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Solomon, S, Kinnison, D, Garcia, RR et al. (8 more authors) (2016) Monsoon circulations and tropical heterogeneous chlorine chemistry in the stratosphere. Geophysical Research Letters, 43 (24). pp. 12624-12633. ISSN 0094-8276

https://doi.org/10.1002/2016GL071778

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Monsoon circulations and tropical heterogeneous chlorine chemistry in the stratosphere

Susan Solomon¹, Doug Kinnison², Rolando R. Garcia², Justin Bandoro¹, Michael Mills², Catherine Wilka¹, Ryan R. Neely III³, Anja Schmidt³, John Barnes⁵, Jean-Paul Vernier⁶, Michael Höpfner⁸

¹Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MA 02139
²Atmospheric Chemistry Observations and Modeling Laboratory, National Center for Atmospheric Research, Boulder, CO 80307
³School of Earth and Environment, University of Leeds, Leeds, UK
⁴National Centre for Atmospheric Science, University of Leeds, Leeds, UK
⁵NOAA/Mauna Loa Observatory, Hilo, HI 96720
⁶NASA Langley Research Center, Hampton, VA
⁷Science Systems and Applications, Inc., Hampton, VA
⁸Institute of Meteorology and Climate Research, Karlsruhe Institute of Technology, Karlsruhe, Germany

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 non-volcanic particles.

• Heterogeneous chlorine activation contributes to the ozone budget and to tropical lowermost stratosphere ozone trends.
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 et al., 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 testbed 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%; 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, 1999; Randel and Thompson, 2011) and
are thought to be largely dynamical in origin (e.g., WMO/UNEP 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 anti-
cyclonic 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.,
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 non-volcanic 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., 2013; 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 dynamics 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\textsubscript{X}, NO\textsubscript{X}, HO\textsubscript{X}, ClO\textsubscript{X}, and BrO\textsubscript{X} chemical families, along with gas phase and heterogeneous reactions on liquid binary and ternary sulfate aerosols. About 5 pptv of bromine from very-short lived substances (VSLS) contributes to the modeled stratospheric bromine levels, along with CH\textsubscript{3}Br and halon sources. Chlorine from CH\textsubscript{3}Cl, CH\textsubscript{3}CCl\textsubscript{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 using gas phase sulfur and related chemistry along with an aerosol model in SD-WACCM. A database of volcanic SO\textsubscript{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 OCS, anthropogenic SO2, etc.) 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 non-volcanic 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., N₂O₅+H₂O) 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 Figure 3 of Froidevaux et al., 2008). The wind vectors superimposed in Figure 1 show the anti-cyclonic 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 the bottom panel. While temperatures near the tropopause in the summer monsoon regions are warmer than in winter, they are nevertheless much colder than temperatures at mid-latitudes 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 to mid-latitudes 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., 2005; 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 (ACE). 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 airmasses, in which chlorine is largely expected to be tied up in unreactive organic chlorine source gases (mainly CH$_3$Cl 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 supports 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., 2010; Ploeger et al., 2012; 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 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. Supplemental figure S1 shows the distributions of the rates of chemical processes that serve to activate chlorine, and Table S1 indicates sensitivities of 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 194-196K 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 sub-polar 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 0-30°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 tropical average ozone trends are about 1-4% per decade from 17-19 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 inter-halogen 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, 15N in summer, vary between 1-2DU 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 gradient in ClONO$_2$ from about 16-18 km and from about 10-25N 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 14-20°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 15-20 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 different y-axes for model and data in the bottom panel of Figure 4). Jaeger and Hofmann (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 Fig. 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 summer ClO and ClONO₂ abundances in this region when heterogeneous chlorine reactions are simulated for non-volcanic conditions are of 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 of the order of 10 pptv for ClO and 5-8 pptv for ClONO₂ 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 Figure 1 in Solomon et al., 2011).

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 mid-latitudes 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 10-20N in the altitude range from 16-18 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 datasets 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$_2$, HOCl, etc. may also be useful to probe the impacts of this heterogeneous chemistry. Laboratory studies of these reactions have used H$_2$SO$_4$/H$_2$O and H$_2$SO$_4$/H$_2$O/HNO$_3$ solutions, and those studies form the basis for the chemistry recommended in JPL (2011) and imposed in models. Even for pure H$_2$SO$_4$/H$_2$O solutions, uncertainties in liquid heterogeneous reactivities are poorly quantified, especially for temperatures below about 200K. Further, direct measurements of particle composition in the tropical tropopause region have revealed substantial amounts of other components, such as non-volatile species and pollutants including organic compounds (Murphy, 2009; 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 non-volcanic 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 non-volcanic 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 and Data. We thank Dan Murphy and Brian Toon for helpful
discussions. SS and JB acknowledge funding under NSF-1539972 and NSF-1419667.
RN is supported by the Natural Environment Research Council (NERC) through the
National Centre for Atmospheric Science (NCAS) in the UK. AS was supported by an
Academic Research Fellowship from the University of Leeds and a NCAR visiting
researcher grant. JB is funded by NOAA/ESRL/GMD. The National Center for
Atmospheric Research (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 (CISL). 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.

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**Figure Captions**

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

**Figure 2.** Model calculated monthly mean distributions of ClO (pptv, top panel), ClONO$_2$ (pptv, bottom panel) for July 2011 at 17 km, with superimposed wind vectors.
Figure 3. Zonally averaged ClONO$_2$ abundances (pptv) in July 2011 versus latitude and altitude in SD-WACCM model calculations with (top) and without (bottom) 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.

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 ClO (top), and ClONO$_2$ (second from top). 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 at 15, 16, and 17 km (third from top). Aerosol backscatter integrated over 15-20 km (bottom) at Mauna Loa (per steradian) from observations (right axis) and from the model, assuming an extinction-to-backscatter conversion factor of 40 (left axis). Note change in scale of the two y-axes in the bottom panel.
Figure 1.
Figure 2.
Figure 3.
Figure 4.