Mechanisms and feedbacks causing changes in upper stratospheric ozone in the 21st century

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Driving forces behind 21st century ozone evolution

One of the important science questions that need to be address is concerning how ozone will evolve in the future and what factors are causes this change. Ozone is a very important atmospheric gas that absorbs damaging ultraviolet radiation, so changes in the total amount above us can have important consequences for our biosphere. The ability of ozone to absorb sunlight, mainly in the ultraviolet but also some in the visible range, as well as some of Earth’s outgoing longwave radiation causes heating of the upper layers of our atmosphere which can have many impacts, including changing the winds.

A new study by scientists at NASA’s Goddard Space Flight Center (GSFC) and Johns Hopkins University used a state-of-the-art chemistry climate model to explain what could potentially be driving changes in ozone in the upper levels of our atmosphere over the 21st century. They found that in the upper stratosphere, the region from 20 to 30 miles above the surface, the reduction in chlorine and cooling temperatures contribute about equally to future increases in ozone in the tropics. The future reduction in chlorine, which is formed mostly from the breakdown of chlorofluorocarbons (CFC’s), is the expected result of the successful implementation of the Montreal Protocol and its subsequent amendments and adjustments. The continued cooling of the stratosphere is a response largely caused by increasing concentrations of carbon dioxide (CO2), which is opposite of the warming that CO2 causes closer to the surface.

The technique that was developed in this study helps to separate the relative contributions of several factors that can influence ozone and can be applied to a wide range of greenhouse gas scenarios as well as to other chemistry climate models. This method can potentially be very useful in explaining differences in ozone trends among models and will be used in an upcoming assessment for this purpose. This work is part of a larger chemistry climate project at GSFC with the ultimate goal of using observations and computer modeling to improve our knowledge of Earth’s climate system.
Figure caption: Vertical variation of trends in ozone (solid black curve) and individual contribution of different mechanisms over the tropics (10°S-10°N) for the 21st century in GEOSCCM. The dominate impacts are from temperature (T, blue curve) changes and chlorine (EESC, red curve) changes with negligible contribution from hydrogen (HOx, green curve) and nitrogen (NOy, orange curve) oxides for the A1b (mid-range) greenhouse gas scenario.
Abstract

Stratospheric ozone is expected to increase during the 21st century as the abundance of halogenated ozone-depleting substances decrease to 1960 values. However, climate change will likely alter this "recovery" of stratospheric ozone by changing stratospheric temperatures, circulation, and abundance of reactive chemical species. Here we quantify the contribution of different mechanisms to changes in upper stratospheric ozone from 1960 to 2100 in the Goddard Earth Observing System Chemistry-Climate Model (GEOS CCM), using multiple linear regression analysis applied to simulations using either A1b or A2 greenhouse gas (GHG) scenarios. In both these scenarios upper stratospheric ozone has a secular increase over the 21st century. For the simulation using the A1b GHG scenario, this increase is determined by the decrease in halogen amounts and the greenhouse gas induced cooling, with roughly equal contributions from each mechanism. There is a larger cooling in the simulation using the A2 GHG scenario, but also enhanced loss from higher NOy and HOx concentrations, which nearly offsets the increase due to cooler temperatures. The resulting ozone evolutions are similar in the A2 and A1b simulations. The response of ozone due to feedbacks from temperature and HOx changes, related to changing halogen concentrations, are also quantified using simulations with fixed halogen concentrations.

1 Introduction
One of the critical questions of Earth’s climate system is how ozone concentrations will evolve during the 21st century. The concentration of ozone-depleting substances (ODS) increased rapidly during the 1960s to 1980s, peaked in 1990s, and is expected to decrease almost back to 1960s levels by the end of this century. As the abundance of stratospheric halogens returns to 1960s values, stratospheric ozone, if there were no other changes, would be expected to increase back to 1960s values. However, the concentrations of greenhouse gases (GHGs) are expected to continue to increase, causing other changes in the thermal, dynamical, and chemical structure of the stratosphere. These changes could alter the “expected” recovery of stratospheric ozone by a variety of mechanisms. For example, the upper stratosphere is expected to continue to cool due to the continued increase of CO$_2$. This cooling will slow the rate of gas-phase reactions that destroy ozone, and hence increase ozone concentrations [e.g., Haigh and Pyle, 1979; Brasseur and Hitchman, 1988, Shindell et al., 1998; Rosenfield et al., 2002].

Increases in N$_2$O and CH$_4$ could also impact the recovery of ozone by increasing nitrogen and hydrogen ozone-loss cycles [e.g., Randeniya et al., 2002; Rosenfield et al., 2002; Chipperfield and Feng, 2003; Portmann and Solomon, 2007]. Increases in GHGs have also been linked to changes in stratospheric transport that could impact the ozone recovery [Waugh et al., 2009; Li et al., 2009].

Projections of the ozone evolution in the 21st century use models that couple stratospheric chemistry and climate. Until WMO [2007] global ozone projections were made primarily with two-dimensional (2D) models, most of which did not include coupling between future temperature changes and the chemistry. Some projections were made with 2D models including this coupling [e.g., Rosenfield et al., 2002; Chipperfield
and Feng, 2003; Portmann and Solomon, 2007], however these models did not fully
capture circulation changes due to changes in wave driving from the troposphere or
changes in the polar vortices. More recently, three-dimensional models that include full
representations of dynamical, radiative, and chemical processes in the atmosphere, and
the couplings between these processes, have been developed, and these “chemistry-
climate models” (CCMs) have been used to make projections of ozone through the 21st
century [e.g. Austin and Wilson, 2006; Eyring et al., 2007; Shepherd, 2008].

While there have been detailed analyses of the simulated ozone in these CCMs
there has been rather limited quantitative attribution of these ozone changes to the
different mechanisms. Although several studies have attributed increases in upper
stratospheric ozone and decreases in lower stratosphere ozone to cooling and circulation
changes respectively [e.g., Eyring et al., 2007; Shepherd, 2008; Li et al., 2009], the
relative role of the different mechanisms has not been quantified. Newchurch et al.
[2003] examined 10 years of HALOE observations to attribute changes in ozone to
different mechanisms, however it was limited by the time period and available
observations of trace gases. Quantitative attribution has been performed for some CCMs
with simulations using either fixed GHGs [e.g., WMO, 2007] or fixed ODSs [e.g., Waugh
et al., 2009]. However, such analysis does not isolate the relative role of different GHG-
related mechanisms in causing changes in ozone. This attribution is needed to understand
exactly how changes in different GHGs will impact stratospheric ozone. There are often
multiple mechanisms by which an increase in a GHG can impact ozone, and the sign of
the ozone changes are not necessarily the same for each mechanism. Without knowledge
of the relative role of different mechanisms it is difficult to know how ozone projections
will change for different GHG scenarios (e.g., whether the GHG impact on ozone will simply scale with GHG concentrations). This is important as the recent CCM projections of the 21st century have all used the same GHG scenario [Eyring et al., 2007], and there have not been comparisons of projections for different scenarios (other than the unrealistic case of fixed GHGs).

Here we use multiple linear regression (MLR) to estimate the relative contribution of changes in halogens, temperature, reactive nitrogen (NOy), and reactive hydrogen (HOx) to changes in the simulated ozone from the NASA Goddard Earth Observing System Chemistry-Climate Model (GEOS CCM) [Pawson et al., 2008]. We consider simulations using two different scenarios of future GHG emissions: The IPCC (2001) A1b scenario that has been used in most recent CCM simulations and the A2 scenario which has larger increases in all GHGs. Even though there are significant differences in the GHG concentrations in the latter half of the 21st century, the ozone changes in these two simulations are very similar. The MLR indicates that the net changes in upper stratospheric ozone are similar because of the compensating effects of larger cooling and larger abundances of reactive nitrogen and hydrogen in the simulation with larger GHGs changes.

The model, simulations and evolution of ozone in the GEOS CCM simulations are described in the next Section. The simulated changes in ozone and quantities that can impact ozone are described in Section 3. Methods used in the analysis are presented in Section 4. Then in Section 5 we quantify the relative contribution of different
mechanisms to ozone changes in the upper stratosphere. Section 6 compares the results to a fixed halogen simulation and concluding remarks are given in Section 7.

2 Model

We consider here GEOS CCM [Pawson et al., 2008] simulations of the past (1960-2004) and future (2000-2100). The past simulations use the observed Hadley sea surface temperatures (SST) and sea ice data set from Rayner et al. [2003], while the future simulations use SST and sea ice data from AR4 integrations of the NCAR Community Climate System Model, version 3 (CCSM3) for both the IPCC [2001] A1b or A2 GHG scenario. Observed surface concentrations of GHGs and halogens are used for past simulations. Future simulations use the A1b or A2 scenario for surface concentrations of GHGs and the WMO [2003] Ab scenario for surface concentrations of halogens. The time series of the surface concentrations of the GHGs and total chlorine, normalized by their 1960 values, are shown in Figure 1a. The two GHG scenarios are fairly similar until about 2040, when the A2 scenario shows faster increases of CO₂ and N₂O. CH₄ continues to increase in this scenario whereas it peaks around 2050 in the A1b scenario.

Comparisons of the simulated temperature, ozone, water vapor, and other constituents with observations have been discussed in Pawson et al. [2008], Eyring et al. [2006, 2007], and Oman et al. [2008]. These studies have shown that GEOS CCM performs reasonably well compared to observations. Two noted deficiencies are a high
bias in total O\textsubscript{3} at high latitudes when chlorine loading is low (in the 1960s) and the late break up of the Antarctic polar vortex [Pawson et al., 2008].

There is a 5 year overlap (2000-2004) in the above two simulations. In the analysis presented below we join the simulations together in January 2001 to form a single time series from January 1960 to December 2099. We use “A1b” to denote the combination of the first reference past simulation (P1) and the A1b future simulation, and “A2” for the combination of the second reference past (P2) and A2 future simulation. The P2 simulation is a second ensemble member of P1, varying only in initial conditions [Oman et al., 2009]. A small discontinuity at January 2001, apparent in the time series for some quantities at some locations, does not impact results presented here. Below when we refer to a single simulation we are referring to the composite past and future simulations joined in January 2001.

3 Modeled Changes 1960 to 2100

Before examining the mechanisms responsible for ozone changes, we examine the changes in ozone and the quantities that can impact ozone changes in the GEOS CCM simulations, focusing on the long-term changes between 1960 and 2100 for the two simulations. Evolution of the 60\degree S-60\degree N average total column ozone and the partial columns above and below 20 hPa is similar for the A1b (solid) and A2 (dashed) simulations (Figure 1b).

In both, column ozone (black curves) decreases from 1960 to around 2000, and
then increases back to values similar to 1960 in 2100. This evolution of total column ozone is qualitatively similar to that of the negative of the tropospheric total chlorine (see Figure 1a), except the total chlorine peaks a few years earlier and has not quite returned to 1960 values by 2100. Although the extra-polar total column ozone in 2100 is similar to that in 1960s this is not necessarily the case for the ozone mixing ratio at a given location. In general, upper stratospheric ozone in the 2090s exceeds the 1960s values whereas the opposite is true for lower stratospheric ozone. This can be seen in the evolution of partial columns of ozone above and below 20 hPa, see Figure 1b (note that 80 DU was added to partial column above 20 hPa for graphical purposes).

Further details of the differences in long-term evolution are shown in Figures 2a and b, which show the change in decadal-averaged ozone between 1960s and 2090s for the (a) A1b and (b) A2 simulations. Here, and below, “1960s” ozone refers to the ozone averaged over the years 1960 to 1969, and “2090s” ozone is the average from 2090 to 2099. These plots show that in both simulations the decadal-averaged 2090s extra-polar ozone is larger than that in the 1960s in the upper stratosphere, similar to 1960s in the mid stratosphere, and less than 1960s in the lower stratosphere.

As discussed in the Introduction, a number of mechanisms can influence the evolution of ozone concentrations in the stratosphere. To help understand the changes in ozone between the 1960s and 2090s we show in Figures 2c-l the change between 1960s and 2090s in several quantities that influence ozone. As shown in Figures 2c and d, equivalent effective stratospheric chlorine (“EESC”; where EESC = Cl_y + α Br_y, with α = 5) in 2090s has returned to values similar to those in the 1960s in the lower stratosphere, and is only around than 0.3 to 0.4 ppb larger in the upper stratosphere.
(compare to the peak EESC values of around 3-4 ppb in 2000). (We use $\alpha = 5$ in the
definition as Daniel et al. [1999] show this is an appropriate value for the upper
stratosphere, which is the focus of this study.) As a result, changes in EESC only make a
minor contribution to the 1960 to 2100 changes in ozone (see below). This is not
necessarily the case, however, for temperature, $\text{NO}_y$, $\text{HO}_x$, and residual vertical velocity.

In both simulations there is stratospheric cooling (Figures 2e,f), associated primarily with
increasing concentrations of GHGs. The A2 simulation shows the largest cooling
consistent with the higher GHG concentrations in this scenario (cf., Figure 1a). This
larger cooling in the A2 simulation alone causes slower destruction of ozone and larger
increase in ozone compared to the A1b simulation. However, as discussed above, the net
ozone is similar in the A1b and A2 simulations implying that other compensating
changes in ozone are occurring.

Two other mechanisms for changes in ozone concentrations are changes in
nitrogen and hydrogen ozone-loss cycles. Figures 2g-j shows that the magnitude of
changes in $\text{NO}_y$ and $\text{HO}_x$ between 1960s and 2090s are different in the A1b and A2
simulations, with a larger increase in upper stratospheric $\text{NO}_y$ and $\text{HO}_x$ in the A2
simulation (again, consistent with higher GHG concentrations in this scenario, see Figure
1a). It is important to note that changes in $\text{HO}_x$ and $\text{NO}_y$ do not simply follow changes in
$\text{CH}_4$ and $\text{N}_2\text{O}$, respectively. This can be seen by comparing Figures 2g,i with Figure 1a:
There are negative changes in some areas in $\text{NO}_y$ and $\text{HO}_x$ from 1960s-2090s despite
large increases in $\text{N}_2\text{O}$ and $\text{CH}_4$. The difference between $\text{HO}_x$ and $\text{CH}_4$ trends is because
methane oxidation is not the only source of stratospheric $\text{H}_2\text{O}$, changes in the tropical
tropopause cold point also influence stratospheric $\text{H}_2\text{O}$ [See Oman et al., 2008]. $\text{HO}_x$
formation can be influenced additionally by changes in ultra-violet radiation and ozone concentration. NO\textsubscript{y} - N\textsubscript{2}O trend differences occur because the loss of NO\textsubscript{y} is influenced by temperature [Rosenfield and Douglass, 1998] and also could be affected by circulation changes.

Changes in transport also influence the ozone evolution, and Figures 2k and 1 show the change in residual vertical velocity, as a proxy for circulation changes. There is a similar increase in the tropical vertical velocity between the 1960s and 2090s in the two simulations, with a slightly larger change in the A2 simulation.

In summary, Figure 2 shows that there are larger changes in temperature, NO\textsubscript{y}, and HO\textsubscript{x} in the A2 simulation, but the ozone change is similar in the two simulations. This suggests compensating ozone changes due to different mechanisms, which is quantified below.

4 Linear Regression Analysis

We wish to estimate the contribution of the different mechanisms to the simulated changes in ozone. The principal analysis method used to do this is multiple linear regression (MLR). For a given location and time, MLR is applied to determine the coefficients \( m_x \) such that

\[
\Delta O_3(t) = \sum_j m_{x_j} \Delta X_j(t) + \epsilon(t),
\]

where the \( X_j \) are the different quantities that could influence ozone, the coefficients \( m_x \),
are the sensitivity of ozone to the quantity $X$, i.e., $m_x = \partial O / \partial X$, and $\epsilon$ is the error in the fit. MLR analysis has been extensively applied to observations or simulations to isolate a long-term linear trend in ozone (and more recently long-term variations in ozone correlated with EESC) (e.g. WMO [2007] and references therein).

To apply equation (1) we need to decide which mechanisms we wish to isolate, and the quantities $X_j$ that are the “proxies” for these different mechanisms. In the MLR calculations presented below we focus on ozone-changes due to changes in halogen, nitrogen, and hydrogen ozone-loss cycles as well as changes in temperature. To do this four explanatory variables ($X_j$) are used in (1): EESC, reactive nitrogen ($NO_x = NO + NO_2 + NO_3 + 2(N_2O_5) + HNO_3 + HO_2NO_2 + ClONO_2 + BrONO_2$), reactive hydrogen ($HO_x = OH + HO_2$), and temperature ($T$). Each term on the right hand side of the equation (1) then gives the “contribution” of the response in ozone due to a change in $X$, and the role the corresponding mechanism plays in the ozone evolution (i.e., $m_{EESC}\Delta EESC$ is the contribution due to changes in EESC, and the role of changes in halogen ozone-loss cycles). We chose $HO_x$ as an explanatory variable rather then $H_2O$ even though it is a shorter lived species to address feedbacks which are discussed in section 6 which would not be seen using $H_2O$.

Rather than using the above four quantities as explanatory variables $X$ in the MLR analysis, an alternative approach would be to use the surface concentrations of the ODSs and GHGs as the independent variables $X$. Stolarski et al. [2009] used this approach when examining temperature changes in the GEOS CCM simulations considered here. Also, Shepherd and Jonsson [2008] used ODSs and CO$_2$ to separate their impact on temperature and ozone changes but could not quantify the impact of other
GHGs, although they are likely to have a smaller impact. However, as discussed above, changes in HO_x and NO_y do not simply follow changes in CH_4 and N_2O, respectively, and regressing against CH_4 and N_2O will not necessarily isolate the role of changes in the hydrogen and nitrogen cycles in the response of ozone. Furthermore, the time series of CO_2 and N_2O are not independent in terms of correlation for either scenario, and neither are CO_2 and CH_4 for the A2 scenario (see Figure 1). This means that the MLR could not separate the impact of these fields.

The model output used in the MLR analysis is from instantaneous output from the 1st day of each month since not all variables were saved as monthly averages, however using monthly mean data should not materially affect the results. This analysis was done for individual months as well as annual averages. Here, we focus on presenting results calculated using annual averages. Thus we examine interannual and longer timescale variations in ozone. The above MLR analysis presented below uses all 140 years of the GEOS CCM simulations to determine the coefficients m_x. Calculations using shorter time periods (i.e. different start or end dates) show some sensitivity to the period used (e.g., if the start date is between 1960 and 1990 and the end date between 2050 and 2100 there is some variation in the coefficients).

There are several complications with the above linear regression approach. First, other mechanisms that are not considered in the regression (e.g., transport) could play a role. Second, significant correlations can exist between the temporal variations of the quantities, i.e., the quantities are not necessarily independent. Third, a high correlation between ozone and a quantity does not show causality, as ozone could be causing the quantity to change, or changes in another quantity could be causing both ozone and the
quantity of interest to change in a correlated way. Temperature and ozone in the upper
stratosphere is an example of this third complication: Changes in ozone cause, through
changes in short-wave heating, changes in temperature. At the same time, changes in
temperature cause, through changes in reaction rates, differences in the response of
ozone. Also, the relationship between the variables we use and ozone may not be linear.
Because of the above complications caution must be applied when interpreting the MLR
results presented below. Additional discussion and analysis of these issues is included
below.

5 Relative Contributions to Ozone Changes

We now use the MLR analysis described in Section 4 to quantify the role of
different mechanisms in causing the ozone changes in the A1b and A2 simulations. We
first examine the ozone evolution in the tropical upper stratosphere. As discussed above,
the simulated upper stratospheric ozone in the 2090s is greater than in the 1960s.
Examples are shown in Figures 3a and 3b, where the simulated evolution of annually
averaged ozone over 10°S-10°N, at 2.9 hPa for the A1b and A2 simulations, respectively,
are shown (black curves). This shows that the ozone decreases rapidly from 1960 to
2000, and then increases, at roughly the same rate, back to 1960s values by the 2030s.
The ozone continues to increase, although at a slower rate, and by the end of the century
the ozone is significantly higher (≈ 20%) than in the 1960s.

From the MLR analysis it is possible to estimate the contribution of different
mechanisms to the changes in ozone. Specifically, the coefficients $m_x$ from equation (1) are multiplied by the simulated change in each quantity $\Delta X$ to determine the contribution to the change in ozone (i.e. $m_{EESC} \Delta EESC$ is the contribution due to changes in EESC). The individual “contributions” for each quantity are shown in Figure 3c for A1b and Figure 3d for A2, and the ozone calculated from the sum of these contributions added to the mean ozone value (dotted black curves) are shown as the magenta curves in Figures 3a and 3b. There is excellent agreement between this “reconstruction” and the simulated ozone change. In the A1b simulation the long-term evolution of ozone at 2.9 hPa is dominated by changes in EESC (red curve) and T (blue curve), with negligible contributions from variations in NO$_y$ (orange curve) and HO$_x$ (green curve), see Figure 3c. The situation is somewhat different for the A2 scenario, where there is a larger trend in T, NO$_y$, and HO$_x$ at this level and changes in NO$_y$ and HO$_x$ now contribute to the ozone change. However, the decrease in O$_3$ due to the increase in NO$_y$ and HO$_x$ is canceled out by the larger increase due to the larger T trend, and the net O$_3$ change in A2 is similar to that of A1b.

Figures 3a and 3b show that the ozone reconstruction from the MLR analysis using T, EESC, NO$_y$, and HO$_x$ reproduces the simulated ozone evolution in the tropics at 2.9 hPa. However, this good agreement may not apply throughout the stratosphere. To assess how well the model ozone variability is explained by the MLR analysis the square of the correlation coefficient between the MLR reconstruction and simulated ozone is shown in Figure 4, for (a) the original time series, and (b) a filtered time series with low frequency variability removed. Since significant autocorrelation exists over many locations in the original time series we focus on the time series in Figure 4b which does
not have significant autocorrelations. Figure 4b shows that the fit between the MLR analysis and simulated ozone is very good in the extra-polar upper stratosphere (e.g., in the tropical upper stratosphere over 90% of the interannual variability is explained by the MLR analysis), but the fit is a lot poorer in polar regions and in the middle and lower stratosphere. This poorer fit is most likely due to the larger role of transport, which is not explicitly accounted for in the MLR analysis. Because of the above we focus our MLR analysis on ozone changes in the extra-polar upper stratosphere.

The analysis at 2.9 hPa indicates that changes in NO$_y$ and HO$_x$ make negligible contributions to ozone changes for the A1b simulation, but NO$_y$ and HO$_x$ do make significant contributions for the A2 simulation. However, the contributions of the different quantities vary with altitude. This is illustrated in Figures 3e-h which shows the contributions for 0.9 hPa and 5.6 hPa. (The simulated ozone and MLR reconstruction are not shown as the evolution and agreement is similar to that for 2.9 hPa.) At 0.9 hPa (Figures 3e,f) HO$_x$ related ozone loss is more important than at 2.9 hPa. This is especially evident in the A2 scenario (Figure 3f) where there is a much larger CH$_4$ trend yielding a larger HO$_x$ trend. The larger HO$_x$ related ozone loss is again offset by larger T contributions. In contrast to 0.9 hPa, NO$_y$ related ozone loss is important at 5.6 hPa for the A2 scenario (Figures 3h). In the A1b simulation NO$_y$ variations contribute to year to year variability but not to the long term trend (Figure 3g), whereas in the A2 simulation variations in NO$_y$ contribute to the long-term behavior (Figure 3h). The trend due to increased NO$_y$ results in an ozone decrease of 0.5 ppm from the 1960s to the 2090s. As with the larger changes in T and HO$_x$ at 0.9 hPa, the larger changes in T and NO$_y$ in the A2 simulation at 5.6 hPa cause larger changes in ozone, but these changes are of opposite
sign and the net change in ozone in A2 is similar to that in the A1b simulation.

Close inspection of Figures 3c-h shows the relative contributions of the different mechanisms to changes in ozone vary with time. This is quantified in Figure 5 which shows the vertical variation of the changes in tropical ozone and individual contributions of different mechanisms for the A1b (solid curves) and A2 (dashed curves) simulations, over (a) 1960-2000, (b) 2000-2100, and (c) 1960-2100.

Over the 1960 to 2000 period both simulation have identical forcings and only vary by the initial conditions, so very similar changes occur in each simulation. The largest change in ozone (-0.6 ppm) occurs in the upper stratosphere at about 3 hPa. This change is mostly caused by the increasing levels of EESC (-1.1 ppm) and is somewhat offset by the decreasing temperature (0.5 ppm). The cooling of the upper stratosphere is mostly due to increases in GHGs like CO₂ but also due to decreased ozone (see Section 6). Over the last forty years, NOₓ and HOₓ increases make an insignificant contribution to ozone changes in the upper stratosphere. The ozone changes in the lower stratosphere are much smaller than in the upper stratosphere, and are discussed briefly below.

The ozone change over the 21st century (2000s to 2090s) is very different than from 1960 to 2000: Upper stratospheric ozone increases over this period due to decreases in EESC and decreases in T (Figure 5b). There are very similar ozone evolutions for the two different scenarios, but the contributions from the different mechanisms vary. As discussed above, there is a larger positive increase in upper stratospheric ozone due to temperature changes in A2 than in A1 due to larger temperature decreases in A2. These increases are almost entirely balanced by increased loss from NOₓ and HOₓ increases, with losses due to NOₓ largest between 10 and 3 hPa and those due to HOₓ largest above
5 hPa (consistent with results of Portmann and Solomon, 2007), resulting in very similar ozone evolutions.

Figure 6a shows that the $m_X$ calculated from the two simulations are very similar, implying that the differences in contributions in the two simulations are due to differences in the temperature and composition (Figure 6b) rather than differences in the sensitivities. The $3\sigma$ confidence intervals of the sensitivities are also shown in Figure 6a (thin curves), and these indicate that uncertainties with this analysis are generally largest in the lower portions of the stratosphere while in the upper portions, the confidence intervals are much smaller with, the largest are associated with the calculated NO$_y$ sensitivities. The cooling with respect to 2000s values in A2 is significantly larger (2 to 4 K, see Figure 6b), causing a larger increase in middle and upper stratospheric ozone. The differences in NO$_y$ and HO$_x$ are also larger in the A2 simulation (Figure 6b), consistent with the increased levels of N$_2$O and CH$_4$ respectively, shown in Figure 1a. As discussed above the increases in NO$_y$ and HO$_x$ are not necessarily the same as those in N$_2$O and CH$_4$. For example, the increase in middle-upper stratospheric NO$_y$ is much smaller than the increase in tropospheric N$_2$O, due to cooling in the middle and upper stratosphere, which increases NO$_y$ loss [Rosenfield and Douglass, 1998]. Also, the NO$_y$-related ozone loss rates are only weakly dependent on T [e.g., Jonsson et al., 2004], so the temperature decrease does not cause a significant difference in this loss.

The changes over the complete period of the simulations (1960s to 2090s) are shown in Figure 5c. These are similar to the 21st century change (Figure 5b), except there is only a small contribution for EESC over the complete period, and ozone changes are dominated by the T changes.
Although we focus here on upper stratospheric ozone changes, we briefly comment on the decrease in tropical lower stratospheric ozone (Figure 5). Although the MLR analysis attributed most of this decrease to changes in $T$, the ozone responses are primarily due increases in tropical upwelling. An increase in tropical upwelling in the lower stratosphere will, if no other changes, result in a decrease in ozone. Furthermore, increases in the upwelling and decreases in ozone will both lead to a decrease in temperature (through adiabatic cooling and reduced heating, respectively), and hence produce correlated changes in ozone and temperature. The larger upwelling increases and tropical lower stratospheric ozone decreases in A2 are consistent with larger increases in SSTs within the A2 simulation, see Oman et al. [2009]. The relationship between upwelling and decreases in tropical lower stratospheric ozone concentrations have been the focus of some recent studies including Lamarque et al. [2008] and Li et al. [2009].

The ozone changes and contributions from relative mechanisms for middle latitudes are similar to that for the tropical stratosphere, e.g., compare Figures 7 and Figure 5. In the midlatitudes of both hemispheres (30-50° N and S) there is a decrease in upper stratospheric ozone from the 1960s to 1990s due to increases in EESC (with a small compensating increase due to cooling), while the upper stratospheric ozone is projected to increase over the 21st century due to increases in EESC and further cooling (Figure 7). As in the tropics, the larger ozone increase in the A2 simulation is due to larger cooling, which is canceled by larger ozone losses related to larger changes in NO$_y$ and HO$_x$ in the A2 simulation.
6 Fixed Halogen Simulation

Two questions that arise when using the MLR analysis are: how representative are the calculated sensitivities (i.e. can they be applied to other simulations) and can the MLR represent some of the feedbacks that occur in the climate system (i.e. separating the effect of \( \text{CO}_2 \) on \( T \) from that due to \( \text{O}_3 \) loss from EESC. To examine these issues we use an additional GEOS CCM simulation with the same SSTs and GHGs as the A1b simulation, but with halogens fixed at 1960 levels. As discussed in Waugh et al. [2009], the difference in ozone between the A1b and "fixed-halogen” simulations is the change in ozone due to EESC, with this EESC-induced change including both the direct EESC chemical impact and any ‘indirect’ feedbacks.

We first test whether the regression coefficients (sensitivities) \( m_X \) calculated above can be used to reconstruct the ozone in the fixed-halogen simulation. As above, we multiply the coefficients by the change in each quantity (e.g., EESC, \( T \), \( \text{NO}_y \), \( \text{HO}_x \)) to determine the individual contributions to the ozone change, and then compare the sum of these contributions with the simulated ozone change. Figure 8a shows the evolution of tropical upper stratospheric (10°S-10°N at 2.9 hPa) ozone from the A1b and fixed-halogen simulations, together with the reconstructed ozone (using the coefficients \( m_X \) calculated from the A1b simulation for both reconstructions). There is good agreement between the simulated and reconstructed ozone for the fixed-halogen simulation, showing that the coefficients calculated here can be applied to different simulations.

We now examine the direct and indirect EESC impact on ozone. Waugh et al. (2009) discussed the difference in ozone between the A1b and “fixed-halogen”
This net change in ozone is due to EESC, with this EESC-induced change including both the direct EESC chemical impact and any 'indirect' feedbacks. Equation (1) can also be used to separate different effects if the difference between the A1b and fixed-halogen simulation is used for $\Delta X$. This is opposed to using the temporal change in a single simulation ($\Delta T = \text{difference in } T \text{ due to changes in } EESC$, so that $m_T \Delta T$ reflects the change in $O_3$ due to $T$ feedback). Figure 8b compares the difference in $O_3$ at 2.9 hPa between the A1b and fixed-halogen simulation with the contributions due to differences in EESC, $T$, $NO_y$, and $HO_x$, as well the sum of these contributions. There is again good agreement between the actual and reconstructed $O_3$ (solid and dashed black curves nearly overlain). The direct impact of EESC changes (red curve) dominates the change in $O_3$. The blue curve represents, the negative feedback due to temperature change from the direct $O_3$ loss caused by EESC, and it is significant. For example, in 2000 there is a total $O_3$ loss of around 1.0 ppm which is a balance between a 1.2 ppm loss due to EESC chemical loss and a 0.2 ppm increase due to the cooling associated with this $O_3$ loss.

At 0.9 hPa there is not only a negative feedback from cooler temperatures, but also a negative feedback from $HO_x$ (Figure 8c). This occurs as Cl and HCl destroy $HO_x$ to form $H_2O$ and $O_2$ [Brasseur et al., 1999].

\[ Cl + HO_2 \rightarrow HCl + O_2 \]

\[ OH + HCl \rightarrow Cl + H_2O \]

Net: \[ OH + HO_2 \rightarrow H_2O + O_2 \]
As a result of the temperature and HOx feedback the net ozone loss at 0.9 hPa is around 50% less than that expected from destruction due to EESC. Much smaller feedbacks are calculated at 5.6 hPa, and the direct loss due to EESC is very close to the modeled ozone loss (Figure 8d).

6.1 Chemical Box Model Analysis

As a further test of the robustness of the above MLR results we compare the coefficients $m_x$ obtained from the MLR analysis with the sensitivities obtained from chemical box model calculations [Kawa et al., 1997]. In the upper stratosphere, ozone is close to photochemical steady state, and chemical box model calculations can be used to estimate the sensitivity of ozone to the changes in different inputs.

To estimate the ozone sensitivities a reference box model calculation is first performed using the mixing ratios of chemical species, overhead ozone, and temperature for a particular location and time from the GEOS CCM simulation using the A1b scenario. In this case we used an average 1960-2100 value to represent what was calculated in the MLR analysis. Then a series of perturbation calculations is performed, where a single quantity (e.g. temperature) is increased and decreased from its reference value. For EESC, Cly was perturbed $\pm$ 0.1 ppb and Bry perturbed $\pm$ 1 ppt; temperature was perturbed $\pm$ 5K; and NOy was perturbed $\pm$ 1 ppb. Each simulation was run for 20 days, by which time the solution has closely approached steady state. The resulting change in ozone gives an estimate of the sensitivity of ozone to changes in this quantity, e.g. $\Delta O_3/\Delta X$ provides an estimate of sensitivity of ozone to changes in variable $X$. This
sensitivity can then be directly compared with the coefficients $m_x$ from equation (1).

Figure 6a shows the variation in calculated steady-state ozone to changes in $T$, EESC, and $\text{NO}_y$ (colored X's) for reference calculations based on simulated fields at several levels between 6.9 and 0.9 hPa for July at 2°N. Although we use annual average values for the MLR analysis, tests using other months in the chemical box model produced only small changes. These values are generally in very good agreement with the coefficients from the MLR analysis. Some disagreement is seen at 5.6 and 6.9 hPa with slightly higher EESC, $\text{NO}_y$, $T$ sensitivities from the chemical box. $\text{NO}_y$ sensitivities are in general slightly larger in the box model than calculated in the MLR analysis. It is not clear at this point why there are some differences seen in the sensitivities between the MLR analysis and the box model. Even though there is some disagreement, overall the 2 methods show a similar picture and give us confidence in the MLR-based attribution of the relative contributions of different factors to the changes in ozone.

7 Conclusions

In this study we have quantified the contribution of different mechanisms to changes in upper stratospheric ozone from 1960 to 2100 in GEOS CCM simulations, and separated the direct and indirect impacts of EESC on ozone. Simulations using two different GHG scenarios (A1b and A2 from IPCC 2001) were considered, and even though there are significant differences in the GHG concentrations in the latter half of the 21st century, there is a very similar increase in upper stratospheric ozone over the 21st century. Isolation of different mechanisms using multiple linear regression (MLR) shows
that the similar ozone evolution is because of compensating effects of different mechanisms. In the A1b scenario the increase in ozone is caused by decreases in halogenated ozone-depleting substances and cooling, which is largely due to increased greenhouse gases, which alters the kinetics rate of ozone destruction, with the two mechanisms making roughly equal contributions to the ozone change. Changes in abundance of reactive nitrogen and hydrogen play only a minor role in long-term changes in the A1b scenario. In contrast, in the A2 simulation there are significant increases in NOy and HOx that cause a long-term negative decrease in ozone. These decreases are largely offset by a larger positive contribution from cooler temperatures, and the ozone evolution in A2 ends up being very similar to that in A1b.

The MLR analysis, together with a fixed halogen simulation, was also used to separate the direct chemical impact and indirect feedbacks of EESC on ozone. The indirect impact and mechanisms were shown to vary with altitude. At 5.6 hPa the indirect impacts are small, but make significant contributions at 2.9 and 0.9 hPa. At 2.9 hPa there is a negative feedback due to temperature increases from the direct O3 loss due to EESC chemistry. This feedback is around 15% the direct EESC impact. At 0.9 hPa there are negative feedbacks from temperature and from changes in HOx due to changes in EESC, and the sum of these are around 50% the direct EESC impact.

The results presented above are based on simulations from a single model, and it will be important to consider simulations from other models. Preliminary application of MLR method to A1b simulations from several of the CCMs examined in Eyring et al. [2007] yields very similar results to those presented here for the GEOS CCM (not shown). In particular, the sensitivities are very similar, and differences in ozone
evolution can be related to differences in simulated EESC, T, and NO\textsubscript{y} fields. As well as considering other models it will be important to consider a wider range of GHG scenarios. The very similar ozone evolution for the A1B and A2 GHG scenarios considered here might lead one to think that the ozone evolution would be similar for all likely GHG scenarios. However, the similarity between the A1B and A2 scenarios considered here occurs by the chance cancellation of differences in temperature and nitrogen and hydrogen loss cycles, and this is unlikely to be the case for all possible scenarios (e.g., for the A1FI and B1 scenarios). It will therefore be important to perform simulations with a wider range of GHG scenarios when making projections of stratospheric ozone.

This analysis of models using MLR raises the possibility of using MLR analysis to separate the contributions of changes in EESC and T to observed ozone changes. One difficulty with applying this method to data is the availability of simultaneous time series of observed ozone, EESC, T and other quantities used in the MLR analysis. Another issue is the need to consider time periods over which the different quantities have sufficiently different temporal variations to be isolated in the MLR analysis. For the 140 years of simulation considered here this is possible for EESC and T, but this may not be the case for shorter periods and more analysis is need to determine over which period data will be required to perform this analysis.

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9 References


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Figure Captions

Figure 1. Temporal Variation of (a) surface GHGs (solid – A1b and dashed – A2) and halogens and (b) total or partial column ozone averaged between 60°S and 60°N, between 1960 and 2100 (solid – A1b and dashed – A2).

Figure 2. Difference in ozone (ppm) between 1960s to 2090s (2090s-1960s) for (a) annual for A1b scenario, (b) annual for A2 scenario. Also, for same time period changes in (c) EESC (ppb) for A1b, (d) EESC (ppb) for A2, (e) Temperature (K) for A1b, (f) Temperature (K) for A2.

Figure 2 (cont.). Difference in annual NOy (ppb) between 1960s to 2090s (2090s-1960s) for (g) A1b scenario, (h) A2 scenario, (i) HOx (ppt) for A1b, and (j) HOx (ppt) for A2, (k) w' (mm/s) for A1b, (l) w' (mm/s) for A2.

Figure 3. Evolution of annual average ozone at (a) 2.9 hPa, for A1b and (b) 2.9 hPa, for A2, 10°S-10°N. Also shown is the contribution of different mechanisms for (c,d) 2.9 hPa, (e,f) 0.9 hPa, and (g,h) 5.6 hPa for each scenario.

Figure 4. Annual correlation coefficient squared for the (a) original model ozone time series and MLR fit and, (b) a filtered time series with low frequency variability removed by applying a 1:2:1 filter iteratively 30 times to each quantity.
Figure 5. Vertical variation of changes in ozone (solid black curve) and individual contribution of different mechanisms for annual averages over the tropics. The changes are for (a) 1990s-1960s P1 (solid curve) and P2 (dashed curve), (b) 2090s-2000s A1b (solid curve) for A2 (dashed curve) scenario, 2090s-1960s A1b (solid curve) for A2 (dashed curve) scenario.

Figure 6. Sensitivities (a) of ozone to various factors (thick curves) and 3σ confidence intervals (thin curves) for annual averages over the tropics (10°S-10°N) with the overplotted X’s showing the chemical box model calculations and the 2090s-2000s change (b) in T, EESC, and NOy, and HOx divided by 100, and the contribution for A1b (solid curves) and A2 (dashed curves).

Figure 7. Vertical variation of changes in ozone (solid black curves) and individual contribution of different mechanisms for annual averages over (a,c) 30-30°S and (b,d) 30-50°N. The changes are for (a,b) 1990s-1960s P1 (solid curves) and P2 (dashed curves), and (c,d) 2090s-2000s A1b (solid curves) for A2 (dashed curves) scenario.

Figure 8. Evolution of ozone and from MLR for (a) 2.9 hPa, 10°S-10°N for A1b simulation and for a fixed-halogen (Low Cl) simulation (upper curve, with the fit from A1b MLR sensitivities). Difference in ozone between the A1b and fixed-halogen simulation (solid black curve), and contributions due to EESC (red curve), T (blue), NOy (orange), and HOx (green) as well as the sum of these contributions (dashed black curve) for (b) 2.9 hPa, 10°S-10°N. Also shown are the individual contributions at (c) 0.9 hPa.
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Figure 2 (cont.). Difference in annual NO$_y$ (ppb) between 1960s to 2090s (2090s-1960s) for (g) A1b scenario, (h) A2 scenario, (i) HO$_x$ (ppt) for A1b, and (j) HO$_x$ (ppt) for A2, (k) $w^*$ (mm/s) for A1b, (l) $w^*$ (mm/s) for A2.
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