemical production, particularly at the surface in the vicinity of key emissions hotspots. Deposition, which occurs
via various processes close to the surface, also increases over this period, reflecting more closely the increase in ozone production, rather than the tropospheric burden. Increases in the ozone burden do lead to an increase in OH and HO2, particularly in the free troposphere, with concomitant increase in chemical destruction via reactions L2 and L3.

Figure 2a shows the behavior in the gross global fluxes controlling the ozone burden in both HIST and fODS_LBC. Chemical production and loss were calculated as using reactions P1–P8 and L1–L6 respectively. Figure 2b shows the difference between these terms, net chemical production (NCP), while Figures 2c and 2d show deposition and STE of ozone. The deposition describes the amount of Ox deposited in wet and dry deposition, and the STE encapsulates the net transport of ozone from the stratosphere into the troposphere.

In both simulations, there is some interannual variability, with other transient features also apparent. These are associated with modes of unforced climate variability, such as El Niño-Southern Oscillation (ENSO), with peak and trough in ozone production occurring around strong events in the mid-1980s and in 1997. These climate events are also present in the NOx and CO emissions used in CCMI refC1SD that represent the fire emissions from these events. Spikes in ozone chemical production, loss, and deposition can be seen around 1997 that reflect the strong transient increase in emissions of ozone precursors in the MACCity emissions used for these simulations, and which represent the increase in biomass burning that year, particularly around SE Asia. We examined the effect of these events on the trends and find no statistically significant difference in trends when calculated when the El Niño years are ignored in the analysis. Removing 1997 and 1998 from our data resulted in the early trend changing from $-0.53 \pm 0.34$ Tg per year to $-0.59 \pm 0.31$ Tg per year, and the later trend changing from $+1.07 \pm 0.52$ Tg per year to $+1.10 \pm 0.48$, identical within mutual uncertainty and showing that El Niño has no effect on the retrieved values for the tropospheric ozone burden trend over 1979–2010. Although dynamical effects may also play a part (Voulgarakis et al., 2011), there is little evidence of a transient increase in STE in these integrations around this time.

Chemical production and loss of tropospheric ozone increase over the entire experiment. In HIST, over the period 1979–1996, ozone production increases at a slightly faster rate than loss resulting in an increase in NCP over this period. After 1996, losses increase slightly faster than production, leading to a smaller and slightly net negative trend in NCP. This partially reflects the behavior of the precursor emissions, which

Figure 1. Transient behaviour of annual mean stratospheric (a, upper) and tropospheric (b, lower) ozone burden.
reach a maximum around 1995 and then decline after this point. In HIST, photochemical production of ozone due to lower overhead ozone and higher photolysis rates (Voulgarakis et al., 2013) than in fODS_LBC. STE of ozone (the transport of ozone from the stratosphere into the troposphere) declines sharply from 1979–1994, consistent with the decline in lower stratospheric ozone associated with the use and emission of halogenated ODS, particularly the CFCs, throughout this time. From 1994–2006, modeled STE slowly increases, driven in part by early signs of stratospheric ozone recovery in the mid-latitudes (e.g. (Keeble et al., 2018), and stratospheric dynamical changes resulting from increased GHGs (e.g., Butchart, 2014). We note that these two effects are not isolated, with stratospheric ozone depletion and stratospheric dynamics closely coupled (e.g. Keeble et al., 2014, Polvani et al. (2018)).

In the fODS_LBC experiment, the STE term declines to a minimum in 1994, albeit at a slower rate than in HIST, before increasing from 1994 to the end of the integration. The greater rate of increase in STE after 1994 in the fODS_LBC integration compared with HIST can be attributed to the higher stratospheric ozone burden in this experiment, as the stratosphere-to-troposphere mass transport is identical between simulations. In fODS_LBC NCP is lower than in HIST, particularly as the stratospheric ozone burdens in the two experiments diverge and the photochemical ozone production in HIST increases.

Comparing HIST to fODS_LBC directly quantifies the chemical impacts of stratospheric ozone depletion on the tropospheric ozone budget. Figure 3 shows the difference in NCP, STE, and DD between the HIST simulation with respect to fODS_LBC. The differences for each in the year 1980 are near zero, as the simulations start from the same initial conditions. They diverge after ~5 years, consistent with the time it takes for the surface ODS mixing ratios prescribed by the LBC to be transported into the polar stratosphere. After 1985, STE is lower in the HIST simulation by around 75 Tg yr⁻¹ between 2000–2006, reflecting the lower stratospheric ozone burden, while NCP is up to 50 Tg yr⁻¹ higher, reflecting the increased photochemical
production of ozone. Deposition of ozone follows the tropospheric burden, and so is lower in the HIST simulation by ~20 Tg yr\(^{-1}\).

In conclusion, the HIST integration represents our best estimate of past tropospheric ozone changes as it follows historical emissions and meteorology. fODS_LBC isolates the effect of stratospheric ozone decreases on the tropospheric ozone budget but also shows that the effect of circulation changes has been significant. The behavior of the STE term in fODS_LBC shows that the faster Brewer-Dobson circulation and increased mass flux to the troposphere are also important controls on the budget. The two experiments also show that there is enhanced NCP in HIST, and that this offsets a significant decrease in ozone transport via STE, and thus moderates the effect of decreased stratospheric ozone on tropospheric ozone burden.

5. Summary

Between 1979 and ~1994 there is an increase in NCP of tropospheric ozone in response to increases in anthropogenic ozone precursors and an indirect decrease in transport to the troposphere that is the result of stratospheric ozone depletion caused by halogenated ODS. These drivers are in opposition, similar in magnitude, and are moderated by the change in chemical loss, resulting in a slight decrease in the tropospheric ozone burden despite increases to ozone precursor emissions. From 1994 to 2006, the tropospheric ozone burden has been increasing, driven by decreases to NCP again being offset by changes to STE. These drivers of tropospheric ozone, which are in opposition, turn out to be of similar magnitude, leading to a near-canceling behavior in changes to the budget terms and so a smaller change in ozone than in the \(P_{O_3}\), \(L_{O_3}\) or STE terms that control it.

Over the recent historical period, our study demonstrates that stratospheric ozone depletion has had a large impact on tropospheric ozone. Without the resulting decrease of STE, the large increase in NCP over the period 1979–1994 would have increased the tropospheric ozone burden. After 1994, there is a leveling off in the growth of emissions, and, coincidentally, a slight increase in STE, which together serve to increase the tropospheric ozone burden.

Our study uses two complementary methods to diagnose the stratospheric input. Our chemical budget diagnostics allow us to identify a residual term, which we ascribe to STE. Separately, we use dynamical methods to determine the amount of stratospheric ozone transported to the troposphere. We show that these two methods agree to within 2%, lending confidence to our analysis of the impact of stratospheric transport on tropospheric ozone.

Our results highlight the role of the stratosphere on tropospheric composition, and the utility of whole-atmosphere chemistry schemes with interactive stratospheric chemistry. Comparison with other UKCA models in the CCM project, highlights the critical role of tropospheric NMVOC chemistry in model skill. Finally, our results demonstrate the importance of STT on present (Neu et al., 2014) and future tropospheric ozone (Sekiya & Sudo, 2014), particularly as stratospheric ozone recovers over this century. This will be particularly important in regions affected by downward transport, for example, NH mid-latitudes in springtime (Lin et al., 2015). The complicating effects of circulation changes (see Polvani et al. (2018) necessitate further study at the regional scale using a dynamical model with interactive chemistry to fully understand the implications of stratospheric ozone recovery on tropospheric composition, radiative forcing and air quality.
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