AGU PUBLICATIONS

Geophysical Research Letters

RESEARCH LETTER

10.1002/2016GL071778

Key Points:
- Transport linked to the monsoons brings increased HCl into contact with liquid aerosols in the cold tropical lowermost stratosphere
- Model results indicate that monsoon flows lead to tropical activation of reactive chlorine on volcanic and nonvolcanic particles
- Heterogeneous chlorine activation contributes to the ozone budget and to tropical lowermost stratosphere ozone trends

Supporting Information:
- Supporting Information S1

Correspondence to:
S. Solomon,
solos@mit.edu

Citation:
Solomon, S., et al. (2016), Monsoon circulations and tropical heterogeneous chlorine chemistry in the stratosphere, *Geophys. Res. Lett.*, *43*, 12,624–12,633, doi:10.1002/2016GL071778.

Received 31 OCT 2016
Accepted 6 DEC 2016
Accepted article online 9 DEC 2016
Published online 27 DEC 2016

Monsoon circulations and tropical heterogeneous chlorine chemistry in the stratosphere

Susan Solomon[1], Doug Kinnison[2], Rolando R. Garcia[2], Justin Bandoro[1], Michael Mills[2], Catherine Wilka[1], Ryan R. Neely III[3,4], Anja Schmidt[3], John E. Barnes[5], Jean-Paul Vernier[6,7], and Michael Höpfner[8]

[1]Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, Massachusetts, USA, [2]Atmospheric Chemistry Observations and Modeling Laboratory, National Center for Atmospheric Research, Boulder, Colorado, USA, [3]School of Earth and Environment, University of Leeds, Leeds, UK, [4]National Centre for Atmospheric Science, University of Leeds, Leeds, UK, [5]Mauna Loa Observatory, NOAA, Hilo, Hawaii, USA, [6]NASA Langley Research Center, Hampton, Virginia, USA, [7]Science Systems and Applications, Inc., Hampton, Virginia, USA, [8]Institute of Meteorology and Climate Research, Karlsruhe Institute of Technology, Karlsruhe, Germany

Abstract Model simulations presented in this paper suggest that transport processes associated with the summer monsoons bring increased abundances of hydrochloric acid into contact with liquid sulfate aerosols in the cold tropical lowermost stratosphere, leading to heterogeneous chemical activation of chlorine species. The calculations indicate that the spatial and seasonal distributions of chlorine monoxide and chlorine nitrate near the monsoon regions of the northern hemisphere tropical and subtropical lowermost stratosphere could provide indicators of heterogeneous chlorine processing. In the model, these processes impact the local ozone budget and decrease ozone abundances, implying a chemical contribution to longer-term northern tropical ozone profile changes at 16–19 km.

1. Introduction

Heterogeneous chlorine chemistry on and in liquid polar stratospheric particles is thought to play a significant role in polar and subpolar ozone depletion [*Solomon*, 1999 review, and references therein]. Previous studies have not provided evidence for heterogeneous chlorine chemistry occurring in the tropical stratosphere. Using the current best understanding of liquid stratospheric particle chemistry in a state-of-the-art numerical model, we examine whether such processes should be expected to affect tropical composition, particularly at and slightly above the cold tropical tropopause, in association with the Asian and North American summer (June-July-August) monsoons. Further, we probe whether volcanic emissions of sulfur (which can increase stratospheric sulfate aerosol abundances) could enhance this chemistry. The primary focus of this paper is to examine whether ClO and $ClONO_2$ observations near the monsoon regions in the tropical lowermost stratosphere could provide a novel test bed for understanding stratospheric chlorine activation chemistry, while a secondary focus is on whether such chemistry has the potential to contribute to the budget and trends of the tropical ozone profile below about 20 km. Stratospheric chlorine chemistry has been a subject of interest for decades, but key uncertainties remain in heterogeneous reactions rates (e.g., 1-sigma uncertainties in reaction rates of 40% [*Jet Propulsion Laboratory* (*JPL*), 2011]) that may be testable in new ways in the tropics. The ozone profile trends in the tropical lowermost stratosphere have long been a topic of scientific interest [*Randel et al.*, 1999; *Randel and Thompson*, 2011] and are thought to be largely dynamical in origin [e.g., *World Meterorological Organization/United Nations Environment Programme*, 2014, and references therein]. Understanding whether there may be a potential chemical contribution to tropical lower stratospheric ozone profile trends is hence of substantial scientific interest and a secondary goal of this paper.

Monsoons are primarily driven by continental heating, extend into the lower stratosphere [e.g., *Dunkerton*, 1995], and involve deep convection and formation of strong anticyclonic circulation cells on a seasonal basis, maximizing in summer over Asia and North America [e.g., *Gettelman et al.*, 2004; *Park et al.*, 2007; *Randel et al.*, 2010]. Weaker monsoons are observed over southern hemisphere landmasses. Observations have shown that transport related to the monsoons influences a range of chemicals in the tropical and subtropical tropopause regions, including tracers such as carbon monoxide and hydrogen cyanide [*Randel et al.*, 2010], ozone [*Park et al.*, 2007], volcanic and pollution aerosols [*Vernier et al.*, 2011, 2015], and water vapor [e.g., *Rosenlof et al.*, 1997; *Randel et al.*, 2015; *Schoeberl et al.*, 2013; *Ploeger et al.*, 2013]. Water vapor can play a role in heterogeneous chemistry under cold conditions, both through its influence on formation of ice clouds and through the dependence of chlorine activation reactions on the water content of liquid stratospheric aerosol particles (which contain sulfuric acid and water [see, e.g., *Solomon*, 1999; *Thornton et al.*, 2007; *Anderson et al.*, 2012]). The influences of HCl, water vapor, and temperature changes for stratospheric chlorine chemistry in the tropics are discussed further below.

The primary goal of this paper is to probe the extent to which heterogeneous chlorine chemistry may be expected to occur on liquid sulfate aerosols in the tropical stratosphere. Liquid aerosol effects could represent a lower limit to this chemistry if, for example, similar reactions also take place on tropical cirrus ice clouds, but the potential for ice chemistry is not examined here. Heterogeneous halogen reactions on ice are sensitive to the size distribution of cirrus ice particles [e.g., *Bregman et al.*, 1997] and to the adopted parameterization of cirrus clouds in models. Heterogeneous processing involving chlorine, bromine, and iodine have also been identified on liquid and/or ice aerosols in the troposphere [e.g., *Wang et al.*, 2015; *Schmidt et al.*, 2016; *Saiz-Lopez and Fernandez*, 2016; *Von Hobe et al.*, 2011; see the review by *Simpson et al.*, 2015, and references therein], but the focus here is on stratospheric chlorine chemistry and the role of transport via the monsoon circulations.

Recent progress in stratospheric chemistry modeling underpins this study. State-of-the-art atmospheric chemistry models have been extensively intercompared and tested [e.g., *Eyring et al.*, 2010], and the temperature-sensitive heterogeneous chemistry can be driven by specified dynamics and temperatures from reanalysis fields based on observations; here we use the Community Earth System Model, version 1, with the Whole Atmosphere Community Climate Model version 4, as the atmospheric component (CESM1(WACCM)) [see *Marsh et al.*, 2013]. The model's representation of heterogeneous chemistry was shown to be in broad agreement with polar ozone and constituent observations in *Solomon et al.* [2015], supporting its use to examine other regions.

The stratospheric aerosol distributions employed in this model include representations of both volcanic and nonvolcanic sulfur sources. The calculated aerosol properties were discussed in detail in *Mills et al.* [2016] and shown to compare well to total stratospheric aerosol extinction data from lidars, including the Mauna Loa lidar. Further comparisons to ground-based and satellite lidar backscatter data in the lowermost tropical stratosphere are presented below. During the summer of 2011, tropical stratospheric aerosols were enhanced compared to several other recent years, at least in part due to volcanic inputs from the Nabro eruption in mid-June [*Bourassa et al.*, 2012; *Fairlie et al.*, 2014; *Neely et al.*, 2013], although pollution from Asian sources also contributes to aerosol loading in the monsoon region [*Vernier et al.*, 2015]. In this paper we focus on 2011 as a period when high tropical volcanic aerosol loading should be expected to increase the potential role of the chemistry under consideration, and we compare 2011 to calculations for other years.

2. Model Description

The specified dynamic version of CESM1 (WACCM), herein referred to as SD-WACCM, is nudged to externally specified dynamical fields for temperature, zonal and meridional winds, and surface pressure fields from the Modern Era Retrospective Analysis for Research and Applications (MERRA) [see *Rienecker et al.*, 2011]. The procedure used to constrain the model is described by *Marsh* [2011] and *Kunz et al.* [2011]. The chemistry scheme includes the O_x, NO_x, HO_x, ClO_x, and BrO_x chemical families, along with gas phase and heterogeneous reactions on liquid binary and ternary sulfate aerosols. About 5 parts per trillion by volume (pptv) of bromine from very short lived substances (VSLS) contributes to the modeled stratospheric bromine levels, along with CH_3Br and halon sources. Chlorine from CH_3Cl, CH_3CCl_3, and industrial chlorofluorocarbons is included in the model. Arguably, our results represent a lower limit since chlorine from VSLS may also contribute [see *Hossaini et al.*, 2015] but are not included here, nor is convective lofting of sea salt evaluated [e.g., *Schmidt et al.*, 2016]. Such additional sources of chlorine and bromine could add to the chemical effects identified here if they reach the stratosphere. Iodine chemistry is not included in the model; if there were to be iodine input to the stratosphere akin to that identified in the upper troposphere [see e.g., *Volkamer et al.*, 2015; *Saiz-Lopez and Fernandez*, 2016], that could further affect the chemistry of the region considered, but is not represented in this model. The homogeneous and heterogeneous reactions and rate coefficients used in the simulations in this paper are based on *JPL* [2011] except where indicated in *Solomon et al.* [2015].

We employ monthly averaged atmospheric aerosol distributions from *Mills et al.* [2016], which were calculated by using gas phase sulfur and related chemistry along with an aerosol model in SD-WACCM. A database of volcanic SO_2 emissions and plume altitudes was developed for eruptions between 1990 and 2014 by *Neely and Schmidt* [2016], and these volcanic sulfur inputs along with background sources of sulfur (including carbonyl sulfide and anthropogenic SO_2) were used to simulate stratospheric sulfate aerosols [*Mills et al*., 2016]. Aerosols are modeled as three lognormal modes: Aitken, accumulation, and coarse. The model is capable of representing interactions of aerosol particles including nucleation, condensation, coagulation, and sedimentation; for further details and comparisons to observations, see *Mills et al*. [2016].

Three sets of SD-WACCM chemistry model results probe heterogeneous chlorine chemistry in this paper: (i) simulations including volcanic and nonvolcanic aerosol sources, (ii) volcanically clean simulations that include only background sources of sulfur, and (iii) simulations in which heterogeneous reactions are turned off between 40°N and 40°S (but allowing heterogeneous reactions that do not involve chlorine or bromine (e.g., $N_2O_5 + H_2O$) to continue to occur).

3. Results

Figure 1 shows the distributions of calculated HCl obtained in SD-WACCM along with the temperature distributions for the month of July 2011 at 100 and 85 hPa, compared to HCl observations for the channel centered at 100 hPa from the Microwave Limb Sounder (MLS) instrument [*Froidevaux et al*., 2008], version 4.2. Model meteorological tropopauses in the northern tropics at this time of year are from 90 to 130 hPa depending upon longitude. No MLS data for HCl are available at 85 hPa, and the sounder has a fairly broad vertical weighting function [see *Froidevaux et al*., 2008, Figure 3]. The wind vectors superimposed in Figure 1 show the anticyclonic large-scale circulations associated with the monsoonal flows over Asia and North America, and the temperatures prescribed in SD-WACCM from MERRA are also overlaid in Figure 1 (bottom). While temperatures near the tropopause in the summer monsoon regions are warmer than in winter, they are nevertheless much colder than temperatures at midlatitudes at these altitudes, as can be seen in the overlaid contours of Figure 1.

The HCl gradients in the data and the model are qualitatively similar but display some important quantitative differences. While the model tropical minima near 100 hPa are lower than the MLS minima, a high bias of about 200 pptv at low latitude to midlatitude in MLS was noted in *Froidevaux et al*. [2008]; further, tropical HCl by the infrared Halogen Occultation Experiment (HALOE) are about 15% lower than MLS [*Froidevaux et al*., 2008; see also *Schoeberl et al*., 2008]. *Froidevaux et al*. [2008, Figures 11 and 14] also showed larger local differences of up to 20–50% at 100 hPa in parts of the tropics in comparisons of MLS with HALOE and the Atmospheric Chemistry Experiment. In all of these satellite data sources, however, the HCl abundances are much lower in the tropical lower stratosphere than in the extratropics; this is a robust feature that is key to our analysis as discussed below.

Tropical regions are characterized on average by upwelling air masses, in which chlorine is largely expected to be tied up in unreactive organic chlorine source gases (mainly CH_3Cl and chlorofluorocarbons). When these gases travel upward and poleward in the stratosphere, their chemical breakdown supplies inorganic chlorine. The inorganic chlorine can interact with sufficiently cold and wet surfaces and activate the chlorine (by converting the inactive reservoir species, HCl, into free radical and less stable species, Cl, ClO, $ClONO_2$, and HOCl). In the two polar regions, this chemistry enhances ClO and destroys ozone. Chlorine activation and related chlorine-catalyzed ozone loss has been documented following its discovery in association with the Antarctic ozone hole, but it has been generally assumed that similar chemistry was negligible in the tropics due to insufficient inorganic chlorine (see, e.g., *Solomon* [1999] for a review stating this assertion). However, Figure 1 shows that in our model, the monsoon circulations lead to equatorward transport of inorganic chlorine into the northern subtropics and tropics along the eastern side of the monsoon anticyclones, and the MLS data support these general features. Recent studies have emphasized the importance of quasi-horizontal transport in producing larger abundances of several key chemical constituents (including ozone and HCl) in the northern tropics as compared to the southern tropics [e.g., *Konopka et al*., 2009; *Abalos et al*., 2012; *Stolarski et al*., 2014].

Figure 1 highlights the role of equatorward transport of extratropical air on the eastern flanks of the northern hemisphere monsoon anticyclones, substantially increasing available inorganic chlorine at northern subtropical latitudes in summer in this model and in the observations. The combination of relatively cold temperatures, liquid aerosols, and transport of inorganic chlorine from higher latitudes drives low-latitude

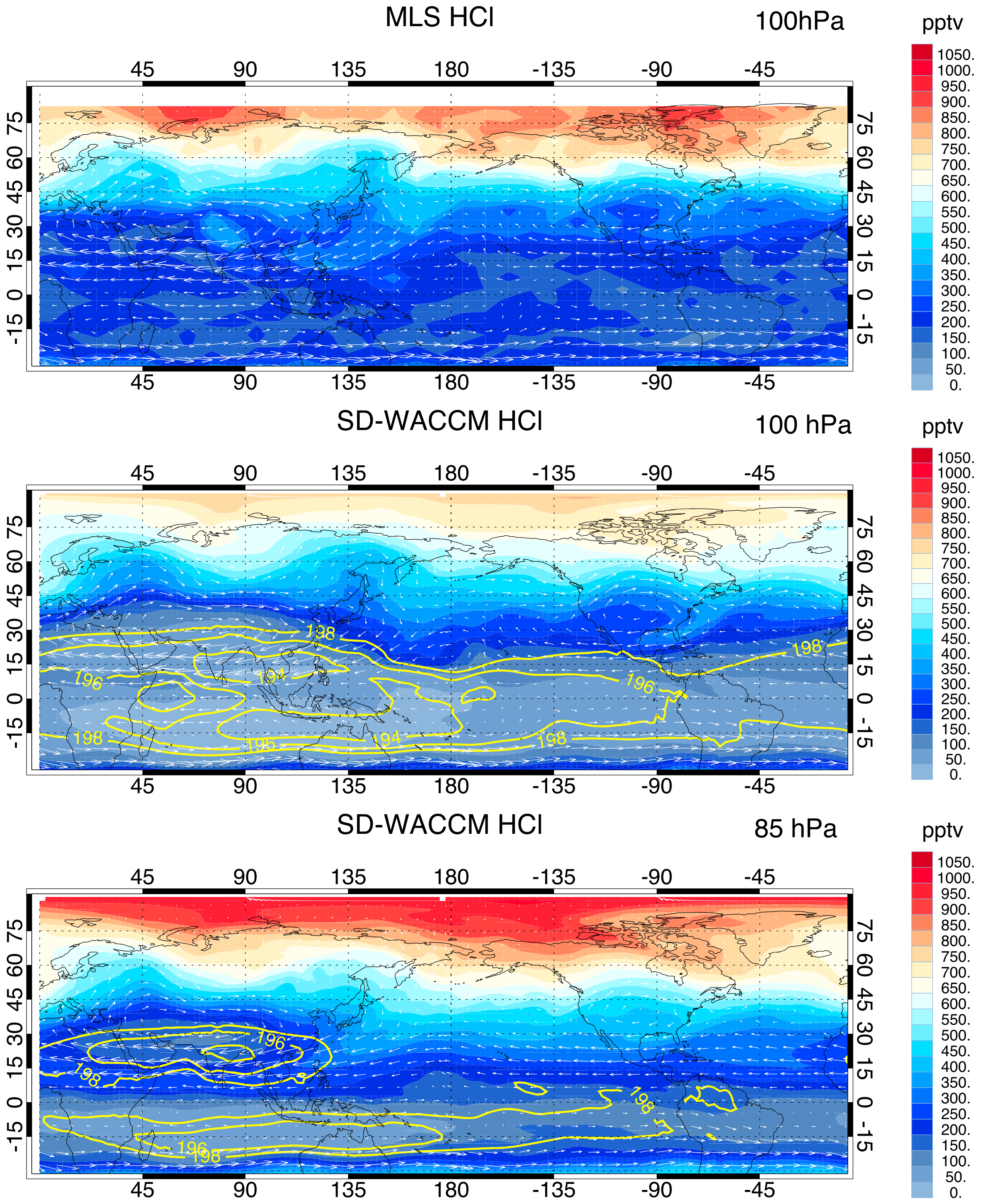


Figure 1. Distributions of HCl from MLS satellite data for the channel centered at (top) 100 hPa and at (middle) 100 and (bottom) 85 hPa in SD-WACCM simulations for July 2011. Wind vectors and temperatures from SD-WACCM are superimposed.

heterogeneous chlorine activation and enhances calculated ClO in our model. Figure 2 presents maps of ClO and $ClONO_2$ calculated in the model at 17 km for July 2011 when low-latitude heterogeneous chlorine chemistry is included. Figure S1 in the supporting information shows the distributions of the rates of chemical processes that serve to activate chlorine, and Table S1 in the supporting information indicates sensitivities of

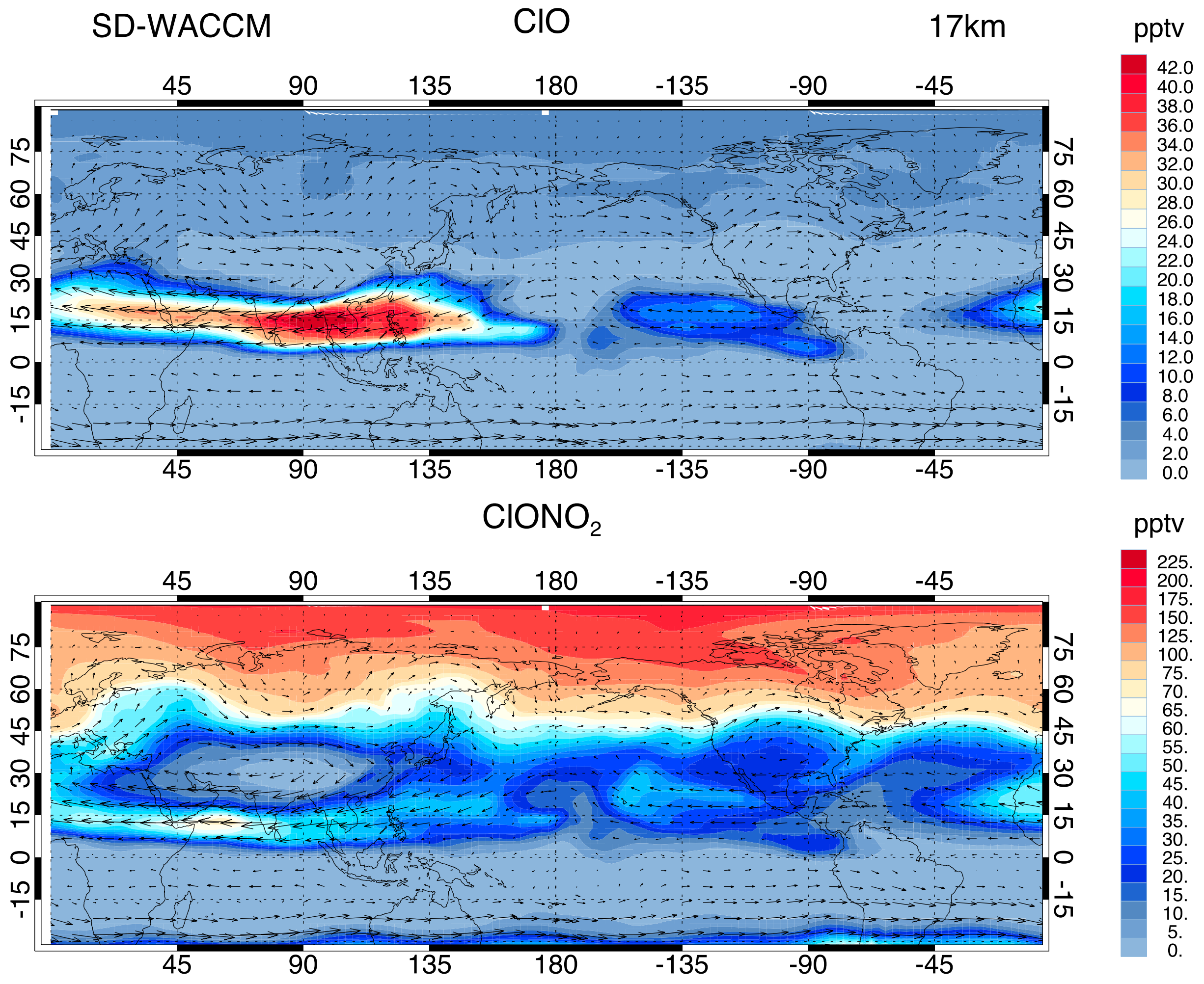
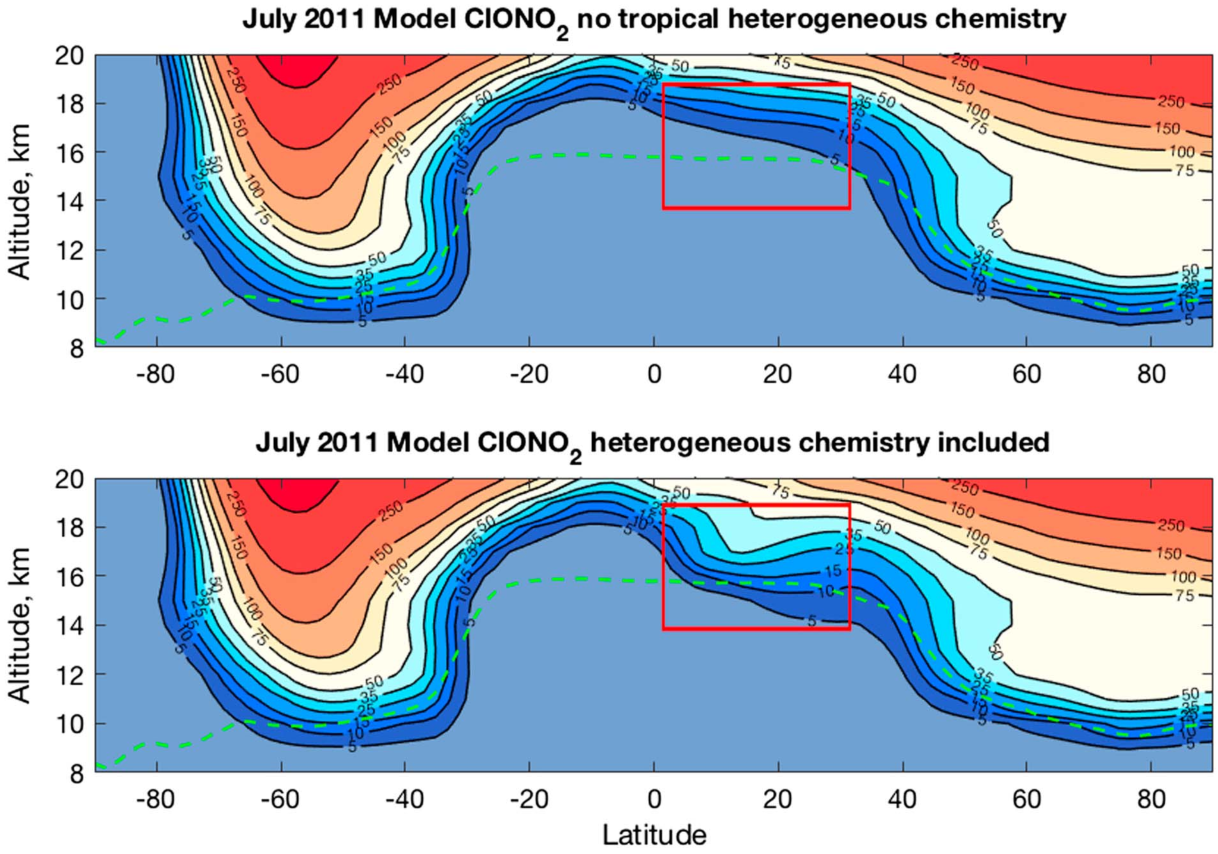


Figure 2. Model calculated monthly mean distributions of (top) ClO (pptv) and (bottom) $ClONO_2$ (pptv) for July 2011 at 17 km, with superimposed wind vectors.

the key activation reaction rate constant to the range of temperature and water vapor changes in the regions of maximum activation, illustrating that the temperature changes are much more important than the water vapor changes for enhancing the chemical reactivity. The largest heterogeneous chlorine activation rates occur near 15–20°N, particularly where the southward flow around the Asian monsoon brings high levels of inorganic chlorine into the coldest part of the subtropical lower stratosphere, where the eastern edge of the anticyclone flows into the Western Pacific. Temperatures as cold as 194–196 K are found even in summer near, for example, 135°E in this region (Figures 1, 2, and S1).

Local maxima in ClO of over 30 pptv (monthly mean) are calculated near the Asian monsoon region near 17 km, while peak values of 15 pptv are obtained near the North American monsoon region (Figure 2). Chlorine activation can be expected to produce enhanced $ClONO_2$ downwind of the main activation region, provided that NO_x is not completely removed by the heterogeneous processing. This chemistry forms the well-known $ClONO_2$ "collar" at subpolar latitudes [e.g., *Toon et al.*, 1989]. Figure 2 shows that the model calculates $ClONO_2$ values as large as 50–75 pptv near the ClO maxima, linked to the North American and Asian summer monsoons. The calculated tropical stratospheric chlorine activation depicted in Figure 2 has not been discussed in previous studies of which we are aware.

A consequence of elevated ClO concentrations is potential destruction of stratospheric ozone. When the tropical heterogeneous chlorine chemistry identified here is included compared to calculations excluding it, we calculate ozone decreases (averaged over the years 2009–2012 and over the northern tropics from 0 to 30°N) of about 2.5% at 16–17 km, about 1.5% at 18 km, and about 1% at 19 km. For comparison, the estimated



July 2011 Model $ClONO_2$ no tropical heterogeneous chemistry

July 2011 Model $ClONO_2$ heterogeneous chemistry included

Figure 3. Zonally averaged $ClONO_2$ abundances (pptv) in July 2011 versus latitude and altitude in SD-WACCM model calculations (top) with and (bottom) without low-latitude heterogeneous chlorine chemistry, including volcanic inputs. The location of the meteorological tropopause has been indicated with a dashed green line, and the red box highlights the region discussed.

tropical average ozone trends are about 1–4% per decade from 17 to 19 km over 1980–2005 [*Randel and Thompson*, 2011; their Figure 12].

The catalytic cycle involving chlorine and hydrogen radicals (in which the rate limiting step is $ClO + HO_2$) dominates our calculated ozone decreases, but the interhalogen reaction between ClO and BrO also represents about 25% of the modeled ozone decrease. These numbers imply an effect on the local ozone budget due to heterogeneous chlorine chemistry, and whether this change represents anthropogenic ozone depletion (as opposed to a change in the ozone background state) depends upon the balance between chlorine and bromine from industrial chemicals versus natural sources in this region, particularly very short-lived species (VSLS) with biogenic origins. In our model, the balance between industrial and VSLS sources of chlorine and bromine suggests that about three quarters of the calculated ozone change is traceable to anthropogenic emissions. While it remains likely that most of the ozone trend in tropical lower stratosphere ozone since 1979 is linked to dynamical changes [*Randel and Thompson*, 2011], our work implies that heterogeneous chlorine chemistry may have made some contributions to the vertical profile of trends in ozone in this region. The changes are confined to a narrow height range, and the corresponding decreases in column ozone for calculations including heterogeneous chemistry to those without them at, for example, 15°N in summer, vary between 1–2 Dobson unit over 2009–2011. Whether the changes in ozone profile or column due to the chemistry discussed here can be detected in observations would depend not only on the precision and accuracy of the ozone measurements but also on the ability to quantify dynamical factors to sufficient accuracy. More detailed analysis of tropical ozone trends is outside the scope of the present paper.

Figure 3 presents the zonally averaged distributions of $ClONO_2$ versus latitude and altitude for July 2011 for these SD-WACCM simulations. The location of the meteorological tropopause is indicated in the figure. When low-latitude heterogeneous chlorine chemistry is included in the model, the calculated stratospheric

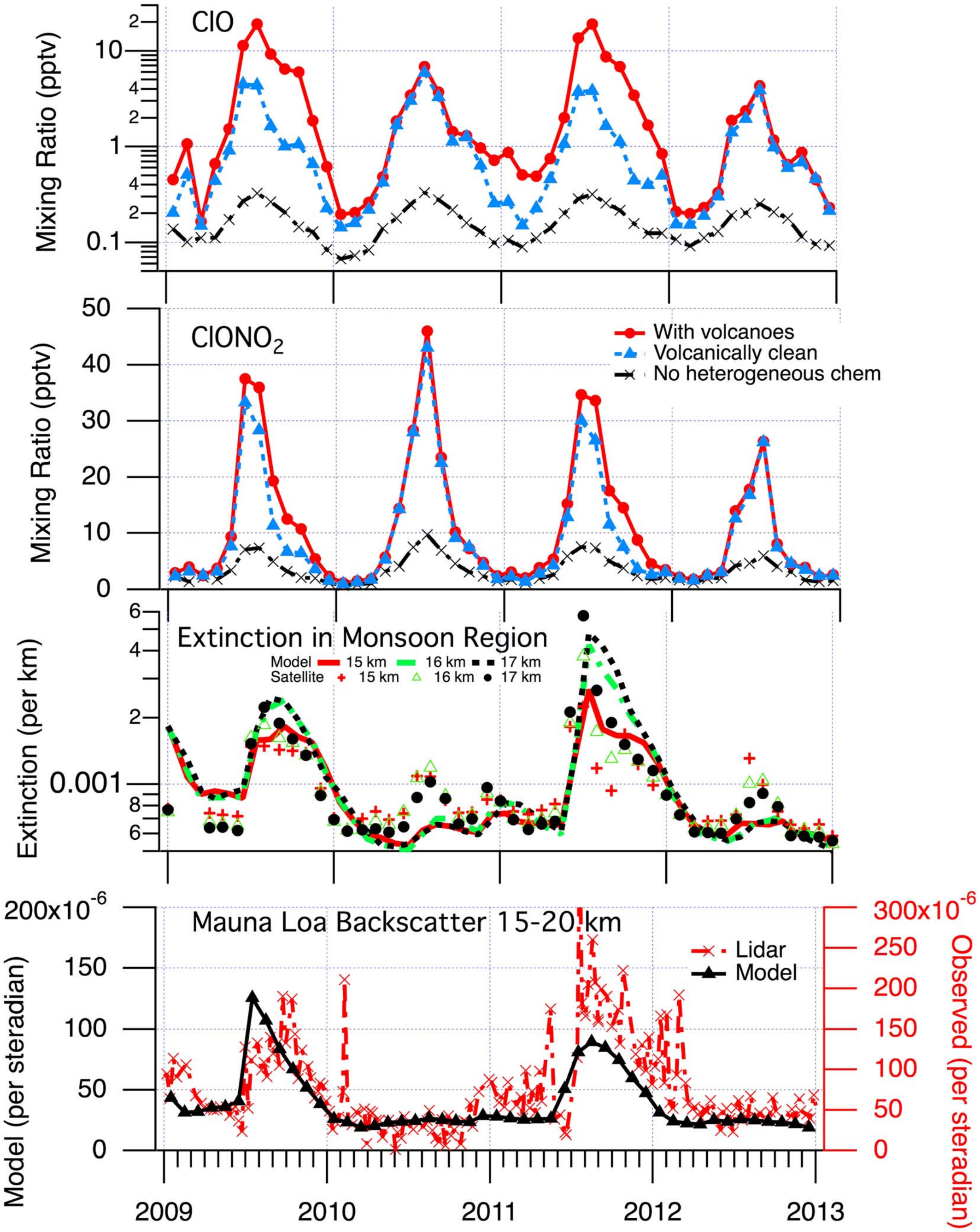


Figure 4. Model-calculated chemical constituents (pptv) averaged over the latitude band 14–20°N versus month at 17 km, for simulations with and without volcanic inputs, and without low-latitude heterogeneous chlorine chemistry, for 2009–2012 for (first panel) ClO and (second panel) $ClONO_2$. The time series of extinction at 532 nm measured by satellite lidar, averaged over the monsoon region (15–45°N, 5–105°E; adapted from Figure 2 of *Vernier et al*. [2015]), compared to the model values (third panel) at 15, 16, and 17 km. Aerosol backscatter integrated over 15–20 km at Mauna Loa (per steradian) from observations (right axis) and from the model (fourth panel), assuming an extinction-to-backscatter conversion factor of 40 (left axis). Note the change in scale of the two *y* axes in the fourth panel.

gradient in $ClONO_2$ from about 16 to 18 km and from about 10 to 25°N in July 2011 displays a pronounced "tongue," with peak zonal mean abundances of over 40 pptv, while no such tongue is obtained in the model without heterogeneous chemistry. Figure 3 illustrates that the region substantially affected by the chemistry considered here is confined to a limited range of height and latitude.

Figure 4 presents seasonal changes in ClO and $ClONO_2$ over several years at 17 km averaged over the latitude band from 14 to 20°N for the three model test cases noted above: with volcanic sulfur inputs, for volcanically clean conditions, and with the heterogeneous chlorine activation chemistry turned off. Figure 4 shows that the calculated heterogeneous chemical processes greatly increase the modeled concentrations of ClO and $ClONO_2$ compared to calculations without heterogeneous chemistry. The changes in these two species as compared to the no heterogeneous chemistry case exceed their interannual variability and are robust to substantial seasonal changes in HCl from month to month (i.e., June-July-August) or interannually (see Figures 4 and S2). Considerably smaller relative changes that lie within interannual variations are expected for HCl (Figure S2). Figure 4 also presents averaged measured satellite extinction in the monsoon region (15–45°N, 5–105°E) at 15, 16, and 17 km (adapted from Figure 2 in *Vernier et al*. [2015]) as compared to the model. As a further check on the modeled aerosols over broader parts of the tropics, Figure 4 compares observations of lidar backscatter from Mauna Loa observatory (19°N) integrated from 15 to 20 km to that from the model at the same site; the modeled extinction has been converted to backscatter here using a backscatter to extinction conversion factor of 40 (note the different *y* axes for model and data in Figure 4, bottom). *Jäger and Deshler* [2002, 2003] suggest values of about 20–60 for this conversion factor depending on particle sizes, with lower values for larger particles following major eruptions. Figure 4 shows that the model captures the timing and magnitudes of the volcanic enhancements that are apparent in both sets of observations. The modeled absolute values are generally close to the *Vernier et al*. [2015] data but are somewhat lower than the Mauna Loa data.

The calculated chlorine activation that is evident in Figure 4 varies from year to year and month to month depending on multiple factors: the strength of the transport associated with the monsoons (which affects total chlorine), changes in temperature, and changes in stratospheric aerosol amounts (see Figure S1). It is likely that the quasi-biennial oscillation plays a role in modulating transport of HCl from year to year [*Schoeberl et al*., 2008], and the El Niño is also important for temperature variations, particularly in the warm pool region of maximum activation [e.g., *Rosenlof and Reid*, 2008; *Nishimoto and Shiotani*, 2012].

The model results shown in Figure 4 suggest that heterogeneous chlorine chemistry in this region greatly enhances reactive chlorine species even for volcanically clean conditions, with substantial increases above what would be expected without heterogeneous processing. Figure 4 suggests that summer ClO and $ClONO_2$ abundances in this region when heterogeneous chlorine reactions are simulated for nonvolcanic conditions are on the order of 5 and 25–40 pptv, respectively, compared to only a few tenths of a pptv and 5–10 pptv when these reactions are neglected. Further increases on the order of 10 pptv for ClO and 5–8 pptv for $ClONO_2$ are simulated in volcanically perturbed summers, particularly 2011 (after Nabro) and 2009 (when transport of aerosol to the tropics from the Sarychev eruption has been documented [see *Solomon et al*., 2011, Figure 1].

4. Discussion and Conclusions

Heterogeneous chlorine chemistry has been well established in polar regions through extensive measurements and modeling, and it should be expected to operate in other latitudes if conditions allow. In this paper, we have shown that numerical model simulations indicate that the appropriate conditions occur in association with the northern hemisphere summer monsoons based on current chemical understanding.

Figures 1 and 2 taken together illustrate how the input of inorganic chlorine from midlatitudes and the relatively cold conditions of the tropical lowermost stratosphere region combine to produce a rapid rate of chlorine activation on liquid sulfate aerosols near the northern monsoon regions in SD-WACCM. The largest rates of calculated chlorine activation are associated with flow around the Asian monsoon into the especially cold lower stratosphere near the Western Pacific warm pool. Our model results suggest that heterogeneous chlorine activation should greatly increase average ClO and $ClONO_2$ abundances from about 10 to 20°N in the altitude range from 16 to 18 km as compared to simulations neglecting this chemistry. Volcanic increases in liquid sulfate aerosols enhance the perturbations, but the heterogeneous reactions are thought to be sufficiently rapid that substantial changes are also indicated for volcanically clean conditions.

Many stratospheric chlorine chemistry measurements have focused on polar and subpolar regions. We are not aware of any available data sets that have validated measurements of ClO or $ClONO_2$ in the 16–18 km region of the tropics and subtropics against which our findings could be further tested. Stratospheric chemistry is tightly coupled, and other constituents including HCl, NO, NO_2, and HOCl may also be useful to probe the impacts of this heterogeneous chemistry. Laboratory studies of these reactions have used H_2SO_4/H_2O and $H_2SO_4/H_2O/HNO_3$ solutions, and those studies form the basis for the chemistry recommended in *JPL* [2011] and imposed in models. Even for pure H_2SO_4/H_2O solutions, uncertainties in liquid heterogeneous reactivities are poorly quantified, especially for temperatures below about 200 K. Further, direct measurements of particle composition in the tropical tropopause region have revealed substantial amounts of other components, such as nonvolatile species and pollutants including organic compounds [*Murphy et al.*, 1998; *Murphy et al.*, 2014; *Borrmann et al.*, 2010]. Whether these components could alter the stratospheric liquid aerosol reactivity is unknown. If so, then particle reactivities might differ in volcanic versus nonvolcanic years, since the volcanic particles would contain a much larger fraction of sulfuric acid, and hence provide a closer correspondence to the laboratory data compared to nonvolcanic conditions. Our simulations provide a testable framework for examining whether or not heterogeneous chlorine chemistry takes place in the tropical lowermost stratosphere, either under volcanically clean or volcanically perturbed conditions, or both.

Acknowledgments
We thank Dan Murphy and Brian Toon for their helpful discussions. S.S. and J.B. acknowledge funding under NSF-1539972 and NSF-1419667. R.N. is supported by the Natural Environment Research Council through the National Centre for Atmospheric Science in the UK. A.S. was supported by an Academic Research Fellowship from the University of Leeds and a National Center for Atmospheric Research (NCAR) visiting researcher grant. J.E.B. is funded by NOAA/ESRL/GMD. NCAR is sponsored by the U.S. National Science Foundation. Any opinions, findings, and conclusions or recommendations expressed in the publication are those of the author(s) and do not necessarily reflect the views of the National Science Foundation. WACCM is a component of the Community Earth System Model (CESM), which is supported by the National Science Foundation (NSF) and the Office of Science of the U.S. Department of Energy. Computing resources were provided by NCAR's Climate Simulation Laboratory, sponsored by NSF and other agencies. This research was enabled by the computational and storage resources of NCAR's Computational and Information System Laboratory. We thank NASA Goddard Space Flight Center for the MERRA data (accessed freely online at http://disc.sci.gsfc.nasa.gov/) and the Aura MLS team for HCl data (accessed freely online at http://disc.sci.gsfc.nasa.gov/Aura/data-holdings/MLS). Mauna Loa lidar data shown in this paper may be accessed at http://ndacc-lidar.org/. Model results shown in this paper are available on request to the WACCM liaison, Michael Mills mmills@ucar.edu.

References

Abalos, M., W. J. Randel, and E. Serrano (2012), Variability in upwelling across the tropical tropopause and correlations with tracers in the lower stratosphere, *Atmos. Chem. Phys.*, *12*, 11,505–11,517, doi:10.5194/acp-12-11505-2012.

Anderson, J. G., D. M. Wilmouth, J. B. Smith, and D. S. Sayres (2012), UV dosage levels in summer: Increased risk of ozone loss from convectively injected water vapor, *Science*, *337*, 835–839, doi:10.1126/science.1222978.

Borrmann, S., et al. (2010), Aerosols in the tropical and subtropical UT/LS: In-situ measurements of submicron particle abundance and volatility, *Atmos. Chem. Phys.*, *10*, 5573–5592, doi:10.5194/acp-10-5573-2010.

Bourassa, A. E., A. Robock, W. J. Randel, T. Deshler, L. A. Rieger, N. D. Lloyd, E. J. Llewellyn, and D. A. Degenstein (2012), Large volcanic aerosol load in the stratosphere linked to Asian monsoon transport, *Science*, *337*, 78–81, doi:10.1126/science.1219371.

Bregman, A., M. van den Broek, K. S. Carslaw, R. Mueller, T. Peter, M. P. Scheele, and J. Lelieveld (1997), Ozone depletion in the late winter lower Arctic stratosphere: Observations and model results, *J. Geophys. Res.*, *102*, 10,815–10,828, doi:10.1029/97JD00006.

Dunkerton, T. J. (1995), Evidence of meridional motion in the summer lower stratosphere adjacent to monsoon regions, *J. Geophys. Res.*, *100*(D8), 16,675–16,688, doi:10.1029/95JD01263.

Eyring, V., T. G. Sheperd, and D. W. Waugh (Eds) (2010), SPARC report on the evaluation of chemistry-climate models SPARC Rep. No. 5, WRCP-132, WMO-TD No. 1526, World Met. Org., Geneva, Switzerland.

Fairlie, T. D., J.-P. Vernier, M. Natarajan, and K. M. Bedka (2014), Dispersion of the Nabro volcanic plume and its relation to the Asian summer monsoon, *Atmos. Chem. Phys.*, *14*, 7045–7057, doi:10.5194/acp-14-7045-2014.

Froidevaux, L., et al. (2008), Validation of Aura Microwave Limb Sounder HCl measurements, *J. Geophys. Res.*, *113*, D15S25, doi:10.1029/2007JD009025.

Gettelman, A., D. E. Kinnison, T. J. Dunkerton, and G. P. Brasseur (2004), Impact of monsoon circulations on the upper troposphere and lower stratosphere, *J. Geophys. Res.*, *109*, D22101, doi:10.1029/2004JD004878.

Hossaini, R., M. P. Chipperfield, S. A. Montzka, A. Rap, S. Dhomse, and W. Feng (2015), Efficiency of short-lived halogens at influencing climate through depletion of stratospheric ozone, *Nat. Geosci.*, *8*, 186–190.

Jäger, H., and T. Deshler (2002), Lidar backscatter to extinction, mass and area conversions for stratospheric aerosols based on midlatitude balloonborne size distribution measurements, *Geophys. Res. Lett.*, *29*(19), 1929, doi:10.1029/2002GL015609.

Jäger, H., and T. Deshler (2003), Correction to "Lidar backscatter to extinction, mass and area conversions for stratospheric aerosols based on midlatitude balloonborne size distribution measurements", *Geophys. Res. Lett.*, *30*(7), 1382, doi:10.1029/2003GL017189.

Jet Propulsion Laboratory (JPL) (2011), Chemical kinetics and photochemical data for use in atmospheric studies evaluation number 15, JPL Publication, 06-2.

Konopka, P., J.-U. Grooß, F. Ploeger, and R. Müller (2009), R.: Annual cycle of horizontal in-mixing into the lower tropical stratosphere, *J. Geophys. Res.*, *114*, D19111, doi:10.1029/2009JD011955.

Kunz, A., L. L. Pan, P. Konopka, D. E. Kinnison, and S. Tilmes (2011), Chemical and dynamical discontinuity at the extratropical tropopause based on START08 and WACCM analyses, *J. Geophys. Res.*, *116*, D24302, doi:10.1029/2011JD016686.

Marsh, D. R. (2011), Chemical-dynamical coupling in the mesosphere and lower thermosphere, in *Aeronomy of the Earth's Atmosphere and Ionosphere, IAGA Spec. Sopron Book Ser.*, vol. 2, edited by M. Abdu, D. Pancheva, and A. Bhattacharyya, pp. 3–17, Springer, Dordrecht, Netherlands.

Marsh, D. R., M. J. Mills, D. E. Kinnison, J. F. Lamarque, N. Calvo, and L. M. Polvani (2013), Climate change from 1850 to 2005 simulated in CESM1(WACCM), *J. Clim.*, *26*, 7372–7391, doi:10.1175/JCLI-D-12-00558.1.

Mills, M. J., et al. (2016), Global volcanic aerosol properties derived from emissions, 1990–2014, using CESM1(WACCM), *J. Geophys. Res. Atmos.*, *121*, 2332–2348, doi:10.1002/2015JD024290.

Murphy, D. M., D. S. Thomson, and M. J. Mahoney (1998), *In situ* measurements of organics, meteoric material, mercury, and other elements in aerosols at 5 to19 km, *Science*, *282*, 1664–1669.

Murphy, D. M., K. D. Froyd, J. P. Schwarz, and J. C. Wilson (2014), Observations of the chemical composition of stratospheric aerosol particles, *Q. J. R. Meteorol. Soc.*, *140*, 1269–1278.

Neely III, R. R. and A. Schmidt (2016), VolcanEESM (Volcanic Emissions for Earth System Models): Volcanic sulphur dioxide (SO2) emissions database from 1850 to present, Centre for Environmental Data Analysis. [Available at http://catalogue.ceda.ac.uk/uuid/bfbd5ec825fa422f9a858b14ae7b2a0d.]

Neely, R. R., III, et al. (2013), Recent anthropogenic increases in SO_2 from Asia have minimal impact on stratospheric aerosol, *Geophys. Res. Lett.*, *40*, 999–1004, doi:10.1002/grl.50263.

Nishimoto, E., and M. Shiotani (2012), Seasonal and interannual variability in the temperature structure around the tropical tropopause and its relationship with convective activities, *J. Geophys. Res.*, *117*, D02104, doi:10.1029/2011JD016936.

Park, M., W. J. Randel, A. Gettelman, S. T. Massie, and J. H. Jiang (2007), Transport above the Asian summer monsoon anticyclone inferred from Aura Microwave Limb Sounder tracers, *J. Geophys. Res.*, *112*, D16309, doi:10.1029/2006JD008294.

Ploeger, F., G. Günther, P. Konopka, S. Fueglistaler, R. Müller, C. M. Hoppe, A. Kunz, R. Spang, and J.-U. Grooß (2013), Horizontal water vapor transport in the lower stratosphere from subtropics to high latitudes during boreal summer, *J. Geophys. Res. Atmos.*, *118*, 8111–8127, doi:10.1002/jgrd.50636.

Randel, W. J., and A. M. Thompson (2011), Interannual variability and trends in tropical ozone derived from SAGE II satellite data and SHADOZ ozonesondes, *J. Geophys. Res.*, *116*, D07303, doi:10.1029/2010JD015195.

Randel, W. J., R. S. Stolarski, D. M. Cunnold, J. A. Logan, M. J. Newchurch, and J. M. Zawodny (1999), Trends in the vertical distribution of ozone, *Science*, *285*, 1689–1692.

Randel, W. J., M. Park, L. Emmons, D. Kinnison, P. Bernath, K. A. Walker, C. Boone, and H. Pumphrey (2010), Asian monsoon transport of pollution to the stratosphere, *Science*, *328*, 611–613.

Randel, W. J., K. Zhang, and R. Fu (2015), What controls stratospheric water vapor in the NH summer monsoon regions?, *J. Geophys. Res. Atmos.*, *120*, 7988–8001, doi:10.1002/2015JD023622.

Rienecker, M. M., et al. (2011), MERRA: NASA's Modern-Era Retrospective Analysis for Research and Applications, *J. Clim.*, *24*, 3624–3648, doi:10.1175/JCLI-D-11-00015.1.

Rosenlof, K. H., and G. C. Reid (2008), Trends in the temperature and water vapor content of the tropical lower stratosphere: Sea surface connection, *J. Geophys. Res.*, *113*, D06107, doi:10.1029/2007JD009109.

Rosenlof, K. H., A. F. Tuck, K. K. Kelly, J. M. Russell III, and M. P. McCormick (1997), Hemispheric asymmetries in water vapor and inferences about transport in the lower stratosphere, *J. Geophys. Res.*, *102*, 13,213–13,234, doi:10.1029/97JD00873.

Saiz-Lopez, A., and R. P. Fernandez (2016), On the formation of tropical rings of atomic halogens: Causes and implications, *Geophys. Res. Lett.*, *43*, 2928–2935, doi:10.1002/2015GL067608.

Schmidt, J. A., et al. (2016), Modeling the observed tropospheric BrO background: Importance of multiphase chemistry and implications for ozone, OH, and mercury, *J. Geophys. Res. Atmos.*, *121*, 11,819–11,835, doi:10.1002/2015JD024229.

Schoeberl, M. R., et al. (2008), QBO and annual cycle variations in tropical lower stratosphere trace gases from HALOE and Aura MLS observations, *J. Geophys. Res.*, *113*, D05301, doi:10.1029/2007JD008678.

Schoeberl, M. R., A. E. Dessler, and T. Wang (2013), Modeling upper tropospheric and lower stratospheric water vapor anomalies, *Atmos. Chem. Phys.*, *13*, 7783–7793, doi:10.5194/acp-13-7783-2013.

Simpson, W. R., S. S. Brown, A. Saiz-Lopez, J. A. Thornton, and R. von Glasow (2015), Tropospheric halogen chemistry: Sources, cycling, and impacts, *Chem. Rev.*, *115*, 4035–4062.

Solomon, S. (1999), Stratospheric ozone depletion: A review of concepts and history, *Rev. Geophys.*, *37*, 275–316, doi:10.1029/1999RG900008.

Solomon, S., J. S. Daniel, R. R. Neely, J.-P. Vernier, E. G. Dutton, and W. L. Thomason (2011), The persistently variable "background" stratospheric aerosol layer and global climate change, *Science*, *333*(6044), 866–870, doi:10.1126/science.1206027.

Solomon, S., D. Kinnison, J. Bandoro, and R. R. Garcia (2015), Polar ozone depletion: An update, *J. Geophys. Res. Atmos.*, *120*, 7958–7974, doi:10.1002/2015JD023365.

Stolarski, R. S., D. W. Waugh, L. Wang, L. D. Oman, A. R. Douglass, and P. A. Newman (2014), Seasonal variation of ozone in the tropical lower stratosphere: Southern tropics are different from northern tropics, *J. Geophys. Res. Atmos.*, *119*, 6196–6206, doi:10.1002/2013JD021294.

Thornton, B. F., et al. (2007), Chlorine activation near the midlatitude tropopause, *J. Geophys. Res.*, *112*, D18306, doi:10.1029/2006JD007640.

Toon, G. C., C. B. Farmer, L. L. Lowes, P. W. Schaper, J.-F. Blavier, and R. H. Norton (1989), Infrared aircraft measurements of stratospheric composition over Antarctica during September 1987, *J. Geophys. Res.*, *94*, 16,571–16,596, doi:10.1029/JD094iD14p16571.

Vernier, J.-P., L. W. Thomason, and J. Kar (2011), CALIPSO detection of an Asian tropopause aerosol layer, *Geophys. Res. Lett.*, *38*, L07804, doi:10.1029/2010GL046614.

Vernier, J.-P., T. D. Fairlie, M. Natarajan, F. G. Wienhold, J. Bian, B. G. Martinsson, S. Crumeyrolle, L. W. Thomason, and K. M. Bedka (2015), Increase in upper tropospheric and lower stratospheric aerosol levels and its potential connection with Asian pollution, *J. Geophys. Res. Atmos.*, *120*, 1608–1619, doi:10.1002/2014JD022372.

Volkamer, R., et al. (2015), Aircraft measurements of BrO, IO, glyoxal, NO_2, H2O, O_2-O2, and aerosol extinction profiles in the tropics: Comparison with aircraft- and ship-based in situ and lidar measurements, *Atmos. Meas. Tech.*, *8*, 2121–2148.

Von Hobe, M., et al. (2011), Evidence for heterogeneous chlorine activation in the tropical UTLS, *Atmos. Chem. Phys.*, *11*, 241–256, doi:10.5194/acp-11-241-2011.

Wang, S., et al. (2015), Active and widespread halogen chemistry in the tropical and subtropical free troposphere, *Proc. Natl. Acad. Sci. U.S.A.*, *112*, 9281–9286.

World Meteorological Organization/United Nations Environment Programme (2014), Scientific assessment of ozone depletion: 2014 World Meterorological Organization Global Ozone Research and Monitoring Project, Report 55, Geneva, Switzerland.