The Spillover of Tropospheric Ozone Increases has hidden the Extent of Stratospheric Ozone Depletion by Halogens

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Key Points:

- Our world has seen damaging levels of ozone depletion over the past several decades, and these will continue into this century
- Ozone column changes are a combination of halogen-driven stratospheric decreases counteracted by pollution-driven tropospheric increases
- Tropospheric increases spillover into the stratosphere and thus the observed recovery of assumed halogen-driven loss is overestimated

Abstract

Stratospheric ozone depletion from halocarbons is partly countered by pollution-driven increases in tropospheric ozone. While recognizing this, the ozone assessment's evaluation of observations and processes have often split the chapters at the tropopause boundary. Using a chemistry-transport model we find that air-pollution ozone enhancements in the troposphere spill over into the stratosphere at significant rates, i.e., 13%-34% of the excess tropospheric burden appears in the lowermost extra-tropical stratosphere. As we track the anticipated recovery of the observed ozone depletion, we should recognize that two tenths of that recovery may come from the transport of increasing tropospheric ozone into the stratosphere.

Plain Language Summary

The world has made great strides in phasing out the halocarbons that drive ozone loss, such as the chlorofluorocarbons 11 and 12. While living with the well-documented depletion of the ozone layer, we are now watching the slow recovery (increase) of stratospheric ozone over this century after our phaseout of halocarbon production and use. Projecting this recovery date also depends on the impact of other changing greenhouse gases on stratospheric chemistry as well as changes in tropospheric ozone. Both observations and models identify tropospheric ozone as increasing due to air-quality pollution in the lower atmosphere. Here, using a global chemistry-transport model, we find that this ozone increase carries over into the stratosphere at rates affecting the recovery expected from the decay of atmospheric halocarbons. This process is inherently included in our chemistry-climate models but is not diagnosed as such. The ozone assessments need consider that what happens in the troposphere does not stay in the troposphere, complicating our of interpretation of ozone changes over this century.

0 Prologue

The *Climatic Impact Assessment Program* (CIAP, 1974) in the early 1970s completed an integrated U.S. assessment of the ozone (O_3) layer as being under future threat from a proposed fleet of high-flying Concorde-like supersonic transport aircraft (SSTs). The threat of depletion of the ozone layer was based on the catalytic ability of oxides of nitrogen (NOx) emitted from the engines to destroy stratospheric ozone (Johnston, 1971; McElroy et al., 1974). The hypothetical threat of SSTs was quickly replaced by real ozone depletion caused by chlorofluorocarbons (Molina and Rowland, 1974; Stolarski and Cicerone, 1974; Wofsy and McElroy, 1974). Ozone assessments became international and remained focused on halogen-driven ozone depletion (e.g., WMO, 1981; 1985; 2022). In 1988 the NASA *High Speed Research Program* revived the dream of a commercial SST fleet and initiated the *Atmospheric Effects of Stratospheric Aircraft* (AESA) to re-assess SST impacts based on the maturity of stratospheric science. In the first AESA report, a figure appeared (Schmeltekopf, 1992; reproduced here as **Fig. 1**) that predicted increases in lowermost stratospheric O_3 from the aircraft NOx due to "smog reactions" that include methane (CH_4). This result was surprising at first to those focusing on O_3 depletion, and it may be the first assessment to show increased lower stratospheric O_3 production associated with human pollution.

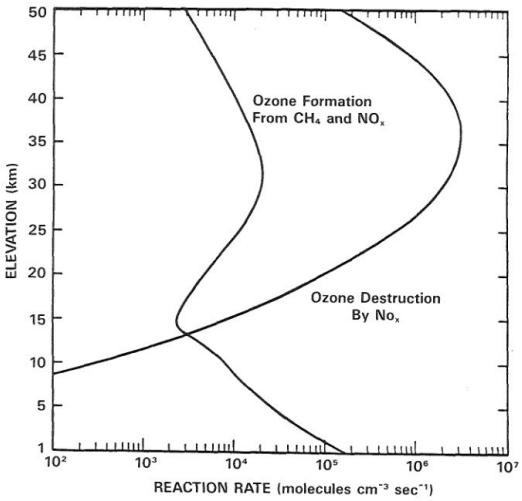

Fig. 1. Ozone formation from the smog reactions based on methane and nitrogen oxides (45° latitude, spring). The primary perturbation shown here is that of added NOx from a fleet of SSTs. Fig. 1, page 166 from Schmeltekopf (1992).

1 Introduction

The community has continued to study pollution of the lower stratosphere whereby ozone precursors or ozone-depleting substances are transported from the troposphere into the stratosphere, thereby altering the chemical production and loss of O_3. Some examples include the convective overshooting at the tropical tropopause (Oman et al., 2016; Wales et al., 2018), the South Asian Monsoon (Fu et al., 2006; Randall et al., 2010; Lelieveld et al., 2018; Dubé et al., 2022), and extensive wildfires (Hirsch and Koren, 2021; Santee et al., 2022; Solomon et al., 2022), all of which can lead to increases or decreases of stratospheric O_3. What is less studied is the direct impact of enhanced tropospheric O_3 on the stratosphere. This spillover effect, whereby tropospheric O_3 pollutes the stratosphere directly rather than through precursors, is not readily diagnosed because separating the chemistry and transport of O_3 across the tropopause region is impossible with just O_3 observations and remains a difficult task in most models.

In climate forcing, increased tropospheric O_3 dominates stratospheric depletion. Gauss et al. (2006) in their multi-model assessment recognized that "tropospheric ozone increase since preindustrial times has moderated lower stratospheric ozone depletion", but they did not have the scenarios or diagnostics to evaluate it. Other model studies (Shindell et al., 2013; Reader et al., 2013) derived the amount of tropospheric "pollution" O_3 in the stratosphere but their pollution scenarios included also the increase in CH_4. Given the very large impact CH_4 has on stratospheric O_3 (see Fig. 1, and Fig. 14 of Zeng et al., 2022) this obfuscates their results. In the AerChemMIP study (Collins et al., 2016) a scenario singling out the O_3-precursor emissions without changing CH_4 provided an opportunity for Zeng et al. (2022) to identify direct O_3 transport, but, even with this scenario, O_3 precursors are emitted directly into the lower stratosphere (e.g., 18%-44% of aviation NOx, Gettelman and Baughcum, 1999) or transported there.

In this paper, a set of carefully designed chemistry-transport model (CTM) simulations is used to assess the impact of direct O_3 influx from the troposphere into the stratosphere. These simulations follow from the use of direct O_3 emissions to derive the lifetime of tropospheric O_3 (Prather and Zhu, 2024). Given a 20th century tropospheric column O_3 ($trpcolO_3$) increase of

about 9 Dobson Units (DU) (Gauss et al., 2006; Young et al., 2013; Griffiths et al., 2021), this work identifies a 2-3 DU increase in stratospheric column O_3 (strcolO_3) without including any stratospheric increase in O_3 precursors such as NOx and CH_4. Failure to recognize trends of this level can notably alter the projected year-of-recovery for stratospheric ozone depletion in response to policy options (see Fig. ES-1 and 3-24 of WMO, 2022) and also the projected net integrated ozone depletion (Pyle et al., 2022). While this trpcolO_3 spillover is inherently included in current models, it is likely misdiagnosed in both models and observations as reduced levels of strcolO_3 depletion and earlier recovery. Modeling is covered in Section 2; analysis of past and future ozone changes are in Section 3; and a summary discussion is in Section 4.

2 Modeling

2.1 The UCI chemistry modules

The UC Irvine CTM, like many early CTMs, developed separate chemistry modules for stratosphere (Linoz: McLinden et al., 2000; Hsu and Prather, 2009; 2010) and troposphere (ASAD: Wild and Prather, 2000; Wild et al., 2003). The current stratospheric chemistry module (Linoz version 3) calculates the chemical production and loss of O_3, NOy (the family of nitrogen oxides except N_2O), N_2O, and CH_4 as a first-order Taylor expansions about 3D climatological means (monthly, latitude by pressure) of these species. The expansion also allows for independent variations in temperature and overhead column O_3. Local stratospheric H_2O is inferred from CH_4 decay through conservation of H and a tropopause boundary condition of 3.65 ppm (micromol mol^{-1}) H_2O. For the present-day (circa year 2000) simulations shown here the CTM uses lower tropospheric boundary conditions (LBCs) of 30 ppb (nmol mol^{-1}) for O_3, 0.02 ppb for NOy, 316 ppb for N_2O, and 1800 ppb for CH_4. Rapid O_3 loss driven by heterogeneous chemistry on polar stratospheric clouds uses the Cariolle et al. (1990) parameterization, which produces an excellent simulation of the mean and interannual variability of the Antarctic ozone hole (e.g., Fig. 8 of Ruiz and Prather, 2022).

To calculate the chemical rates and the Taylor expansions, a stratospheric chemistry box model (Pratmo: e.g., Dubé et al., 2022) is linearized about the climatological mean values of the independent species scaled to the LBCs for N_2O and CH_4, plus stratospheric climatologies for the nitrogen (NOy), chlorine (Cly) and bromine (Bry) families of species. The Pratmo calculation forces all the individual species in each of the three families to be in 24-hour photo-stationary state. During a CTM simulation, stratospheric CH_4, N_2O, and NOy may evolve in response to changing LBCs, but the Cly and Bry remain fixed per the initial calculation of the Linoz tables, i.e., 3.24 ppb peak Cly and 16.8 ppt peak Bry for year 2000. The tropospheric chemistry module ASAD includes about 30 species with a reduced set of hydrocarbon reactions, but no halogen chemistry. Many ASAD species are set to decay slowly in the stratosphere; but the NOy species are reconciled to the Linoz production and loss of NOy by adjusting NO, NO_2 and HNO_3 to ensure the observed relative influx of these species into the troposphere generated from the N_2O loss.

The choice of which chemistry to apply in each air parcel is triggered by the e90 surface tracer (Prather et al., 2011) using a threshold of 90 ppb. Thus, a full-chemistry CTM simulation includes both a standard O_3 tracer that experiences Linoz chemistry when in the stratosphere and ASAD chemistry when in the troposphere. It also includes a tagged tracer O_3S that experiences only Linoz chemistry plus the LBC, which is invoked by the Linoz module. A recent example of the full-chemistry simulations are shown in Prather and Zhu (2024, see their Table 1). Present-

day tropospheric O_3 budgets are similar to recent model intercomparison projects (Young et al., 2018; Griffiths et al., 2021).

2.2 Identifying the Spillover Effect

The work here was triggered by the belated discovery that the O_3 and O_3S tracers in the UCI CTM differed, not just in the troposphere as expected (where O_3 has ASAD chemistry and O_3S has only a LBC reset), but also in the lower stratosphere (where both are subject only to the same Linoz chemistry). To study this effect we set up some diagnostic experiments. First, we calculate O_3S with two Linoz-only simulations using O_3S LBCs of (a) 10 and (b) 30 ppb. Finally, we run a full-chemistry simulation (c) with O_3 calculated from the chemical rates in the troposphere and the O_3S tracer in that run with a 30 ppb LBC. All simulations here are run for two years using years 2000-2001 meteorological data, with diagnostics taken from the final year 2001. All O_3 diagnostics here are based on sampling all grid cells (320 x 160 x 57) on the 1st of each month to ensure a clean separation of stratosphere and troposphere based on the e90 tracer value in each cell. The typical approach using monthly means destroys the tropopause information, creating a high bias for O_3 (see Prather and Zhu, 2024, who chose 5-day sampling for better temporal resolution). The global, annual mean, 60°S-60°N profiles of tropospheric O_3 (or O_3S) averaged on model layers are shown in Figure 2a. These profiles include only and all of tropospheric air. Mean trpcolO_3 values are (a) 8.5 DU, (b) 20.9 DU, and (c) 32.0 DU. The full chemistry (c) values for trpcolO_3 are our best simulation of the 2000s decade and are consistent with the observed columns (about 30 DU) and the seasonal cycle (minimum in DJF) found by Ziemke et al. (2012). The annual mean strcolO_3 for the full chemistry run is 280 DU. As expected, the O_3S profiles with 30 ppb LBC, either alone (b) or with tropospheric chemistry (c), are essentially identical and not shown.

The profiles in Figure 2b are for stratospheric air only and show the percent difference of O_3 (full) – O_3S (30 ppb) *(blue)* and O_3S (10 ppb) – O_3S (30 ppb) *(red)*. The annual mean strcolO_3 difference in these two pairs is +3.8 DU and -1.6 DU, respectively. For both cases the relative differences in stratospheric O_3 are largest (5-20%) below 16 km and negligible above 22 km. Absolute differences in the lowermost stratosphere below 19 km for these two cases are nearly constant at about +30 ppb and -15 ppb, respectively (not shown, but see Fig. 3). Both trace species O_3 and O_3S experience only Linoz chemical tendencies in the lower stratosphere. These tendencies drive the O_3 species toward the O_3S profile, the preferred chemical state in the stratosphere, and thus damp any injection of tropospheric O_3. Any flux of pollution precursors (e.g., ASAD's NO, CO, H_2O_2) into the stratosphere will be ignored by Linoz. Thus we are certain that the stratospheric enhancements observed here are due entirely to the transport of tropospheric O_3 into the stratosphere.

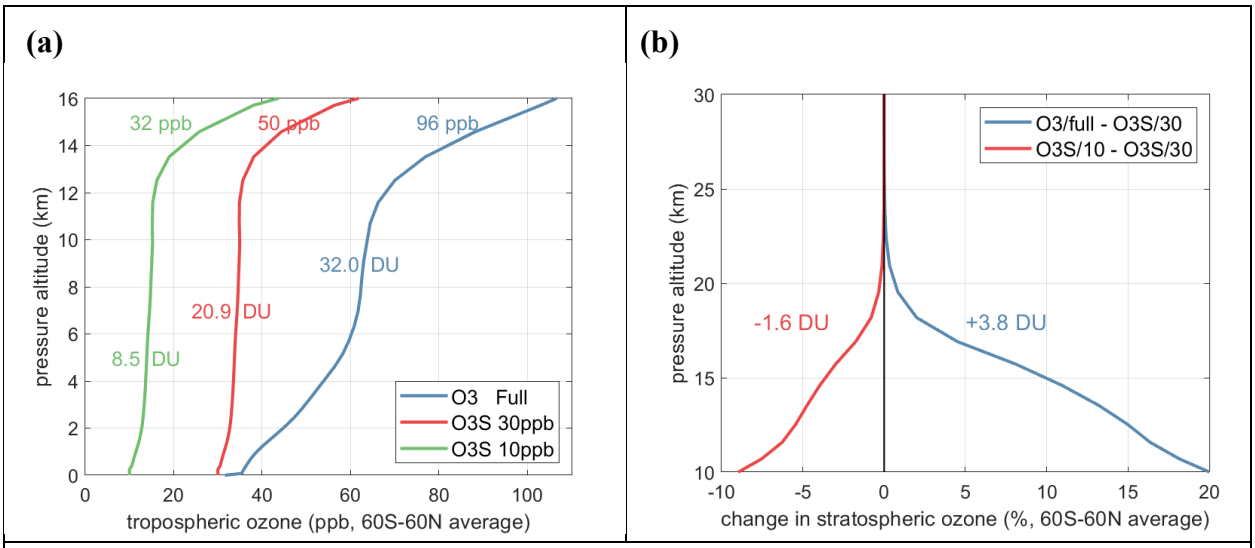

Fig. 2. **(a)** Mean profiles of tropospheric O_3 (ppb, nmol mol^{-1}) vs. pressure altitude (z*, km). Only tropospheric air as defined by e90 is included, and results are area-averaged over 60°S-60°N. Three profiles are shown along with their global mean tropospheric column (trpcolO_3 in DU = 10^{-3} cm-amagat): ***(green)*** No tropospheric chemistry plus Linoz with 10 ppb LBC; ***(red)*** ditto with 30 ppb LBC; and ***(blue)*** Full tropospheric chemistry plus Linoz with 30 ppb LBC. Each curve is also labeled with mean tropospheric abundance (ppb) for two model layers from 88 to 123 hPa, which lie in the tropical upper troposphere, see text. **(b)** Relative change in stratospheric O_3 (%) vs. pressure altitude (km). Only stratospheric air as defined by the e90 tracer is included. O_3 is area-averaged over 60°S-60°N. The positive profile ***(blue)*** shows difference O_3 (full tropospheric plus stratospheric ozone chemistry) minus O_3S (Linoz stratospheric chemistry only with 30 ppb LBC). The negative profile ***(red)*** contrasts two Linoz-only runs: 10 ppb LBC minus 30 ppb LBC.

Figure 3 provides a latitude by pressure-altitude color map of the absolute increase in stratospheric O_3 attributable to excess tropospheric O_3, calculated as O_3 minus O_3S with a 30 ppb LBC. We calculate that 99% of the increased mass occurs below 21 km. As in Fig. 2, stratospheric values from troughs and folds appear well below the mean tropopause. Based on this map, the enhanced tropospheric O_3 finds its way into the stratosphere through isentropic flow across the jet streams into the extratropical lowermost stratosphere and also partly through ascent across the tropical tropopause. The stratospheric increases are asymmetric favoring the northern hemisphere because the tropospheric O_3 changes (O_3 minus O_3S) in the full chemistry model are driven by predominantly northern hemisphere emissions of ozone precursors. For our full chemistry run, the northern hemisphere (NH) and southern hemisphere (SH) trpcolO3 are 35.2 and 28.7 DU, respectively. For O_3S (30 ppb LBC), these values are 21.2 and 20.6 DU. Thus, the increase in trpcolO_3 is about twice as large in the NH as evidenced in Fig. 3. The small NH-SH difference in tropospheric O_3S reflects the nearly balanced STE O_3 flux in the UCI CTM (Ruiz and Prather, 2022), even though the SH flux has been reduced by about 14% due to the Antarctic ozone hole.

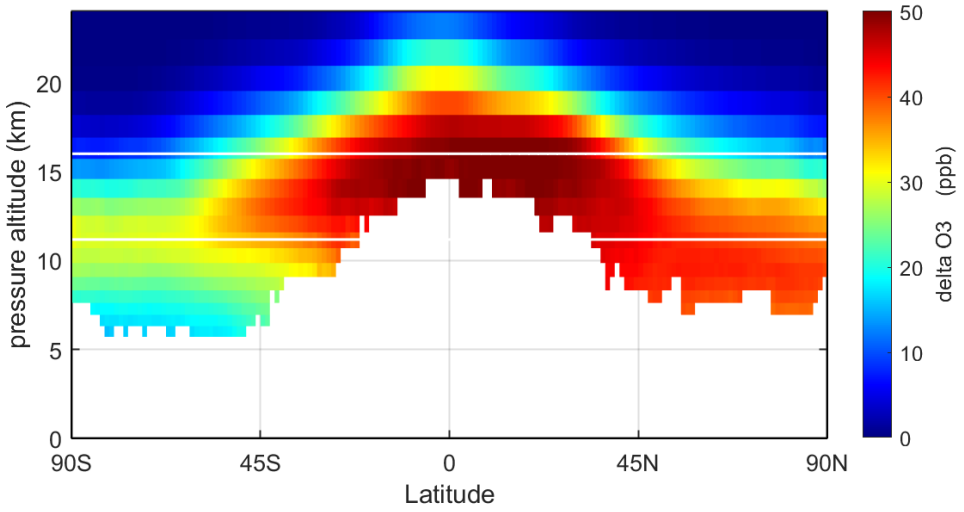

Figure 3. Latitude-by-altitude color map of the spillover effect, i.e., the stratospheric O_3 excess (ppb) due to injection tropospheric O_3. Values shown here are for stratospheric air parcels only (using e90). The color map is calculated as the difference between full chemistry simulation (O_3) and the stratospheric tagged tracer O_3S calculated using only stratospheric chemistry (Linoz) with a lower boundary condition (LBC) of 30 ppb, see text. The plot shows the annual, zonal mean taken from the 1st of each month for year 2001 and includes stratospheric air parcels in folds or troughs below the climatological mean tropopause. For perspective, horizontal white lines mark pressure altitudes of 12 km and 16 km.

Given our ability to measure trpcolO_3 from satellites (e.g. Ziemke et al., 2012) and the ready diagnostic of trpcolO_3 from the model intercomparison projects (MIPs: Young et al., 2013; Griffiths et al., 2021; Zeng et al., 2022), it would be great if can derive a spillover factor that relates tropospheric column changes to the induced stratospheric column changes. For this study, we have available two independent cases: (i) the two Linoz runs with different LBCs, and (ii) the single modern full chemistry run that contrasts O_3 with O_3S. For these cases, the change in trpcolO_3 is an extremely poor predictor of strcolO_3 : (i) spillover factor of 0.13 DU per DU (1.6/12.4), and (ii) 0.34 DU per DU (3.8/11.0). Searching for a better predictor and considering Fig. 3, we identified the O_3 abundance (mole fraction) in the upper tropical troposphere, specifically the two model levels from 88 to 123 hPa. The predictor now is consistent for the two cases, 0.083 DU per ppb, but it is difficult, if not impossible, to observe the troposphere-only mole fraction of O_3 between 88 and 123 hPa except with sondes. Likewise, such a diagnostic for the MIPs would not work.

3 Analysis of Past and Future Ozone Changes

How can we use our limited set of CTM simulations to estimate the magnitude of the spillover effect from pre-industrial (PI) to present day (PD)? The change in trpcolO_3 from 1900 to 2000 based on multi-model assessments give values of about +9 DU (Gauss et al., 2006; Young et al., 2013; Griffiths et al., 2021; Zeng et al., 2022), consistent with observed trends over the past two decades (Gaudel et al., 2018; Tarasick et al., 2019). We do not have the resources for a full PI to PD CTM simulation here and, further, lack the necessary PI meteorological data to drive the

transport. We propose that our Linoz 30 ppb simulation is similar to PI because: (1) trpcolO_3 is 11 DU less than our PD simulation with full chemistry; (2) tropospheric O_3S is remarkably north-south symmetric; and (3) in most models tropospheric pollution-driven changes in O_3 are largest in the upper troposphere (e.g., Fig. 8 of Young et al., 2013, converting mass to abundance). Thus, assuming that the PI to PD profile of tropospheric O_3 has changed as in our O_3S to O_3 simulation, we scale our spillover (3.8 DU) with trpcolO_3 (from 11 to 9 DU) and get 3.1 DU. Thus, our best estimate of the increase in strcolO_3 from PI to PD due simply to the increase in tropospheric O_3 is 3 DU. It is difficult to provide a formal error analysis, but our estimate would be ±1.5 DU, due primarily to abundance uncertainty in the upper tropical troposphere.

How important is 3 DU spillover into strcolO_3? The difficulty, but necessity, of separating trends in total column O_3 (totcolO_3) into pollution-driven tropospheric and halogen-driven stratospheric is discussed in Box 3-3 of WMO (2022), but a reconciliation was not made. A global mean loss of about 8.0 DU in totcolO_3 is observed between 1980 and 2020 with most occurring before 1995 (see Fig. 3-6 of WMO, 2022). The return to 1980 O_3 levels is the established measure of "recovery" (Prather and Watson, 1990). The observed trpcolO_3 trend gives an increase of 3.6 DU for these four decades, and thus the true loss in strcolO_3 since 1980 is 11.6 DU. The tropospheric spillover based on the increase in trpcolO_3 means that this inferred halogen-driven loss is further underestimated by 0.5 to 1.2 DU (The upper and lower range is based on trpcolO_3 spillover factors ranging from 0.34 (full chemistry O_3-minus-O_3S) to 0.13 (Linoz 30 ppb-minus-10 ppb cases)).

It is useful to examine the MIP-based attribution study of Zeng et al. (2022), which presented PI-PD changes in strcolO_3 and trpcolO_3. Here we use year 2000 as PD for reading numbers from their figures. The PI-PD total change in trpcolO_3 is about +9.0 DU (consistent with previous studies); it is comprised of +4.0 DU from CH_4 increases and +7.5 DU from increased emissions of other O_3 precursors (e.g., NOx, CO) minus the decreases driven by halocarbons and N_2O. The total change in strcolO_3 is predominantly negative (-14.5 DU) but with some large positive changes from CH_4 (+6.5 DU) and the other O_3 precursors (+2.5 DU) that parallel the tropcolO_3 changes. The large direct role of CH_4 in stratospheric chemistry is well known and expected. What is unclear from the Zeng et al. analysis is whether the +2.5 DU from non-CH_4 precursors is a direct O_3 spillover effect from the +7.5 DU in trpcolO_3 or if it results from increased stratospheric chemical production of O_3 from the tropospheric NOx entering the stratosphere or direct stratospheric emissions of aviation NOx as described by Schmeltekopf (1992).

For the future, the multi-model assessments project changes in trpcolO_3 over the 21st century that vary by scenario from –5.6 DU (RCP2.6) to +5.3 DU (RCP8.5) to +7.3 DU (SSP3-7.0) (Archibald et al., 2020). This wide range is due primarily to changes in the O_3 precursor emissions and secondarily to recovery of halogen-driven depletion combined with overall climate change (e.g., warmer wetter troposphere, colder stratosphere). The spillover effect on strcolO_3 with the large factor (0.34 DU per DU) then ranges from –1.9 to +2.4 DU; but because these future changes likely preserve the current O_3 profile shape and hence have a smaller factor (0.13), the spillover is likely much smaller, -0.7 to +0.9 DU. For perspective, the totcolO_3 loss from 1900 to 2000 attributed to ozone depleting substances is about 20 DU, and the loss from all emissions is 14 DU (Zeng et al., 2022). In terms of the observed totcolO_3 loss since 1980, we are looking for recovery of about 8 DU. Thus the scenario range of projected changes in trpcolO_3 is comparable to size of the recovery (-70% to +90%), and the spillover effect onto

strcolO_3 will still be an important fraction (~25%). With fully diagnosed models, we should be able recognize and correct for this, but with observations, the spillover effect is hidden within the recovery and cannot be readily diagnosed.

4. Discussion

The spillover effect will vary depending on what is driving tropospheric O_3 changes and how that is manifest in the upper tropical troposphere. It is necessary for other models to quantify this effect, and to examine a range of scenarios. In simulating the spillover effect with other models, one should avoid the use of tagged tracers such as labeling tropospheric O_3 and watching its buildup in the stratosphere. Such experiments give unreliable results because tropospheric O_3 molecules entering the stratosphere are not differentiable from stratospheric O_3 molecules. There are chemical feedbacks on O_3 and its lifetime (in parallel with tropospheric CH_4), and thus addition of O_3 changes the whole of stratospheric O_3 chemistry, a process that cannot be simply simulated with a tagged tracer (see the problems with O_3S as a measure of stratospheric influence in Prather and Zhu, 2024). It is important that other model studies are able to differentiate between the transport of O_3 (e.g., 10–30 % spillover) and that of chemical precursors (NOx, CH_4), and thus warrant such diagnostics in future ozone assessments.

The reverse of this process is well known, i.e., strcolO_3 changes propagate into the troposphere through STE fluxes and alter trpcolO_3. Recent results allow us to quantify this. The Antarctic ozone hole is shown to reduce the southern hemisphere STE ozone flux by on average 30 Tg-O_3 y^{-1} with interannual variations of ±20 Tg-O_3 y^{-1} (Ruiz and Prather, 2022). Using the 24-day perturbation lifetime for tropospheric O_3 from STE sources, Prather and Zhu (2024) calculate that the total STE perturbation is only 8%, and hence the SH mean reduction in trpcolO_3 from the current ozone hole is only 0.4 DU. These relatively large ozone fluxes have much less impact in the troposphere because the photochemistry is much more reactive (shorter lifetime) there than in the lower stratosphere.

Unfortunately, this spillover effect exacerbates the conflicts inherent in environmental mitigation strategy. For example, the RCP2.6 scenario greatly improves air quality by reducing tropospheric O_3, but this leads to reductions in stratospheric O_3. Even the integrated O_3 depletion metric envisaged by Pyle et al. (2022) needs to be calculated with a full chemistry-transport model that includes spillover effects when emission scenarios include O_3 precursors.

Acknowledgments

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Open Research - Data Availability Statement

The UCI CTM output data used in the study are archived as netcdf files along with the plotted data in Prather (2024).

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