Impact of Volcanic Aerosols on Stratospheric Ozone Recovery

Short/Running Title: Impact of volcanic aerosols on stratospheric ozone

Vaishali Naik¹, Larry W. Horowitz¹, M. Daniel Schwarzkopf¹, and Meiyun Lin¹,²

¹NOAA Geophysical Fluid Dynamics Laboratory, Princeton, NJ 08540
²Program in Atmospheric and Oceanic Sciences, Princeton University, Princeton, NJ 08540

Corresponding Author: V. Naik (Vaishali.Naik@noaa.gov)

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Key Points:

- Elevated volcanic aerosol in the RCP4.5 and RCP8.5 scenarios lead to earlier ozone recovery.
- Volcanic aerosols contribute to uncertainty in stratospheric ozone recovery
- Projections of stratospheric ozone should consider volcanic aerosols
Abstract

We use transient chemistry-climate model simulations over the 2006-2100 time period to show how the influence of volcanic aerosols on the extent and timing of ozone recovery varies with a) future greenhouse gas scenarios (RCP4.5 and RCP8.5) and b) halogen loading. With background aerosol loadings, global mean stratospheric ozone is simulated to return to 1980 levels around 2050 in the RCP8.5 scenario but remains below 1980 levels throughout the 21st century in the RCP4.5 scenario. In contrast, with elevated volcanic aerosol loadings, ozone column recovers more quickly to 1980 levels, with recovery dates ranging from the mid-2040s in RCP8.5 to the mid-2050s to early 2070s in RCP4.5. The ozone response in both future emission scenarios is greater for moderate compared with low volcanic aerosol loadings. These responses are consistent with our current understanding of the influence of volcanic aerosols on ozone under conditions of high and low halogen loadings. For the range of aerosol loadings considered here, by 2100, the 1980-baseline adjusted global stratospheric ozone column is projected to be about 20-40% greater in RCP8.5 and 110-200% greater in RCP4.5 with elevated volcanic aerosols compared to simulations with background aerosols. The ozone response to elevated volcanic aerosols appears to be sensitive to the factor of 2.5 greater methane in RCP8.5 compared with that in RCP4.5. Our results demonstrate the substantial uncertainties in stratospheric ozone projections and expected recovery dates induced by volcanic aerosol perturbations that need to be considered in future model ozone projections.
1. Introduction

Stratospheric aerosols affect stratospheric ozone directly by affecting heterogeneous chemistry and photolysis rates and indirectly by influencing stratospheric temperature and large-scale circulation patterns [SPARC, 2006]. Recent measurements indicate that there has been a continuous increase in stratospheric aerosols over the last decade following a period (1998-2002) of “background” (non-volcanic) aerosol levels. This increase has been attributed to a series of moderate tropical volcanic eruptions [Vernier et al., 2011]. However, the impact of volcanic perturbations on the evolution of stratospheric ozone in the 21st century has not been considered in projections of long term stratospheric ozone changes using chemistry-climate models [Eyring et al., 2010a, 2013]. For example, volcanic aerosols were set to zero or to near-zero background in future climate projections conducted for the Coupled Model Intercomparison Project Phase 5 (CMIP5) [Collins et al., 2014; see their Table 12.1]. Here we explore the evolution of stratospheric ozone for the 2006-2100 time in response to two future climate forcing scenarios under three different fixed levels of volcanic aerosol loading. We highlight the contrasting effects of volcanic aerosol amounts under high (e.g., present-day) and low (e.g., future) halogen loading (e.g., Austin et al. [2013]), the differing responses to greenhouse gas abundances, and resulting influence on the timing of ozone recovery.

Volcanic eruptions enhance the background stratospheric aerosol layer, first identified by Junge et al. [1961], by injecting large amounts of sulfur dioxide (SO₂) and ash. SO₂ oxidizes to sulfuric acid (H₂SO₄) which nucleates homogeneously or condenses on existing particles to form sulfate aerosols (H₂SO₄-H₂O). Volcanic sulfate aerosols affect the Earth’s radiative balance by increasing the scattering of incoming solar radiation and enhancing the infrared absorption depending on the particle size, thus cooling the Earth’s surface and the troposphere, and warming
the stratosphere [McCormick et al., 1995]. The influence of volcanic aerosols on stratospheric ozone, particularly in the mid-latitudes, via heterogeneous chemistry is also well known, as briefly discussed below.

Observational and modeling studies conducted after the Pinatubo volcanic eruptions provided evidence of decreases in nitrogen oxides (NO$_x$ = NO + NO$_2$) and increases in reactive halogen radicals via heterogeneous chemistry on sulfate aerosols. As a result, the NO$_x$-catalyzed ozone loss is suppressed, particularly in the middle stratosphere where the NO$_x$ cycle is efficient at destroying ozone [Brasseur et al., 1999]. The reduction in NO$_x$ also limits the formation of reservoir species, such as chlorine nitrate (ClONO$_2$) and bromine nitrate (BrONO$_2$), increasing the abundance of reactive halogen (ClO$_x$, BrO$_x$), and to a lesser extent, hydrogen oxides (HO$_x$). Reactive halogen radicals are also enhanced due to heterogeneous activation on sulfate aerosols. Thus, the efficiency of ozone destruction by ClO$_x$, BrO$_x$, and HO$_x$ cycles [Wennberg et al., 1994; Lary et al., 1996; Solomon et al., 1996] is enhanced in the presence of volcanic sulfate aerosols (see Solomon [1999] for a detailed review). The net impact of enhanced volcanic aerosols in the present atmosphere is to increase ozone in the middle stratosphere and decrease ozone in the lower stratosphere, resulting in a net decrease of ozone column. The overall effect on global ozone burden has been shown to depend on the halogen loading of the atmosphere [Tie and Brasseur, 1995; Austin et al., 2013].

Multi-model projections of future ozone levels and the dates of ozone recovery to 1980 levels vary by latitude region and are dependent upon the assumed projection of well-mixed greenhouse gases (WMGGs), including carbon dioxide (CO$_2$), methane (CH$_4$) and nitrous oxide (N$_2$O), and ozone depleting substances (ODSs), and the resulting climate and stratospheric circulation changes [Pawson et al., 2014]. The possibility of significant changes in stratospheric
aerosol levels has been identified to be a key uncertainty in predicting future ozone abundance by the World Meteorological Organization (WMO) and United Nations Environment Programme (UNEP) Scientific Assessment of Ozone Depletion [Bekki et al., 2011]. In this study, we perform transient 21st century simulations with the U.S. NOAA Geophysical Fluid Dynamics Laboratory (GFDL) fully interactive chemistry-climate model (GFDL-CM3) to assess ozone recovery in response to the Representative Concentration Pathway (RCP) 4.5 and 8.5 climate forcing scenarios under three different assumptions of stratospheric aerosol loading.

2. Model and Simulations

We employ the GFDL-CM3 chemistry-climate model [Donner et al., 2011; John et al., 2012; Austin et al. 2013; Westervelt et al., 2015; Barnes et al., 2016] in this study. Transient historical (1860-2005) and future (2006-2100) simulations of CM3 were conducted in support of the Coupled Model Intercomparison Project (CMIP5) and informed the Intergovernmental Panel on Climate Change Assessment Report 5 (IPCC AR5). CM3 uses a finite-volume dynamical core on a cubed-sphere horizontal grid composed of six faces, each with a horizontal domain of 48 x 48 grid cells, denoted as C48 horizontal resolution, and 48 vertical hybrid sigma-pressure levels extending from the surface to 0.01 hPa (~80 km). The model simulates tropospheric and stratospheric gas phase and heterogeneous photochemical processes over the full model domain [Austin et al., 2013; Naik et al., 2013]; the simulated three dimensional ozone distribution influences radiation calculations. Stratospheric chemistry includes gas-phase reactions describing the HOx, NOx, ClOx, and BrOx catalytic cycles and heterogeneous reactions on solid nitric acid trihydrate (NAT) and water-ice polar stratospheric particles, and liquid binary and ternary sulfate polar stratospheric cloud (PSC) particles [Austin and Wilson, 2010]. Global mean tropospheric
volume mixing ratios of ozone depleting substances (ODSs) – including chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), halons, and bromine from very short-lived substances (VSLS; shown to be important during periods of elevated aerosol surface area) – are specified as a function of time providing a parametrized source of reactive halogens to the stratosphere [Austin et al., 2013].

Direct injection of aerosols or their precursors into the stratosphere is not considered explicitly as the stratospheric aerosol life cycle is not represented in the model. Instead, the radiative influence of stratospheric volcanic aerosols is accounted for by implementing vertically resolved spatial and temporal distributions of aerosol optical properties (monthly mean aerosol extinction, single scattering albedo, and asymmetry factor) following Stenchikov et al. [1998]. This dataset originally developed for the Pinatubo eruption based on satellite measurements by Stenchikov et al. [1998] has been extended to cover the historical time period (1850-1999) based on volcanic aerosol optical depths from Sato et al. [1993] and its updates. Volcanic aerosol surface area density (SAD) is derived from aerosol extinction centered at 1.0-μm following the relationship of Thomason et al. [1997], and is used for calculating heterogeneous reaction rates.

The historical CM3 simulations have been shown to generally reproduce well the observed total ozone column over the past several decades, except for a high bias in the tropics and southern mid-latitudes [Austin et al., 2013]. The positive bias in the southern mid-latitudes is likely due to excessive transport of ozone by the Brewer Dobson circulation from the tropics, where ozone is already high, to the mid-latitudes [Austin et al., 2013; Eyring et al., 2013]. These deficiencies in the model will most likely have minor impact on our results as our analysis focuses on relative differences. Additionally, we evaluate the response of ozone to volcanic aerosols by comparing monthly mean total ozone anomalies for the 5-year period encompassing
the Mt. Pinatubo eruption computed with historical CM3 simulations [Austin et al., 2013] against observations [Frith et al., 2013; Bodeker et al., 2005] (Figure 1). The anomalies are calculated relative to the mean over 1990-1999 period and the contributions due to quasi-biennial oscillation (QBO), El Nino Southern Oscillation (ENSO), solar cycle, and changing stratospheric chlorine and bromine have not been removed. Globally, the observations show a slow decline in monthly total column ozone after Mt. Pinatubo eruption reaching a minimum of about -8 Dobson Units (DU) in early 1993. The ensemble mean model is able to capture the observed variation in global monthly column ozone, although it has some difficulty in reproducing the observed minimum (Figure 1a). At least one ensemble member reproduces the observed global mean ozone minimum. Additionally, a simulation of the atmospheric component of CM3 (AM3) with a similar configuration as the historical CM3 simulations but nudged to NCEP-NCAR reanalysis winds over the 1980-2012 period [Lin et al., 2014; 2015] is able to better match the observed variations in global mean column ozone (blue lines on Figure 1a), suggesting that the response to Pinatubo aerosols in the free-running CM3 is strongly influenced by dynamical variability and feedbacks.

Despite depletion of stratospheric NO\textsubscript{2} in both the hemispheres after the Pinatubo eruption [Pawson et al., 2014 and references therein], observations indicate an interhemispheric asymmetry in the mid-latitude ozone response to Pinatubo aerosols with enhanced ozone loss in the Northern Hemisphere (NH) mid-latitudes and a small increase of ozone column in the Southern Hemisphere (SH) mid-latitudes [Randel et al., 1995]. Recent studies have attributed this asymmetry to enhanced ozone transport in the SH that counterbalances the aerosol-induced ozone loss [Poberaj et al., 2011; Aquila et al., 2013; Dhomse et al., 2015]. Observations show total column ozone decreases of up to 10 DU and 30 DU in December 1991 and January 1993,
respectively, in the NH mid-latitudes (Figure 1b), and about 10 DU increase after the eruption from July to December 1991 and then a sharp decline reaching a minima of -10 DU in late 1992 in the SH mid-latitudes (Figure 1c). The mean model does not reproduce variations in NH mid- latitudes, although at least one ensemble member is able to capture the column ozone decrease in December 1991 (Figure 1b). In the SH mid-latitudes, the mean model is able to reproduce variability to some extent but has difficulty in capturing the timing of the increase in ozone column immediately after the eruption (Figure 1c). Discrepancies in chemistry-climate model simulations of the interhemispheric asymmetry in the ozone response to Pinatubo have been a problem [SPARC 2010, chapter 8]. Models forced with re-analyzed meteorological fields show better skill in simulating the enhanced ozone loss in NH and the smaller ozone loss in SH pointing to the importance of dynamical forcing on ozone changes [Shepherd et al., 2014; Dhomse et al., 2015]. Indeed, the AM3 simulation nudged to NCEP-NCAR reanalysis winds over the 1980-2012 period [Lin et al., 2014; 2015] shows much better skill in reproducing the observed interhemispheric asymmetry in the ozone response to Pinatubo aerosols (blue lines on Figure 1b, c).

We analyze results from three-member ensembles of transient CM3 simulations for the 2006-2100 time period, with concentrations of WMGGs, ODSs, and short-lived species emissions, following either the RCP 4.5 [Thomson et al., 2011] or RCP 8.5 [Riahi et al., 2011] climate forcing scenarios (Table 1 and Figure 2). These ensemble members are initialized from the respective members of the historical CM3 simulation [Austin et al., 2013]. For each climate forcing scenario, we consider three fixed levels of monthly-varying stratospheric aerosol loading repeated over the 95 years of each simulation: background (BG) levels of sulfate aerosols during non-volcanic periods (represented by values for year 1999) [Morgenstern et al., 2010], periods of
weak volcanic activity (represented by year 1860), and moderate volcanic activity (represented by the historical mean (HM) over the 1860-2000 period) (Table 1). The 1860 and historical mean aerosol loadings are chosen arbitrarily from the volcanic aerosol dataset implemented in CM3 [Stenchikov et al., 1998] to denote low and moderate volcanic aerosol loadings. The simulations are denoted as RCP.X_BG, RCP.X_1860, and RCP.X_HM, where X.X represents either 4.5 or 8.5.

The global annual mean volcanic aerosol optical depth (AOD) in the visible wavelength (550 nm) in RCP.X_BG, RCP.X_1860, and RCP.X_HM simulations is 0.0005, 0.0045, and 0.013, respectively. The volcanic AOD in RCP.X_1860 is close to that observed for tropical volcanic eruptions occurring in the 2000-2010 period, while that in RCP.X_HM is similar to AOD observed for the moderate volcanic events in the mid 1980s [Vernier et al. 2011]. Annual average zonal mean volcanic aerosol SAD in the BG, 1860 and HM simulations are shown in Figure 3.

For the analysis discussed below, we average results across ensemble members to better isolate the forced response to volcanic aerosols. Stratospheric ozone column is defined here as ozone concentrations integrated above 200 hPa. For each RCP scenario, we evaluate the impact of increased volcanic aerosols by comparing the results for 1860 and HM simulations against those of the corresponding BG simulation.

3. Impact of Volcanic Aerosols on Stratospheric Ozone

3.1 Ozone Column

We first analyze the long term evolution of stratospheric ozone column relative to 1980 levels in a manner consistent with previous multi-model projections [Eyring et al., 2010b; 2013].
Figure 4 shows the 1980 baseline-adjusted time series of annual mean stratospheric ozone column from 1960 to 2100, globally and averaged over five selected latitude bands. Results are plotted for 1960-2005 from the historical simulations with time-varying stratospheric aerosols [Austin et al., 2013] and for 2006-2100 from the RCPX.X_* simulations discussed above. Values are smoothed with a 1:2:1 filter applied 30 times iteratively [see Eyring et al., 2010b; smoothing was performed 50 times for polar region] to reduce interannual variability. In the 2000-2020 timeframe, stratospheric ozone column recovery in the RCPX.X_1860 simulations (blue lines) is similar to that in the RCPX.X_BG simulations (black lines) but it is slower in the RCPX.X_HM simulations (red lines; Figure 4a). After the mid-2020s, the adjusted stratospheric ozone columns in both the RCPX.X_1860 and RCPX.X_HM simulations exceed the respective RCPX.X_BG simulations and recover to 1980 levels earlier than in the RCPX.X_BG simulations. Global stratospheric ozone column returns to 1980 levels in the RCP8.5_HM and RCP8.5_1860 simulations three to seven years earlier (2045-2049) than in the RCP8.5_BG simulation (2052), while for the RCP4.5 scenario, return dates range from 2056 to 2071 compared to RCP4.5_BG in which ozone remains below 1980 levels throughout the 21st century. By 2100, the global stratospheric ozone column relative to 1980 levels is projected to range from 0.5-3 DU in the RCP4.5 and 11-13 DU in the RCP8.5 simulations with 1860 and HM aerosol loading compared to -2.6 and 9.3 DU in the RCP4.5_BG and RCP8.5_BG simulations, respectively. The response of global mean stratospheric ozone column to elevated volcanic aerosols results from the combination of different responses in the tropics, mid-latitudes, and polar regions as discussed below.

In the tropics, the annual mean stratospheric ozone column does not recover to 1980 levels (Figure 4b) in any of the simulations; however, it is greater in RCPX.X_1860 and
RCPX.X_HM compared to the respective RCPX.X_BG simulations from about 2020 through the end of the 21st century. Previous multi-model studies [Eyring et al., 2010; 2013] attribute the non-recovery of tropical stratospheric ozone column in simulations with increasing WMGGs and declining ODSs to a combination of a) decreases in lower stratospheric ozone due to enhanced tropical upwelling from WMGG-induced warming and b) increases in middle to upper stratospheric ozone from WMGG-induced cooling that slows down ozone destruction. Elevated volcanic aerosol loading in RCPX.X_1860 and RCPX.X_HM leads to warming of the tropical lower stratosphere relative to RCPX.X_BG (not shown) due to the absorption of longwave radiation, consistent with results of geoengineering model experiments in which stratospheric sulfate aerosols are artificially enhanced [Tilmes et al., 2009; Heckendorn et al., 2009; Pitari et al., 2014]. This warming causes lower stratospheric ozone to decrease due to enhanced upwelling of ozone-poor air through the end of the 21st century. In contrast, ozone increases in the middle to upper tropical stratosphere in RCPX.X_1860 and RCPX.X_HM relative to RCPX.X_BG due to the suppression of the NOX-catalyzed ozone loss (discussed in the next section). The net effect of these opposing ozone responses is that at 2100 the annual mean tropical adjusted-stratospheric ozone column ranges from -7.9 to -6 DU in RCP4.5 and -4 to -5 DU in RCP8.5 simulations with 1860 and HM aerosol loading, a smaller decrease relative to 1980 values than the -9.2 and -6.0 DU found in the RCP4.5_BG and RCP8.5_BG simulations, respectively.

In the mid-latitudes, the RCPX.X_1860 and RCPX.X_HM projections of the adjusted-stratospheric ozone column (Figures 4c and 4d) evolve in a similar manner as that for the global mean. The ozone return dates to 1980 values are significantly earlier in RCP4.5_1860 (2062) and RCP4.5_HM (2046) than in the RCP4.5_BG simulation in the Northern Hemisphere mid-
latitudes but not in the Southern Hemisphere mid-latitudes. The ozone return dates are not statistically significantly different in the RCP8.5_1860 and RCP8.5_HM relative to RCP8.5_BG at either the northern or southern mid-latitudes. At 2100, the annual mean adjusted-stratospheric ozone column in the northern mid-latitudes is 0, 3, and 7 DU for RCP4.5 and 19, 22, and 25 DU for RCP8.5 with BG, 1860 and HM aerosol loadings, respectively. In southern mid-latitudes, the adjusted-stratospheric ozone column is 5, 10, and 12 DU for RCP4.5, and 24, 26, and 28 DU for RCP8.5 with BG, 1860 and HM aerosol loadings, respectively. Figure 4 also shows that ozone column in the mid-latitudes has greater sensitivity to the WMGG scenarios than in the tropics. This likely results from a) stronger WMGG-induced stratospheric cooling that slows down ozone loss rates in the upper stratosphere leading to enhanced ozone [e.g., Eyring et al., 2010a,b; 2013], b) a factor of 2.5 higher methane concentration in RCP8.5 [Meinshausen et al., 2011] leading to greater ozone increase in lower stratosphere and troposphere [Revell et al., 2012; Young et al., 2013], and c) greater WMGG-induced acceleration of Brewer-Dobson circulation resulting in increased stratosphere-troposphere exchange and ozone flux, particularly in the northern mid-latitudes [Bekki et al., 2011; Pawson et al., 2014].

The long-term evolution of stratospheric ozone column in the polar regions appears to be insensitive to the volcanic aerosol loading (Figures 4e and 4f). Over the Arctic in March, ozone recovery is mostly similar amongst the three aerosol loadings (BG, 1860 and HM) with similar 1980 return dates across the RCPs (Figure 1e). Post recovery, ozone column remains insensitive to aerosol loadings but is sensitive to the RCP scenario as indicated by the ~ 40 DU difference between RCP4.5 and RCP8.5 at 2100 attributed to the stronger effect of transport-induced changes and chemical impacts in RCP8.5 consistent with previous studies [Eyring et al., 2010b; 2013]. Over the Antarctic in October, ozone recovery is sensitive to neither volcanic aerosol
loadings nor the RCP scenarios considered here (Figure 4f) consistent with previous multi-model projections [Eyring et al., 2013].

3.2 Vertical Distribution of Zonal Mean Ozone Concentration

To decipher the trends in the stratospheric ozone columns, we analyze the difference in the zonal mean ozone concentrations simulated for RCPX.X_1860 and RCPX.X_HM relative to the respective RCPX.X_BG simulations for the mean 2006-2015 and 2091-2100 time periods. In the 2006-2015 period (Figure 5, top) when stratospheric halogen loading is still sufficiently high (Figure 2), annual mean ozone concentrations are simulated to increase in the middle stratosphere and decrease in the lower stratosphere for RCPX.X_1860 and RCPX.X_HM relative to the respective RCPX.X_BG. These differences are weaker for the RCPX.X_1860 simulations with smaller volcanic aerosol loading compared to the RCPX.X_HM simulations with greater aerosol loading. The zonal mean ozone differences are similar in the two RCPs ranging from -0.1 to +0.2 ppmv in the RCP4.5_1860 and RCP8.5_1860 simulations, and -0.14 to +0.4 ppmv in the RCP4.5_HM and RCP8.5_HM simulations relative to the respective RCPX.X_BG. This similarity in ozone response to volcanic aerosols between the two RCPs is driven by the similarity in the WMGG and ODS projections in the early 21st century consistent with the findings of Eyring et al. [2013].

In the 2091-2100 time period (Figure 5, bottom) when stratospheric halogen loading has diminished significantly (but is still above the natural background), stronger increases in annual mean ozone concentrations in the middle stratosphere and negligible decreases in the lower stratosphere are simulated for RCPX.X_1860 and RCPX.X_HM relative to the respective RCPX.X_BG. The importance of halogen chemistry has diminished over this time period as...
evidenced by the absence of statistically significant differences in ozone in the lower stratosphere where ozone decreased in response to volcanic aerosols for the 2006-2015 period (Figure 5). This is consistent with the results of Austin et al. [2013] who found a temporary increase in ozone column in response to volcanic eruptions in the pre-halogen era. Like the 2006-2015 period, ozone response to volcanic aerosols is stronger in the HM simulations with greater aerosol loading. The increase in ozone from increasing volcanic aerosol loadings at 2091-2100 is consistently weaker for RCP8.5 than that simulated for RCP4.5, reflecting the role of greater methane loading in RCP8.5 which we discuss in the next section.

3.3 Chemical Partitioning versus Aerosol Surface Area Density

Next, we analyze the mechanisms of stratospheric ozone response by examining the differences in chemical partitioning of reactive nitrogen (NO\textsubscript{y}), reactive chlorine (Cl\textsubscript{y}), and reactive bromine (Br\textsubscript{y}), as a function of volcanic SADs, focusing on the northern mid-latitudes. At 50°N the simulated activated chlorine and bromine, measured as annual mean ClO/Cl\textsubscript{y} and BrO/Br\textsubscript{y} ratios increase with increasing aerosol SAD while activated NO\textsubscript{x} (NO\textsubscript{y}/NO\textsubscript{x}) decreases in both RCP4.5 (Figures 6 a-e’) and RCP8.5 (Figures 6 f-j’) scenarios; ClO/Cl\textsubscript{y} and BrO/Br\textsubscript{y} increase more strongly in the near term (2006-2015) when halogen loading is still high than in the future, particularly in the upper (17hPa) stratosphere (Figures 6 a, e, f, j). Similar dependencies are simulated for the southern mid-latitudes (not shown).

These differences in the partitioning of NO\textsubscript{y} and halogens are attributed to heterogeneous reactions occurring on stratospheric aerosol surfaces [see review of Solomon 1999]. The key reaction linking volcanic aerosol changes to ozone depletion is the hydrolysis of N\textsubscript{2}O\textsubscript{5} to nitric acid (HNO\textsubscript{3}) that depletes NO\textsubscript{x}:
$\text{N}_2\text{O}_5 + \text{H}_2\text{O} \text{ (sulfate aerosol)} \rightarrow 2\text{HNO}_3 \quad (1)$

Due to enhanced hydrolysis of $\text{N}_2\text{O}_5$ to $\text{HNO}_3$ as volcanic aerosol SAD increases, $\text{NO}_x$ is depleted in RCPX.X_1860 and RCPX.X_HM relative to RCPX.X_BG resulting in lower $\text{NO}_y/\text{NO}_x$ (Figures 6 a, a’, f, f’) and higher $\text{HNO}_3/\text{NO}_x$ (Figure 6 c, c’, h, h’). This repartitioning causes $\text{NO}_x$-catalyzed ozone loss to be suppressed at both the time periods. Since $\text{NO}_x$-induced ozone loss is dominant in the middle stratosphere [Brasseur et al., 1999], this is where ozone is most enhanced in response to elevated volcanic aerosols (Figure 5).

Depleted $\text{NO}_x$ not only reduces $\text{NO}_x$-catalyzed ozone loss but also perturbs halogen partitioning, enhancing the $\text{ClO}_x$- and $\text{BrO}_x$-catalyzed ozone loss in the lower stratosphere where these catalytic cycles dominate. Since less $\text{NO}_2$ is available to combine with $\text{ClO}$ to produce the reservoir species, $\text{ClONO}_2$, more chlorine remains activated. Activated bromine is similarly increased by reduced formation of $\text{BrONO}_2$ although to a lesser extent. Thus, $\text{ClO}/\text{Cl}_y$ and $\text{BrO}/\text{Br}_y$ increase with increasing aerosol SADs, particularly in the 2006-2015 timeframe with elevated halogen levels in the atmosphere (Figure 6). Additional heterogeneous reactions on sulfate aerosols also increase halogen activation:

$\text{ClONO}_2 + \text{H}_2\text{O} \text{ (aerosol)} \rightarrow \text{HOCl} + \text{HNO}_3 \quad (2)$

$\text{BrONO}_2 + \text{H}_2\text{O} \text{ (aerosol)} \rightarrow \text{HNO}_3 + \text{HOBr} \quad (3)$

$\text{ClONO}_2 + \text{HCl} \text{ (aerosol)} \rightarrow \text{HNO}_3 + \text{Cl}_2 \quad (4)$

Typically, these occur on polar stratospheric clouds (solid NAT and water ice) in the extremely cold polar stratosphere; however, with enhanced aerosol surface areas, these reactions can proceed on liquid sulfate aerosols in the northern mid-latitudes due to temperature and water vapor fluctuations [Solomon, 1999 and references therein].
Finally, gas-phase formation of HNO$_3$ via OH + NO$_2$ + M reaction competes with reaction 1. Higher aerosol SAD leads to OH increases (not shown) that enhance the HO$_x$-catalyzed ozone loss and increase the gas-phase conversion of hydrochloric acid (HCl) to reactive chlorine [Granier and Brasseur, 1992] via:

\[
\text{HCl} + \text{OH} \rightarrow \text{Cl} + \text{H}_2\text{O}
\]

Reactions 4 and 5 lead to decreases in HCl as evident from decreasing HCl/Cl$_2$ with increasing aerosol SAD in both the RCP4.5 (Figure d, d’) and RCP8.5 simulations (Figure 6 i, i’).

For RCP4.5, the HNO$_3$/NO$_x$ ratio is similar over the 2006-2015 and 2091-2100 time periods (Figure 6 c, c’), but for RCP8.5 the HNO$_3$/NO$_x$ ratio increases significantly between the two periods (Figure 6 h, h’) due to the increased OH from the higher water vapor driven by a factor of 2.5 methane increase projected for RCP8.5 (as opposed to a small decrease for RCP4.5; see Figure 2). The increased OH in RCP8.5 increases the gas-phase production of HNO$_3$, thus making the chemistry less sensitive to aerosol SAD increases as evident from the gradual change in the NO$_y$/NO$_x$ ratio with increasing SAD at 2091-2100 (Figure 6 g, g’). This leads to a weaker ozone enhancement in RCP8.5 from elevated volcanic aerosols as compared to that in RCP4.5 at 2091-2100 (Figure 5).

The net effect on ozone of changes in Cl$_y$, Br$_y$, and NO$_y$ partitioning in response to volcanic aerosols is thus a balance between competing effects on NO$_x$-, HO$_x$- and halogen-catalyzed ozone loss cycles, with the net impact depending on the altitude, atmospheric halogen (and methane) loading, and volcanic aerosol loading. For the range of aerosol loadings considered here, the ozone response to volcanic aerosols does not saturate as suggested by Prather et al. [1992].
4. Conclusions and Discussion

Analyses of transient three-member ensemble simulations of GFDL CM3 following two climate scenarios (RCP4.5 and RCP8.5) indicate that stratospheric ozone exhibits opposing changes in response to elevated volcanic aerosols at different altitudes and halogen levels. In the early 21\textsuperscript{st} century, increased halogen-catalyzed ozone loss in the lower stratosphere offsets the suppressed NO\textsubscript{x}-catalyzed ozone loss in the middle stratosphere, resulting in largely similar recovery of global mean stratospheric ozone column in RCPX.X\_1860 and RCPX.X\_BG simulations; the RCPX.X\_HM simulations with greater volcanic aerosols exhibit slow ozone column recovery during this period due to the greater activation of halogen radicals causing increased ozone loss. After about the mid-2020s, when halogen levels have diminished (but are still above the natural background), the NO\textsubscript{x} suppression by volcanic aerosols dominates, leading to stronger stratospheric ozone recovery in scenarios with elevated volcanic aerosols. Ozone column returns to 1980 levels in the mid-2040s in RCP8.5\_1860 and RCP8.5\_HM simulations (three to seven years earlier than in RCP8.5\_BG), while its recovery date ranges from mid 2050s to early 2070s in the RCP4.5\_1860 and RCP4.5\_HM simulations compared to RCP4.5\_BG in which it remains below 1980 levels through 2100. These results are sensitive to the amount of aerosol loading, as indicated by weaker responses in RCPX.X\_1860 compared to those in RCPX.X\_HM simulations. Further, stratospheric ozone recovery by year 2100 in simulations with elevated volcanic aerosols relative to background is greater in RCP4.5 versus RCP8.5 due to a factor of 2.5 greater methane in RCP8.5 compared to RCP4.5.

The long-term evolution of stratospheric ozone column in response to different future emissions scenarios varies by different latitude regions [e.g., Eyring et al., 2013]; elevated volcanic aerosols in the future act to enhance this variability. In the tropics, stratospheric ozone
column does not respond to elevated aerosols until about 2020, but thereafter is enhanced by elevated volcanic aerosols in both RCP scenarios, although it remains below 1980 levels in all simulations. In the mid-latitudes, stratospheric ozone column shows more sensitivity to elevated volcanic aerosols in the Northern Hemisphere than in the Southern Hemisphere. The sensitivity is generally greater in RCP4.5 than in the RCP8.5 emission scenario. Over the polar regions, the long term evolution of stratospheric ozone column is insensitive to the amount of volcanic aerosol loading relative to the background, but Arctic ozone column is sensitive to the greenhouse gas scenario.

Our findings are generally consistent with those of previous modeling studies that have analyzed the impact of volcanic aerosols [Granier and Brasseur, 1992; Tie and Brasseur, 1995; Solomon et al., 1996; Austin et al., 2013; Aquila et al., 2013] and the impact of geoengineering via sulfate aerosols [Heckendorn et al., 2009; Tilmes et al., 2009; Pitari et al., 2014] on stratospheric ozone in the presence of varying amounts of halogens following different WMGG scenarios. Our simulated ozone response in RCP4.5_HM can be directly compared with those simulated in multi-model geoengineering experiments conducted by imposing a constant sulfate aerosol surface area increase similar to that produced following the Pinatubo eruption in the RCP4.5 reference scenario [Pitari et al., 2014]. Pitari et al. find that increased aerosols would cause global ozone column to decrease in the 2040-2049 decade relative to the base RCP4.5 scenario but to increase after 2050, similar to RCP4.5_HM results, although the timing of the ozone response is somewhat different. Pitari et al. also find a net reduction of 5% in polar ozone from elevated sulfate aerosols resulting from enhanced PSC formation, consistent with the results of a more recent study in which an imposed factor of three enhancement in stratospheric sulfate over 2011 levels increased ozone loss by up to 20 DU in the Antarctic and 15 DU in the
Arctic [Solomon et al., 2015]. This conflicts with our result that polar stratospheric ozone column appears to be insensitive to the amount of volcanic aerosol loading, especially in the 2006-2020 period when halogen levels are still high. Differences in the simulated polar temperatures, chemical reaction rates, aerosol SAD, and halogen levels could potentially explain some of this discrepancy over the polar regions.

As with any modeling study, our results are subject to errors resulting from model deficiencies. Model biases in the ozone and atmospheric circulation response to volcanic aerosols and other forcing agents (e.g., WMGGs, ODSs) will likely affect our results. For example, the better simulation of ozone response to Pinatubo aerosols by the nudged AM3 simulation compared to the free-running CM3 simulations demonstrates the influence of biases in atmospheric circulation. The stratospheric halogen source is treated in a simplified manner in our model to reduce computational cost; simulated Cl\textsubscript{y} and Br\textsubscript{y} have been shown to agree generally with existing observations but have some discrepancies, particularly in the tropics [Austin and Wilson, 2010], which may affect our results. CM3 does not explicitly simulate the emission of stratospheric aerosol precursors, aerosol formation, transport, growth and loss processes after volcanic eruptions – processes that determine the aerosol SAD distribution and therefore affect the rate of heterogeneous reactions. Similar experiments with other global models that include these processes will help provide more robust estimates of the influence of stratospheric volcanic aerosols on ozone recovery. Further, our results are specific to the idealized experiments conducted here, with imposed fixed levels of volcanic aerosols through the 21\textsuperscript{st} century. In reality, stratospheric volcanic aerosol loadings will fluctuate, causing the timing and extent of ozone recovery to vary correspondingly. It would be worth exploring the influence of variable volcanic eruptions in the 21\textsuperscript{st} century on the long term evolution of stratospheric
Finally, idealized volcanic-perturbation experiments conducted in support of Model Intercomparison Project on the climatic response to Volcanic forcing (VolMIP) [Zanchettin et al., 2016] can help assess the robustness of the stratospheric ozone response to strong volcanic forcings simulated across chemistry-climate models and can help identify the causes of differences in these responses.

Uncertainties in ozone projections and expected recovery dates have been recognized to come from uncertainties in assumed ODS and WMGG emission scenarios, interannual variability of ozone column, and diversity in model projections [Eyring et al., 2013]. We show here that volcanic aerosol perturbations also contribute to this uncertainty, thus providing a knowledge base to interpret ozone results from future multi-model projections with volcanic forcing prescribed to be equal to a constant historical mean value [O’Neill et al., 2016]. The novelty of our study lies in the use of transient simulations to 2100 using a state-of-the-art chemistry-climate model to demonstrate that the influence of volcanic aerosols on the extent and timing of the ozone recovery varies with: a) greenhouse gas scenarios, and b) halogen loading. We have also highlighted the need to explore further the influence of increased methane concentrations on stratospheric ozone column under conditions of elevated volcanic aerosols.

Predicting the timing and magnitude of volcanic eruptions on a global scale several decades into the future is currently impossible. Model simulations that consider hypothetical volcanic aerosol distributions based on recent measurements could help provide a lower limit of the influence of volcanic aerosols on stratospheric ozone. The response of stratospheric ozone column to observed SAD over the 2000-2014 period for which we now have observational constraints [Kremser et al., 2016 and references therein] can help provide estimates of the net effect of recent observed SAD on stratospheric ozone column.
Acknowledgments

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**Tables**

**Table 1**: Overview of GFDL-CM3 three-member ensemble simulations conducted to assess the influence of elevated volcanic aerosols on stratospheric ozone recovery.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Volcanic aerosol surface area density (SAD)</th>
<th>Greenhouse gases (CO$_2$, CH$_4$, N$_2$O) and Ozone Depleting Substances (ODSs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RCP4.5_BG</td>
<td>1999</td>
<td>RCP4.5</td>
</tr>
<tr>
<td>RCP4.5_1860</td>
<td>1860</td>
<td>RCP4.5</td>
</tr>
<tr>
<td>RCP4.5_HM</td>
<td>Mean 1860-1999</td>
<td>RCP4.5</td>
</tr>
<tr>
<td>RCP8.5_BG</td>
<td>1999</td>
<td>RCP8.5</td>
</tr>
<tr>
<td>RCP8.5_1860</td>
<td>1860</td>
<td>RCP8.5</td>
</tr>
<tr>
<td>RCP8.5_HM</td>
<td>Mean 1860-1999</td>
<td>RCP8.5</td>
</tr>
</tbody>
</table>
**Figures**

**Figure 1.** Total column ozone monthly mean anomalies [DU] from two observational datasets and model simulations for a) global, (b) NH and (c) SH mid-latitudes. Anomalies were calculated relative to monthly mean total column ozone averaged over 1990-1999 period. Observed monthly average total ozone columns are taken from version 8.6 Solar Backscattered Ultra Violet (SBUV) data from the Nimbus-4 BUV, Nimbus-7 SBUV, and NOAA-9 through 18 SBUV/2 instruments [Frith et al., 2013] (NOAA_SBUV) and version 2.8 of the monthly total column ozone from NIWA-BS total column ozone (TCO) database [Bodeker et al., 2005]. Blue-colored P indicates the time of Pinatubo eruption.
Figure 2. Timeseries of carbon dioxide (CO$_2$), methane (CH$_4$), trichlorofluoromethane (CFC-11) and nitrous oxide (N$_2$O) implemented in the simulations described in Table 1. Original data are from Meinshausen et al. (2011).
Figure 3. Annual mean zonal average volcanic aerosol surface area density implemented in the (a) RCPX.X_BG, (b) RCPX.X_1860, and (c) RCPX.X_HM simulations.
Figure 4. The 1980 baseline-adjusted time series of stratospheric ozone column (200 – 0 hPa) from 1960 to 2100 for the background (BG), 1860, and historical mean (HM) volcanic aerosols considered in RCP4.5 and RCP8.5 simulations. The panels show (a) global and annual average, (b) annual average over 25°N-25°S (c) annual average over 35°-60°N (d) annual average over 35-60°S (e) averaged over 60-90°N for March, and (f) averaged over 60-90°S for October. Shaded areas indicate ± 1-standard deviation across the three ensemble members for each simulation.
Figure 5. Difference in annual average zonal mean ozone concentration in RCP4.5 (left) and RCP8.5 (right) with 1860 and historical mean (HM) volcanic aerosols relative background (BG) volcanic conditions. Top and bottom rows show differences for mean 2006-2015 and 2091-2100 time periods, respectively. Only differences significant at 95% confidence level based on student’s t-test are shown.
Figure 6. Annual mean radical ratios as a function of volcanic aerosol surface area density (SAD) for 17hPa and 63hPa at 50°N. Values are individual years within 2006-2015 and 2091-2100 time periods averaged over three ensemble members of the RCPX.X_BG, RCPX.X_1860 and RCPX.X_HM simulations, where X.X = 4.5 (top) and 8.5 (bottom).