On the changing role of the stratosphere on the tropospheric ozone budget: 1979-2010

P.T. Griffiths[1,2], J.M. Keeble[1,2], Y. Matthew Shin[1], N.L. Abraham[1,2], A.T. Archibald[1,2] and J.A. Pyle[1,2]

[1]Chemistry Dept, Cambridge University, Lensfield Road, Cambridge, U.K.

[2]National Centre for Atmospheric Science, Cambridge University, U.K.

Corresponding author: Paul Griffiths (paul.griffiths@ncas.ac.uk)

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 constrained, isolating the chemical response. By using historical forcings and emissions representative, interactions between processes are realistically represented. We use the model to ask how the ozone responds over time and to investigate model responses, sensitivities, feedbacks and trends. We find that the 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, stratospheric ozone recovery, and a levelling off in emissions, effect 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 modelling 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 representative 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.

Introduction

The changes in tropospheric ozone since the pre-industrial are estimated to have resulted in an increase in radiative forcing of 0.4 W m^{-2} (Stevenson et al., 2013, Myhre et al., 2013), 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 a complex scheme of oxidation of 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_{O3}) and downward transport of ozone-rich air from the stratosphere (S_{O3}), and sinks, principally physical losses at the surface (deposition, D_{O3}) and chemical loss throughout the free troposphere (L_{O3}).

Ozone has important impacts on vegetation and human health. In addition, ozone is important since it also indirectly affects the lifetime of other greenhouse gases, particularly methane, through its role in the formation of the hydroxyl radical (OH). OH (and so ozone) also has 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 oxidants like OH 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 modelling 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 (Morgenstern et al., 2017) provided a mechanism to coordinate multi-model 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 recover to 1980s levels between 2045-2059 (Dhomse et al., 2018) but that the timing of this recovery will vary depending on the extent of greenhouse gas emissions. As a result of increased greenhouse gas emissions tropical total column ozone is likely to decrease by the end of the century (Keeble et al., 2018). 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%). Revell et al. (2018) go on to explore the causes of bias in tropospheric ozone in the SOCOL model through performing an extensive series of sensitivity studies (Revell et al., 2018), highlighting that a large sensitivity of the SOCOL model tropospheric column ozone to emissions of ozone precursors in the year 2000. (Abalos et al., 2019) focus on the role of changes in the stratospheric influx of ozone into the troposphere over the coming century and show that models agree that an acceleration of the stratospheric circulation driven by increases in greenhouse gas emissions will result in increased stratosphere-to-troposphere transport (STT).

While we have a good understanding of the current distribution of tropospheric ozone, owing to a large number of different measurements, our understanding of changes to the historic ozone burden and budget are less so. The Tropospheric Ozone Assessment Report (TOAR) estimates that the tropospheric ozone burden averaged between 2010-2014 is 302 (281–318) Tg (Gaudel et al., 2018). This compares well with multi-model means (MMM) from model intercomparisons of 337±23 Tg (ACCMIP,(Young et al., 2013)) and 336±27 (+16 -21) Tg (ACCENT,(Stevenson et al., 2006) (although we note the TOAR burden is restricted to the latitude ±60˚). What controls this burden is still under debate. Archibald et al. (2020) review the recent literature on the chemical production (P_{O3}) and loss (L_{O3}) of tropospheric ozone and highlight a lack of data on the topic to make reliable assessments. P_{O3} is estimated to be much larger than the source from the stratosphere (S_{O3}) in all model simulations

which have calculated this (Young et al., 2018) however there is wide-spread in the magnitude of P_{O3}. Young et al. (2018) review the spread in the tropospheric ozone budget terms for the year 2000 and highlight a factor of ~ 2 spread across each term (P_{O3}, L_{O3}, S_{O3} and D_{O3}). Whilst models agree that $P_{O3}>S_{O3}$ there is less agreement historically on the sign of $P_{O3}-L_{O3}$, with some models suggesting the troposphere is a net sink for ozone.

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 UM-UKCA CCMI nudged dynamics RefC1SD simulation (Morgenstern et al., 2017). Our aim is to quantify how the impacts that changes in emissions of ozone precursors (and so the chemical source of tropospheric ozone) has changed relative to the 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.

Method

Here we assess recent changes to the tropospheric ozone budget using version 7.3 of the HadGEM3-A configuration of the Met Office's Unified Model (Hewitt et al., 2011) coupled with the United Kingdom Chemistry and Aerosol scheme (here-after referred to as UM-UKCA). The simulation follows the experimental design of the IGAC/Stratosphere-troposphere Processes And their Role in Climate (SPARC) Chemistry-Climate Model Initiative (CCMI) REF-C1 SD 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 chemical scheme used in this configuration of the model is a combination of the tropospheric (O'Connor et al., 2014) and stratospheric (Morgenstern et al., 2009) schemes. By using historical emissions, sea surface temperatures and meteorology we are able to accurately capture both the long-term tropospheric ozone changes (driven

predominantly by anthropogenic emissions) and short-term changes (e.g. those driven by ENSO, etc). Further, by using a combined stratosphere-troposphere chemistry scheme, the influence of stratospheric ozone changes on the tropospheric ozone budget are more accurately represented.

A full understanding of recent changes to the tropospheric ozone burden requires detailed analysis of the tropospheric ozone budget, including quantification of the chemical production and loss fluxes, stratosphere-troposphere exchange and the deposition of ozone at the surface. UM-UKCA includes 85 tracers, with 83 involved in chemistry, 59 photolytic reactions, 199 bimolecular reactions and 25 uni- and ter-molecular reactions. The chemistry employs primary emissions of 12 species and dry and wet deposition of a 39 and 14 species. Heterogeneous reactions occurring in the troposphere on sulfate aerosols are included. As a result, the model includes detailed tropospheric ozone chemistry. Dry deposition is parameterised employing a resistance type model (Wesely, 1989) using the implementation described in Archibald et al. (2019), while STT is calculated using an online method every chemical timestep.

For the monthly mean data, the tropopause height was diagnosed using the 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 in Tilmes et al. Ozone production is calculated as the reaction flux through the rate-determining reactions, namely HO_2+NO, the sum of the various RO_2+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 RCO2H, organic nitrates and PAN. Ozone chemical destruction is derived from O^1D+H_2O, HO_2+O_3, $OH+O_3$, ozonolysis of alkenes, as well as indirect terms including loss of the Ox reservoirs, N_2O_5, and reaction of NO_3 with VOCs. Dry deposition of O_3 and NO_y species, as well as wet deposition of NO_y, are also included as ozone loss.

Table 1: tropospheric ozone budget terms, broken down into annual mean sum fluxes. All quantities are given in units of Tg(O3) per year for UM-UKCA integrations for year 2000.

Chemical O3 production / Tg per year	4751	Chemical destruction / Tg per year	4193
P1: HO2 + NO	3185	L1: O1D + H2O	2205
P2: CH3O2 + NO	1092	L2: HO2 + O3	1356
P3: RO2 + NO	345	L3: OH + O3	518
P4: OH + RCO2H	18.9	L4: O3 + ALKENE	58.2
P5: OH + RONO2	7.8	L5: NO3 Loss	50.0
P6: OH + PAN	45.9	L6: N2O5 Loss	6.6
P7: RONO2 + hv	1.8	D1: Dry deposition O3	852
P8: JO2	55.0	D2+D3: Wet + dry deposition NOy	147
STT	451 Tg	Residual (STT)	441

From the table above, it can be seen that the residual STT, calculated from the budget as STT = $L_{O3}+D_{O3}-P_{O3}$ agrees with the diagnosed online STT 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).

Results and Discussion

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 model seasonality is good, 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 is 28.4 DU vs the OMI mean of 35.2DU. The mean ozone value is significantly closer to the OMI/MLS mean than the configuration of UKCA used in the CCMI refC1 integrations, analysed 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, 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. 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 O3 burden (using 125ppbv ozonopause) is 295 Tg for year 2000, which compares well with observational estimates of between 260 Tg and 340 Tg (Gaudel et al., 2018), over the same latitude range. Methane is forced by an LBC CH4 condition that follows CCMI historical concentrations at the surface, from which we derive a tropospheric CH_4 burden of 5000 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 10.6×10^5 cm^{-3} which agrees well with ACCMIP MMM of $(11.7 \pm 1.0) \times 10^5$ cm^{-3} (Naik et al., 2013).

Evolution of tropospheric ozone burden and budget 1979-2009

To determine the trend in chemical production, loss and ozone burden over the period 1979-2009, the model data were deseasonalised by subtracting a monthly mean climatology generated over all years. Figure 1 shows the evolution of the stratospheric and tropospheric burden. It can be seen that there is a strong decrease over the period 1980-1994 in modelled stratospheric ozone as a result of the continuing increase in CFC concentrations in the stratosphere and accompanying ozone destruction via chlorine species (Keeble et al., 2018). In the mid 1990s, the decline in stratospheric ozone burden ceases, and signs of recovery emerge over the next 15 years. Over this period, the trend in tropospheric ozone burden follows the behaviour in stratospheric ozone although less strongly and with a greater effect of interannual variability.
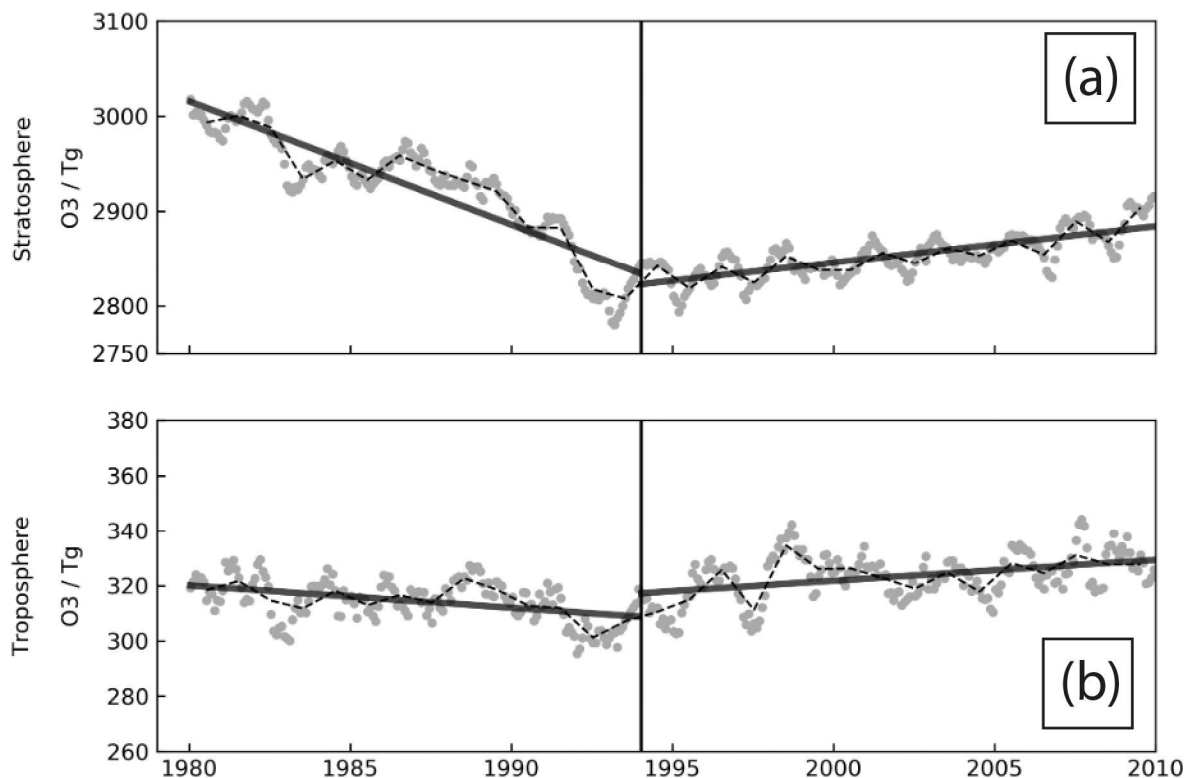
Figure 1 - Transient behaviour of stratospheric (a, upper) and tropospheric (b, lower) ozone burden.   The seasonal cycle in ozone has been removed. The breakpoint at 1994 is a guide for the eye and is explained in the text

Table 2 shows the computed trend either side of the breakpoint in the stratospheric ozone burden.   Small, but statistically significant, trends are calculated independent of the precise choice of break-point year, but the largest trends are observed for a breakpoint of 1994, consistent with the clear minimum in the stratospheric ozone around 1994.   Varying the breakpoint within one year of 1994 does not change the trend within the uncertainty of the linear fit.   The overall uncertainty in the trend shown in the table is the larger of the uncertainty in trend from fitting the data to a linear function, and the uncertainty arising from choice of breakpoint by one year around 1994.

Break- point	Tropospheric Ozone Burden trend / Tg yr-1		NCP trend / Tg yr-2	
	Before breakpoint	**After breakpoint**	**Before breakpoint**	**After breakpoint**
1993	-0.738 ± 0.150	+0.951 ± 0.115	+10.733 ± 1.226	-2.145 ± 0.781
1994	**-0.809 ± 0.133**	**+0.756 ± 0.123**	**+11.400 ± 1.083**	**-2.012 ± 0.867**
1995	-0.759 ± 0.117	+0.558 ± 0.135	+10.918 ± 0.963	-2.509 ± 0.966
	Deposition		STE	
	Before	**After**	**Before**	**After**
1993	+1.912 ± 0.283	+1.445 ± 0.251	-7.822 ± 0.829	+2.889 ± 0.553
1994	**+1.564 ± 0.254**	**+1.087 ± 0.273**	**-8.343 ± 0.736**	**+2.577 ± 0.611**
1995	+1.559 ± 0.225	+0.834 ± 0.305	-8.105 ± 0.647	+2.505 ± 0.690

Table 2 - trends in modelled ozone burden and budget terms around a varying break-point in the mid 1990s

NCP, defined as P_{O3}-L_{O3}, shows the opposite behaviour of this time period, with a strong increase over 1979-1994, and a smaller, negative trend afterwards. There is no statistically significant effect of the breakpoint on the magnitude of this trend. DD shows a positive trend over this period, with little change in the magnitude of the trend over the entire period. It shows a similar behaviour to the tropospheric ozone burden, but with a less pronounced effect of breakpoint on recovered trend. The behaviour of the trend in the STT term more closely parallels the behaviour of the tropospheric ozone burden, changing sign around 1994. Again, the breakpoint does not change the value of the trend, to within the uncertainty of the fit.

Discussion

The MACCCity emission database used for these simulations describe an increase in emissions of tropospheric ozone precursors over the period 1979-2009 in (Morgenstern et al., 2017) which leads to enhanced chemical production, particularly at the surface in the vicinity of the emissions. 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 HO_2, particularly in the free troposphere, with concomitant increase in chemical destruction via reactions L2 and L3.
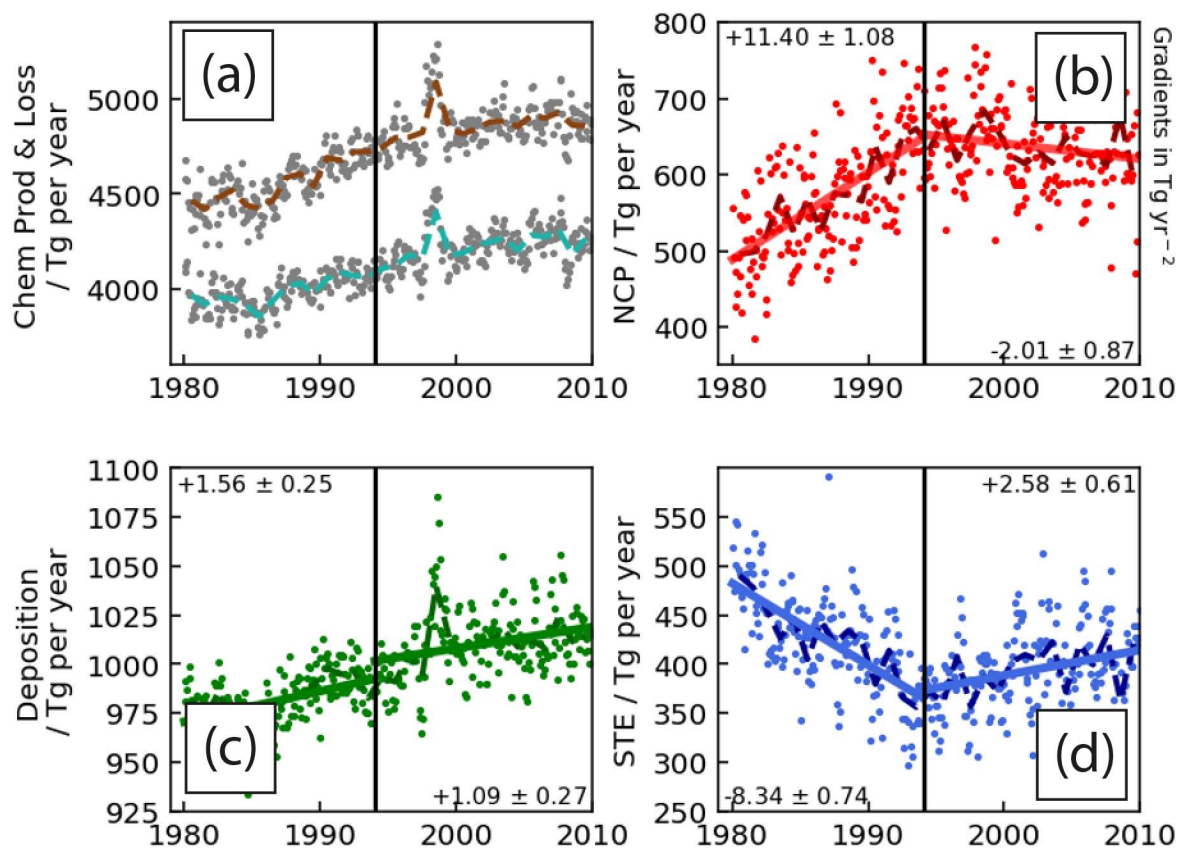
Figure 2: behaviour of the fluxes controlling the tropospheric ozone burden. a: Chemical production and loss. (b): Net (P_{O3}-L_{O3}) chemical production. (c): Deposition of Ox and NOy. (d): Net STT of ozone. Dots represent the deseasonalized global monthly mean fluxes. Dashed lines show annual means. Solid lines show a linear fit to the data, based on a break-point of 1994. Captions show trend in Tg per year.

Figures 2c and 2d show the behaviour in the gross global fluxes controlling the ozone burden. Chemical production and loss were calculated as using reactions P1-P8 and L1-L6 respectively. 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.

There is some interannual variability, with other transient features also apparent. These are associated with modes of unforced climate variability, such as 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 which represent the fire emissions from these events. Spikes in ozone chemical production, loss and deposition can be seen around 1997 which reflect the strong transient increase in emissions of ozone precursors in the MACCCity 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 Nino years are ignored in the analysis. Removing 1997 and 1998 from our data, resulted in the post-1994 trend changing from +0.76 ± 0.12 Tg per year to +0.80 ± 0.11 Tg per year, identical within mutual uncertainty and showing that El Nino 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.

Between 1979 and 1994, production and loss terms increase at a slightly different rate, with production increasing slightly faster than loss, resulting in an increase in NCP over this period. After 1994, the trend in production and loss is more similar, with loss increasing slightly faster, leading to a smaller and slightly net negative trend. This partially reflects the behaviour of the precursor emissions, which reach a maximum around 1995 and then decline after this point.

STE declines sharply from 1979-1994, consistent with the declines in lower stratospheric ozone associated with the use and emission of halogenated ozone depleting substances, particularly the CFCs, throughout this time. From 1994-2010, modelled STE slowly increases, driven in part by early signs of stratospheric ozone recovery in the mid-latitudes (e.g. (James 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)).

There is a direct increase in ozone production in response to increases in anthropogenic ozone precursors (figures S2 and S3) and an indirect decrease in transport to the troposphere which is the result of stratospheric ozone depletion

caused by chlorofluorocarbons. These drivers are in opposition, similar in magnitude, and are moderated by the change in chemical loss. The behaviour of the tropospheric ozone burden reflects the balance between these large budget terms, and the interactions between them, such as chemical loss, which depend non-linearly on the ozone burden itself. The magnitude of NCP, DD and STT are similar, ranging between 300 Tg and 1000 Tg, and change by as much as 40% over this period. These changes partially offset each other and mitigate their individual effect on tropospheric ozone. Since 1994 the tropospheric ozone burden has been increasing, while NCP has been decreasing over the same period. On the other hand, STE decreases up to 1992, then recovers slightly, which partially offsets the decrease in chemical ozone production within the troposphere. These drivers of tropospheric ozone, which are in opposition, turn out to be of similar magnitude, leading to a near-cancelling behaviour in changes to the budget terms and so a smaller change in ozone than in the P_{O3}, L_{O3} or STT terms that control it.

Summary

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 STT, the large increase in NCP over the period 1979-1994 would have increased the tropospheric ozone burden. After 1994, there is a levelling off in the growth of emissions, and, coincidentally, a slight increase in STT, 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 STT. 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 ensembles in the CCMI 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, e.g. NH midlatitudes 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.

Acknowledgements

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