White Rose
university consortium
Universities of Leeds, Sheffield & York

1   Monsoon circulations and

2   tropical heterogeneous chlorine chemistry in the stratosphere

3

4 Susan Solomon[1], Doug Kinnison[2], Rolando R. Garcia[2], Justin Bandoro[1], Michael Mills[2],

5 Catherine Wilka[1], Ryan R. Neely III[3,4], Anja Schmidt[3], John Barnes[5], Jean-Paul

6 Vernier[6,7], Michael Höpfner[8]

7

8 [1]Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology,

9 Cambridge, MA 02139

10 [2]Atmospheric Chemistry Observations and Modeling Laboratory, National Center for Atmospheric

11 Research, Boulder, CO 80307

12 [3]School of Earth and Environment, University of Leeds, Leeds, UK

13 [4]National Centre for Atmospheric Science, University of Leeds, Leeds, UK

14 [5]NOAA/Mauna Loa Observatory, Hilo, HI 96720

15 [6]NASA Langley Research Center, Hampton, VA

16 [7]Science Systems and Applications, Inc., Hampton, VA

17 [8]Institute of Meteorology and Climate Research, Karlsruhe Institute of Technology, Karlsruhe, Germany

18 Key Points.

19 • Transport linked to the monsoons brings increased HCl into contact with liquid

20 aerosols in the cold tropical lowermost stratosphere.

21 • Model results indicate that monsoon flows lead to tropical activation of reactive

22 chlorine on volcanic and non-volcanic particles.

23 • Heterogeneous chlorine activation contributes to the ozone budget and to tropical

24 lowermost stratosphere ozone trends.

25

26 Abstract. Model simulations presented in this paper suggest that transport processes

27 associated with the summer monsoons bring increased abundances of hydrochloric acid

28 into contact with liquid sulfate aerosols in the cold tropical lowermost stratosphere,

29 leading to heterogeneous chemical activation of chlorine species. The calculations

30 indicate that the spatial and seasonal distributions of chlorine monoxide and chlorine

31 nitrate near the monsoon regions of the northern hemisphere tropical and subtropical

32 lowermost stratosphere could provide indicators of heterogeneous chlorine processing.

33 In the model, these processes impact the local ozone budget and decrease ozone

34 abundances, implying a chemical contribution to longer-term northern tropical ozone

35 profile changes at 16-19 km.

36

37 1. Introduction

38

39 Heterogeneous chlorine chemistry on and in liquid polar stratospheric particles is thought

40 to play a significant role in polar and subpolar ozone depletion (Solomon et al., 1999

41 review, and references therein).   Previous studies have not provided evidence for

42 heterogeneous chlorine chemistry occurring in the tropical stratosphere. Using the

43 current best understanding of liquid stratospheric particle chemistry in a state-of-the-art

44 numerical model, we examine whether such processes should be expected to affect

45 tropical composition, particularly at and slightly above the cold tropical tropopause, in

46 association with the Asian and North American summer (June-July-August) monsoons.

47 Further, we probe whether volcanic emissions of sulfur (which can increase stratospheric

48 sulfate aerosol abundances) could enhance this chemistry.   The primary focus of this

49 paper is to examine whether ClO and $ClONO_2$ observations near the monsoon regions in

50 the tropical lowermost stratosphere could provide a novel testbed for understanding

51 stratospheric chlorine activation chemistry, while a secondary focus is on whether such

52 chemistry has the potential to contribute to the budget and trends of the tropical ozone

53 profile below about 20 km.   Stratospheric chlorine chemistry has been a subject of

54 interest for decades, but key uncertainties remain in heterogeneous reactions rates (e.g.,

55 1-sigma uncertainties in reaction rates of 40%; JPL, 2011) that may be testable in new

56 ways in the tropics.   The ozone profile trends in the tropical lowermost stratosphere have

57 long been a topic of scientific interest (Randel, 1999; Randel and Thompson, 2011) and

58 are thought to be largely dynamical in origin (e.g., WMO/UNEP 2014 and references

59 therein).   Understanding whether there may be a potential chemical contribution to

60 tropical lower stratospheric ozone profile trends is hence of substantial scientific interest

61 and a secondary goal of this paper.

62

63 Monsoons are primarily driven by continental heating, extend into the lower stratosphere

64 (e.g., Dunkerton, 1995), and involve deep convection and formation of strong anti-

65 cyclonic circulation cells on a seasonal basis, maximizing in summer over Asia and North

66 America (e.g., Gettelman et al., 2004; Park et al., 2007; Randel et al., 2010).   Weaker

67 monsoons are observed over southern hemisphere landmasses.   Observations have shown

68 that transport related to the monsoons influences a range of chemicals in the tropical and

69 subtropical tropopause regions, including tracers such as carbon monoxide and hydrogen

70 cyanide (Randel et al., 2010), ozone (Park et al., 2007), volcanic and pollution aerosols

71 (Vernier et al., 2011; 2015) and water vapor (e.g., Rosenlof et al., 1997; Randel et al.,

72   2015; Schoeberl et al., 2013, Ploeger et al., 2013).   Water vapor can play a role in

73   heterogeneous chemistry under cold conditions, both through its influence on formation

74   of ice clouds and through the dependence of chlorine activation reactions on the water

75   content of liquid stratospheric aerosol particles (which contain sulfuric acid and water,

76   see, e.g., Solomon, 1999; Thornton et al., 2007; Anderson et al., 2012).   The influences

77   of HCl, water vapor, and temperature changes for stratospheric chlorine chemistry in the

78   tropics are discussed further below.

79

80   The primary goal of this paper is to probe the extent to which heterogeneous chlorine

81   chemistry may be expected to occur on liquid sulfate aerosols in the tropical stratosphere.

82   Liquid aerosol effects could represent a lower limit to this chemistry if, for example,

83   similar reactions also take place on tropical cirrus ice clouds, but the potential for ice

84   chemistry is not examined here.   Heterogeneous halogen reactions on ice are sensitive to

85   the size distribution of cirrus ice particles (e.g., Bregman et al., 1997) and to the adopted

86   parameterization of cirrus clouds in models.   Heterogeneous processing involving

87   chlorine, bromine, and iodine have also been identified on liquid and/or ice aerosols in

88   the troposphere (e.g., Wang et al., 2015; Schmidt et al., 2016; Saiz-Lopez and Fernandez,

89   2016; Von Hobe et al., 2011; see the review by Simpson et al., 2015 and references

90   therein) but the focus here is on stratospheric chlorine chemistry and the role of transport

91   via the monsoon circulations.

92   Recent progress in stratospheric chemistry modeling underpins this study.   State-of-the-

93   art atmospheric chemistry models have been extensively intercompared and tested (e.g.,

94   Eyring et al., 2010), and the temperature-sensitive heterogeneous chemistry can be driven

95   by specified dynamics and temperatures from reanalysis fields based on observations;

96   here we use the Community Earth System Model, version 1, with the Whole Atmosphere

97   Community Climate Model version 4, as the atmospheric component

98   (CESM1(WACCM); see Marsh et al., 2013). The model's representation of

99   heterogeneous chemistry was shown to be in broad agreement with polar ozone and

100 constituent observations in Solomon et al. (2015), supporting its use to examine other

101 regions.

102 The stratospheric aerosol distributions employed in this model include representations of

103 both volcanic and non-volcanic sulfur sources. The calculated aerosol properties were

104 discussed in detail in Mills et al. (2016), and shown to compare well to total stratospheric

105 aerosol extinction data from lidars, including the Mauna Loa lidar. Further comparisons

106 to ground-based and satellite lidar backscatter data in the lowermost tropical stratosphere

107 are presented below. During the summer of 2011, tropical stratospheric aerosols were

108 enhanced compared to several other recent years, at least in part due to volcanic inputs

109 from the Nabro eruption in mid-June (Bourassa et al., 2012; Fairlie et al., 2013; Neely et

110 al., 2013) although pollution from Asian sources also contributes to aerosol loading in the

111 monsoon region (Vernier et al., 2015).   In this paper we focus on 2011 as a period

112 when high tropical volcanic aerosol loading should be expected to increase the potential

113 role of the chemistry under consideration, and we compare 2011 to calculations for other

114 years.

115 2. Model Description

116

117 The specified dynamics version of CESM1 (WACCM), herein referred to as SD-

118   WACCM, is nudged to externally specified dynamical fields for temperature, zonal and

119   meridional winds, and surface pressure fields from the Modern Era Retrospective

120   Analysis for Research and Applications (MERRA; see Rienecker et al., 2011). The

121   procedure used to constrain the model is described by Marsh (2011) and Kunz et al.

122   (2011). The chemistry scheme includes the O_X, NO_X, HO_X, ClO_X, and BrO_X chemical

123   families, along with gas phase and heterogeneous reactions on liquid binary and ternary

124   sulfate aerosols. About 5 pptv of bromine from very-short lived substances (VSLS)

125   contributes to the modeled stratospheric bromine levels, along with CH_3Br and halon

126   sources.   Chlorine from CH_3Cl, CH_3CCl_3, and industrial chlorofluorocarbons is included

127   in the model.   Arguably, our results represent a lower limit since chlorine from VSLS

128   may also contribute (see Hossaini et al, 2015) but are not included here, nor is convective

129   lofting of sea salt evaluated (e.g., Schmidt et al., 2016).   Such additional sources of

130   chlorine and bromine could add to the chemical effects identified here if they reach the

131   stratosphere.   Iodine chemistry is not included in the model; if there were to be iodine

132   input to the stratosphere akin to that identified in the upper troposphere, (see e.g.,

133   Volkamer et al., 2015; Saiz-Lopez and Fernandez, 2016) that could further affect the

134   chemistry of the region considered, but is not represented in this model.   The

135   homogeneous and heterogeneous reactions and rate coefficients used in the simulations in

136   this paper are based on JPL (2011) except where indicated in Solomon et al. (2015).

137   We employ monthly averaged atmospheric aerosol distributions from Mills et al. (2016),

138   which were calculated using gas phase sulfur and related chemistry along with an aerosol

139   model in SD-WACCM.   A database of volcanic SO_2 emissions and plume altitudes was

140   developed for eruptions between 1990 and 2014 by Neely and Schmidt (2016), and these

141 volcanic sulfur inputs along with background sources of sulfur (including OCS,

142 anthropogenic SO_2, etc.) were used to simulate stratospheric sulfate aerosols (Mills et al.,

143 2016). Aerosols are modeled as three lognormal modes: Aitken, accumulation, and

144 coarse. The model is capable of representing interactions of aerosol particles including

145 nucleation, condensation, coagulation, and sedimentation; for further details and

146 comparisons to observations, see Mills et al. (2016).

147 Three sets of SD-WACCM chemistry model results probe heterogeneous chlorine

148 chemistry in this paper: (i) simulations including volcanic and non-volcanic aerosol

149 sources; (ii) volcanically-clean simulations that include only background sources of

150 sulfur and (iii) simulations in which heterogeneous reactions are turned off between 40°N

151 and 40°S (but allowing heterogeneous reactions that do not involve chlorine or bromine

152 (e.g., $N_2O_5+H_2O$) to continue to occur).

153 3. Results

154

155 Figure 1 shows the distributions of calculated HCl obtained in SD-WACCM along with

156 the temperature distributions for the month of July, 2011 at 100 and 85 hPa, compared to

157 HCl observations for the channel centered at 100 hPa from the Microwave Limb Sounder

158 (MLS) instrument (Froidevaux et al., 2008), version 4.2. Model meteorological

159 tropopauses in the northern tropics at this time of year are from 90 to 130 hPa depending

160 upon longitude. No MLS data for HCl are available at 85 hPa, and the sounder has a

161 fairly broad vertical weighting function (see Figure 3 of Froidevaux et al., 2008). The

162 wind vectors superimposed in Figure 1 show the anti-cyclonic large-scale circulations

163 associated with the monsoonal flows over Asia and North America, and the temperatures

164   prescribed in SD-WACCM from MERRA are also overlaid in the bottom panel.   While

165   temperatures near the tropopause in the summer monsoon regions are warmer than in

166   winter, they are nevertheless much colder than temperatures at mid-latitudes at these

167   altitudes, as can be seen in the overlaid contours of Figure 1.

168

169   The HCl gradients in the data and the model are qualitatively similar but display some

170   important quantitative differences. While the model tropical minima near 100 hPa are

171   lower than the MLS minima, a high bias of about 200 pptv at low to mid-latitudes in

172   MLS was noted in Froidevaux et al. (2008); further, tropical HCl by the infrared

173   HALogen Occultation Experiment (HALOE) are about 15% lower than MLS

174   (Froidevaux et al., 2005; see also Schoeberl et al., 2008).   Froidevaux et al. (2008,

175   figures 11 and 14) also showed larger local differences of up to 20-50% at 100 hPa in

176   parts of the tropics in comparisons of MLS with HALOE and the Atmospheric Chemistry

177   Experiment (ACE).   In all of these satellite data sources however, the HCl abundances

178   are much lower in the tropical lower stratosphere than in the extratropics; this is a robust

179   feature that is key to our analysis as discussed below.

180

181   Tropical regions are characterized on average by upwelling airmasses, in which chlorine

182   is largely expected to be tied up in unreactive organic chlorine source gases (mainly

183   CH_3Cl and chlorofluorocarbons).   When these gases travel upward and poleward in the

184   stratosphere, their chemical breakdown supplies inorganic chlorine.   The inorganic

185   chlorine can interact with sufficiently cold and wet surfaces and activate the chlorine (by

186   converting the inactive reservoir species, HCl, into free radical and less stable species, Cl,

187 ClO, ClONO$_2$, and HOCl). In the two polar regions, this chemistry enhances ClO and

188 destroys ozone.   Chlorine activation and related chlorine-catalyzed ozone loss has been

189 documented following its discovery in association with the Antarctic ozone hole, but it

190 has been generally assumed that similar chemistry was negligible in the tropics due to

191 insufficient inorganic chlorine (see, e.g., Solomon, 1999 for a review stating this

192 assertion).   However, Figure 1 shows that, in our model, the monsoon circulations lead

193 to equatorward transport of inorganic chlorine into the northern subtropics and tropics

194 along the eastern side of the monsoon anticyclones, and the MLS data supports these

195 general features.   Recent studies have emphasized the importance of quasi-horizontal

196 transport in producing larger abundances of several key chemical constituents (including

197 ozone and HCl) in the northern tropics as compared to the southern tropics (e.g.,

198 Konopka et al., 2010; Ploeger et al., 2012; Abalos et al., 2012; Stolarski et al., 2014).

199

200 Figure 1 highlights the role of equatorward transport of extratropical air on the eastern

201 flanks of the northern hemisphere monsoon anticyclones, substantially increasing

202 available inorganic chlorine at northern subtropical latitudes in summer in this model and

203 in the observations. The combination of relatively cold temperatures, liquid aerosols, and

204 transport of inorganic chlorine from higher latitudes drives low-latitude heterogeneous

205 chlorine activation and enhances calculated ClO in our model.   Figure 2 presents maps

206 of ClO and ClONO$_2$ calculated in the model at 17 km for July 2011 when low-latitude

207 heterogeneous chlorine chemistry is included.   Supplemental figure S1 shows the

208 distributions of the rates of chemical processes that serve to activate chlorine, and Table

209 S1 indicates sensitivities of the key activation reaction rate constant to the range of

210   temperature and water vapor changes in the regions of maximum activation, illustrating

211   that the temperature changes are much more important than the water vapor changes for

212   enhancing the chemical reactivity.   The largest heterogeneous chlorine activation rates

213   occur near 15-20°N, particularly where the southward flow around the Asian monsoon

214   brings high levels of inorganic chlorine into the coldest part of the subtropical lower

215   stratosphere, where the eastern edge of the anticyclone flows into the Western Pacific.

216   Temperatures as cold as 194-196K are found even in summer near, for example, 135°E in

217   this region (Figures 1, 2, and S1).

218

219   Local maxima in ClO of over 30 pptv (monthly mean) are calculated near the Asian

220   monsoon region near 17 km, while peak values of 15 pptv are obtained near the North

221   American monsoon region (Figure 2). Chlorine activation can be expected to produce

222   enhanced $ClONO_2$ downwind of the main activation region, provided that NO_x is not

223   completely removed by the heterogeneous processing.   This chemistry forms the well-

224   known $ClONO_2$ 'collar' at sub-polar latitudes (e.g., Toon et al., 1989).   Figure 2 shows

225   that the model calculates $ClONO_2$ values as large as 50-75 pptv near the ClO maxima,

226   linked to the North American and Asian summer monsoons. The calculated tropical

227   stratospheric chlorine activation depicted in Figure 2 has not been discussed in previous

228   studies of which we are aware.

229

230   A consequence of elevated ClO concentrations is potential destruction of stratospheric

231   ozone. When the tropical heterogeneous chlorine chemistry identified here is included

232   compared to calculations excluding it, we calculate ozone decreases (averaged over the

233   years 2009-2012 and over the northern tropics from 0-30°N) of about 2.5% at 16-17 km,

234   about 1.5% at 18 km, and about 1% at 19 km.   For comparison, the estimated tropical

235   average ozone trends are about 1-4% per decade from 17-19 km over 1980-2005 (Randel

236   and Thompson, 2011; their figure 12).

237

238   The catalytic cycle involving chlorine and hydrogen radicals (in which the rate limiting

239   step is $ClO + HO_2$) dominates our calculated ozone decreases, but the inter-halogen

240   reaction between ClO and BrO also represents about 25% of the modeled ozone decrease.

241   These numbers imply an effect on the local ozone budget due to heterogeneous chlorine

242   chemistry, and whether this change represents anthropogenic ozone depletion (as

243   opposed to a change in the ozone background state) depends upon the balance between

244   chlorine and bromine from industrial chemicals versus natural sources in this region,

245   particularly very short-lived species (VSLS) with biogenic origins. In our model, the

246   balance between industrial and VSLS sources of chlorine and bromine suggests that

247   about three-quarters of the calculated ozone change is traceable to anthropogenic

248   emissions. While it is remains likely that most of the ozone trend in tropical lower

249   stratosphere ozone since 1979 is linked to dynamical changes (Randel and Thompson,

250   2011), our work implies that heterogeneous chlorine chemistry may have made some

251   contributions to the vertical profile of trends in ozone in this region.   The changes are

252   confined to a narrow height range, and the corresponding decreases in column ozone for

253   calculations including heterogeneous chemistry to those without them at, for example,

254   15N in summer, vary between 1-2DU over 2009-2011.   Whether the changes in ozone

255   profile or column due to the chemistry discussed here can be detected in observations

256   would depend not only on the precision and accuracy of the ozone measurements, but

257   also on the ability to quantify dynamical factors to sufficient accuracy. More detailed

258   analysis of tropical ozone trends is outside the scope of the present paper.

259

260   Figure 3 presents the zonally averaged distributions of $ClONO_2$ versus latitude and

261   altitude for July, 2011 for these SD-WACCM simulations. The location of the

262   meteorological tropopause is indicated in the figure. When low latitude heterogeneous

263   chlorine chemistry is included in the model, the calculated stratospheric gradient in

264    $ClONO_2$ from about 16-18 km and from about 10-25N in July 2011 displays a

265   pronounced 'tongue', with peak zonal mean abundances of over 40 pptv, while no such

266   tongue is obtained in the model without heterogeneous chemistry.   Figure 3 illustrates

267   that the region substantially affected by the chemistry considered here is confined to a

268   limited range of height and latitude.

269

270   Figure 4 presents seasonal changes in ClO and $ClONO_2$ over several years at 17 km

271   averaged over the latitude band from 14-20°N for the three model test cases noted above:

272   with volcanic sulfur inputs, for volcanically clean conditions, and with the heterogeneous

273   chlorine activation chemistry turned off.   Figure 4 shows that the calculated

274   heterogeneous chemical processes greatly increase the modeled concentrations of ClO

275   and $ClONO_2$ compared to calculations without heterogeneous chemistry. The changes in

276   these two species as compared to the no heterogeneous chemistry case exceed their

277   interannual variability, and are robust to substantial seasonal changes in HCl from month

278   to month (i.e., June-July-August) or interannually (see Figures 4 and S2). Considerably

279   smaller relative changes that lie within interannual variations are expected for HCl

280   (Figure S2). Figure 4 also presents averaged measured satellite extinction in the

281   monsoon region (15-45°N, 5-105°E) at 15, 16, and 17 km (adapted from Figure 2 in

282   Vernier et al., 2015) as compared to the model. As a further check on the modeled

283   aerosols over broader parts of the tropics, Figure 4 compares observations of lidar

284   backscatter from Mauna Loa observatory (19°N) integrated from 15-20 km to that from

285   the model at the same site; the modeled extinction has been converted to backscatter here

286   using a backscatter to extinction conversion factor of 40 (note different y-axes for model

287   and data in the bottom panel of Figure 4).   Jaeger and Hofmann (2002, 2003) suggest

288   values of about 20-60 for this conversion factor depending on particle sizes, with lower

289   values for larger particles following major eruptions.   Figure 4 shows that the model

290   captures the timing and magnitudes of the volcanic enhancements that are apparent in

291   both sets of observations. The modeled absolute values are generally close to the Vernier

292   et al. (2015) data but are somewhat lower than the Mauna Loa data.

293

294   The calculated chlorine activation that is evident in Figure 4 varies from year to year and

295   month to month depending on multiple factors: the strength of the transport associated

296   with the monsoons (which affects total chlorine), changes in temperature, and changes in

297   stratospheric aerosol amounts (see Fig. S1).   It is likely that the quasi-biennial oscillation

298   plays a role in modulating transport of HCl from year to year (Schoeberl et al., 2008), and

299   the El Niño is also important for temperature variations, particularly in the warm pool

300   region of maximum activation (e.g., Rosenlof and Reid, 2008; Nishimoto and Shiotani,

301   2012).

302

303   The model results shown in Figure 4 suggest that heterogeneous chlorine chemistry in

304   this region greatly enhances reactive chlorine species even for volcanically clean

305   conditions, with substantial increases above what would be expected without

306   heterogeneous processing.   Figure 4 suggests summer ClO and ClONO$_2$ abundances in

307   this region when heterogeneous chlorine reactions are simulated for non-volcanic

308   conditions are of the order of 5 and 25-40 pptv respectively, compared to only a few

309   tenths of a pptv and 5-10 pptv when these reactions are neglected.   Further increases of

310   the order of 10 pptv for ClO and 5-8 pptv for ClONO$_2$ are simulated in volcanically

311   perturbed summers, particularly 2011 (after Nabro) and 2009 (when transport of aerosol

312   to the tropics from the Sarychev eruption has been documented; see Figure 1 in Solomon

313   et al., 2011).

314

315   4. Discussion and Conclusions

316

317   Heterogeneous chlorine chemistry has been well established in polar regions through

318   extensive measurements and modeling, and it should be expected to operate in other

319   latitudes if conditions allow. In this paper, we have shown that numerical model

320   simulations indicate that the appropriate conditions occur in association with the northern

321   hemisphere summer monsoons based on current chemical understanding.

322

323   Figures 1 and 2 taken together illustrate how the input of inorganic chlorine from mid-

324   latitudes and the relatively cold conditions of the tropical lowermost stratosphere region

325 combine to produce a rapid rate of chlorine activation on liquid sulfate aerosols near the

326 northern monsoon regions in SD-WACCM.   The largest rates of calculated chlorine

327 activation are associated with flow around the Asian monsoon into the especially cold

328 lower stratosphere near the Western Pacific warm pool.   Our model results suggest that

329 heterogeneous chlorine activation should greatly increase average ClO and $ClONO_2$

330 abundances from about 10-20N in the altitude range from 16-18 km as compared to

331 simulations neglecting this chemistry.   Volcanic increases in liquid sulfate aerosols

332 enhance the perturbations, but the heterogeneous reactions are thought to be sufficiently

333 rapid that substantial changes are also indicated for volcanically clean conditions.

334

335 Many stratospheric chlorine chemistry measurements have focused on polar and subpolar

336 regions. We are not aware of any available datasets that have validated measurements of

337 ClO or $ClONO_2$ in the 16-18 km region of the tropics and subtropics against which our

338 findings could be further tested.   Stratospheric chemistry is tightly coupled, and other

339 constituents including HCl, NO, NO_2, HOCl, etc. may also be useful to probe the impacts

340 of this heterogeneous chemistry.   Laboratory studies of these reactions have used

341 H_2SO_4/H_2O and $H_2SO_4/H_2O/HNO_3$ solutions, and those studies form the basis for the

342 chemistry recommended in JPL (2011) and imposed in models.   Even for pure

343 H_2SO_4/H_2O solutions, uncertainties in liquid heterogeneous reactivities are poorly

344 quantified, especially for temperatures below about 200K.   Further, direct measurements

345 of particle composition in the tropical tropopause region have revealed substantial

346 amounts of other components, such as non-volatile species and pollutants including

347 organic compounds (Murphy, 2009; 2014; Borrmann et al., 2010).   Whether these

348   components could alter the stratospheric liquid aerosol reactivity is unknown.   If so, then

349   particle reactivities might differ in volcanic versus non-volcanic years, since the volcanic

350   particles would contain a much larger fraction of sulfuric acid, and hence provide a closer

351   correspondence to the laboratory data compared to non-volcanic conditions.   Our

352   simulations provide a testable framework for examining whether or not heterogeneous

353   chlorine chemistry takes place in the tropical lowermost stratosphere, either under

354   volcanically clean or volcanically perturbed conditions, or both.

355

371   for the MERRA data (accessed freely online at http://disc.sci.gsfc.nasa.gov/) and the

372   Aura MLS team for HCl data (accessed freely online at

373   http://disc.sci.gsfc.nasa.gov/Aura/data-holdings/MLS). Mauna Loa lidar data shown in

374   this paper may be accessed at http://ndacc-lidar.org/.   Model results shown in this paper

375   are available on request to the WACCM liaison, Michael Mills mmills@ucar.edu.

376   References

377   Abalos, M., W. J. Randel, and E. Serrano (2012), Variability in upwelling across the

378   tropical tropopause and correlations with tracers in the lower stratosphere, *Atmos.*

379   *Chem. Phys.*, 12, 11,505–11,517, doi:10.5194/acp-12-11505-2012.

380   Anderson, J. G., Wilmouth, D. M., Smith, J. B., and D. S. Sayres (2012), UV dosage

381   levels in summer: Increased risk of ozone loss from convectively injected water

382   vapor, *Science*, 337, 835-839, doi: 10.1126/science.1222978.

383   Borrmann, S., et al. (2010), Aerosols in the tropical and subtropical UT/LS: in-situ

384   measurements of submicron particle abundance and volatility, *Atmos. Chem.*

385   *Phys.*, 10, 5573–5592, doi:10.5194/acp-10-5573-2010.

386   Bourassa, A. E., Robock, A., Randel, W. J., Deshler, T., Rieger, L. A., Lloyd, N. D.,

387   Llewellyn, E. J., and D. A. Degenstein (2012), Large volcanic aerosol load in the

388   stratosphere linked to Asian monsoon transport, *Science*, 337, 78-81,

389   doi:10.1126/science.1219371, 2012.

390   Bregman, A., M. van den Broek, K. S. Carslaw, R. Mueller, T. Peter, M. P. Scheele, and

391   J. Lelieveld, (1997), Ozone depletion in the late winter lower Arctic stratosphere:

392   Observations and model results, *J. Geophys. Res.*, 102, 10815-10828.

393   Dunkerton, T. J., (1995) Evidence of meridional motion in the summer lower stratosphere

394   adjacent to monsoon regions, *J. Geophys. Res*., 100(D8), 16675–16688,

395   doi:10.1029/95JD01263.

396   Eyring, V., T. G. Sheperd, and D. W. Waugh (Eds.) (2010), SPARC report on the evalua-

397   tion of chemistry-climate models, SPARC Rep. No. 5, WRCP-132, WMO-TD

398   No. 1526, World Met. Org., Geneva.

399   Fairlie, T. D., J.-P. Vernier, M. Natarajan, and K. M. Bedka, (2014), Dispersion of the

400   Nabro volcanic plume and its relation to the Asian summer monsoon, *Atm. Chem.*

401   *Phys*., 14, 7045-7057, doi:10.5194/acp-14-7045-2014.

402   Froidevaux, L., et al. (2008), Validation of Aura Microwave Limb Sounder HCl

403   measurements, *J. Geophys. Res*., 113, D15S25, doi:10.1029/2007JD009025.

404   Gettelman, A., D. E. Kinnison, T. J. Dunkerton, and G. P. Brasseur (2004), Impact of

405   monsoon circulations on the upper troposphere and lower stratosphere, *J.*

406   *Geophys. Res*., 109, D22101, doi:10.1029/2004JD004878.

407   Hossaini, R., M. P. Chipperfield, S. A. Montzka, A. Rap, S. Dhomse, and W. Feng,

408   (2015), Efficiency of short-lived halogens at influencing climate through

409   depletion of stratospheric ozone, *Nat. Geosci*., 8, 186-190.

410   Jäger, H. and T. Deshler: Lidar backscatter to extinction, mass and area conversions for

411   stratospheric aerosols based on midlatitude balloonborne size distribution

412   measurements, *Geophys. Res. Lett*., 29(19), 1929, doi:10.1029/2002GL015609,

413   2002. (correction *Geophys. Res. Lett.*, 30(7), 1382, doi:10.1029/2003GL017189,

414   2003).

415 Jet Propulsion Laboratory JPL (2011), Chemical kinetics and photochemical data for use

416   in atmospheric studies, evaluation number 15, JPL Publication, 06-2.

417 Konopka, P., J.-U. Grooß, F. Ploeger, and R. Müller (2009), R.: Annual cycle of

418   horizontal in-mixing into the lower tropical stratosphere, *J. Geophys. Res.*, 114,

419   D19111, doi:10.1029/2009JD011955.□

420 Kunz, A., L. L. Pan, P. Konopka, D. E. Kinnison, and S. Tilmes, 2011: Chemical and

421   dynamical discontinuity at the extratropical tropopause based on START08 and

422   WACCM analyses. *J. Geophys. Res., 116*, D24302, doi:10.1029/2011JD016686.

423 Marsh, D. R., 2011: Chemical□dynamical coupling in the mesosphere and lower

424   thermosphere, in *Aeronomy of the Earth's Atmosphere and Ionosphere, IAGA*

425   *Spec. Sopron Book Ser.*, *Vol. 2*, edited by M. Abdu, D. Pancheva, and A.

426   Bhattacharyya, pp. 3–17, Springer, Dordrecht, Netherlands.

427 Marsh, D. R., M.J. Mills, D. E. Kinnison, J. F. Lamarque, N. Calvo, and L. M. Polvani,

428   (2013), Climate Change from 1850 to 2005 Simulated in CESM1(WACCM). *J.*

429   *Clim.*, 26, 7372–7391, doi: 10.1175/JCLI-D-12-00558.1

430 Mills, M. J., et al. (2016), Global volcanic aerosol properties derived from emissions,

431   1990–2014, using CESM1(WACCM),□ *J. Geophys. Res.*, 121, 2332–2348,

432   doi:10.1002/2015JD024290. □

433 Murphy, D. M., Thomson, D. S., and M. J. Mahoney (1998), *In situ* measurements of

434   organics, meteoric material, mercury, and other elements in aerosols at 5 to19 km,

435   *Science,* 282, 1664–1669.□

436   Murphy, D. M., Froyd, K. D., Schwarz, J. P., and J. C. Wilson (2014), Observations of

437   the chemical composition of stratospheric aerosol particles, *Q. J. Roy. Met. Soc.,*

438   140, 1269-1278.

439   Neely III, R.R., O.B. Toon, S. Solomon, J.-P. Vernier, C. Alvarez, J.M. English, K.H.

440   Rosenlof, M.J. Mills, C.G. Bardeen, J.S. Daniel and J.P. Thayer (2013), Recent

441   anthropogenic increases in SO_2 from Asia have minimal impact on stratospheric

442   aerosol, *Geophys. Res. Lett.,* 40, doi:10.1002/grl.50263.

443   Neely III, R.R. and A. Schmidt (2016), VolcanEESM (Volcanic Emissions for Earth

444   System Models): Volcanic sulphur dioxide (SO2) emissions database from 1850

445   to present. Centre for Environmental Data Analysis, *(2016).*

446   http://catalogue.ceda.ac.uk/uuid/bfbd5ec825fa422f9a858b14ae7b2a0d.

447   Nishimoto, E., and M. Shiotani (2012), Seasonal and interannual variability in the

448   temperature structure around the tropical tropopause and its relationship□with

449   convective activities, J. Geophys. Res., 117, D02104,

450   doi:10.1029/2011JD016936.

451   Park, M., Randel, W. J., Gettelman, A., Massie, S. T., and J. H. Jiang, (2007), Transport

452   above the Asian summer monsoon anticyclone inferred from Aura Microwave

453   Limb Sounder tracers, *J. Geophys. Res.,*112, D16309,

454   doi:10.1029/2006JD008294.

455   Ploeger, F., et al. (2013), Horizontal water vapor transport in the lower stratosphere from

456   subtropics to high latitudes during boreal summer, *J. Geophys. Res.*, 118, 8111–

457   8127, doi:10.1002/jgrd.50636.□

458 Randel, W. J., R. S. Stolarski, D. M. Cunnold, J. A. Logan, M. J. Newchurch, and J. M.

459   Zawodny (1999), Trends in the vertical distribution of ozone, *Science*, 285, 1689-

460   1692.

461 Randel, W. J., et al. (2010), Asian monsoon transport of pollution to the stratosphere,

462   *Science*, 328, 611-613.

463 Randel, W. J., and A. M. Thompson, (2011), Interannual variability and trends in tropical

464   ozone derived from SAGE II satellite data and SHADOZ ozonesondes, J.

465   Geophys. Res., 116, D07303, doi:10.1029/2010JD015195.

466 Randel, W. J., K. Zhang, and R. Fu (2015), What controls stratospheric water vapor in

467   the NH summer monsoon regions?, *J. Geophys. Res.*, 120, 7988–8001,

468   doi:10.1002/2015JD023622. □

469 Rienecker, M. M., et al. (2011), MERRA: NASA's Modern-Era Retrospective Analysis

470   for Research and Applications, *J. Clim.*, 24, 3624–3648, doi: 10.1175/JCLI-D-11-

471   00015.1.

472 Rosenlof, K. H., and G. C. Reid, (2008), Trends in the temperature and water vapor

473   content of the tropical lower stratosphere: Sea surface connection, J. Geophys.

474   Res., 113, D06107, doi:10.1029/2007JD009109.

475 Rosenlof, K. H., A. F. Tuck, K. K. Kelly, J. M. Russell III, and M. P. McCormick (1997),

476   Hemispheric asymmetries in water vapor and inferences about transport in the

477   lower stratosphere, *J. Geophys. Res.*, 102, 13,213–13,234,

478   doi:10.1029/97JD00873.□

479   Saiz-Lopez, A., and R. P. Fernandez, (2016), On the formation of tropical rings of atomic

480   halogens: causes and implications, *Geophys. Res. Lett.*, 43, 2928–2935,

481   doi:10.1002/2015GL067608.

482   Schoeberl, M. R., A. E. Dessler, and T. Wang (2013), Modeling upper tropospheric and

483   lower stratospheric water vapor anomalies, *Atmos. Chem. Phys.*, 13, 7783–7793,

484   doi:10.5194/acp-13-7783-2013.

485   Schoeberl, M. R., et al. (2008), QBO and annual cycle variations in tropical lower

486   stratosphere trace gases from HALOE and Aura MLS observations, J. Geophys.

487   Res., 113, D05301, doi:10.1029/2007JD008678.

488   Schmidt, J. A., et al. (2016), Modeling the observed tropospheric BrO background:

489   Importance of multiphase chemistry and implications for ozone, OH, and

490   mercury, *J. Geophys. Res. Atmos.*, *121*, doi:10.1002/2015JD024229.

491   Simpson, W. R., S. S. Brown, A. Saiz-Lopez, J. A. Thornton, and R. von Glasow (2015),

492   Tropospheric halogen chemistry: sources, cycling, and impacts, Chem. Rev., 115,

493   4035−4062.

494   Solomon, S. (1999), Stratospheric ozone depletion, A review of concepts and history,

495   *Rev. Geophys.*, 37, 275–316.

496   Solomon, S., Daniel, J. S., Neely, R. R., Vernier, J.-P., Dutton, E. G. and W. L.

497   Thomason, (2011), The persistently variable "background" stratospheric aerosol

498   layer and global climate change, *Science*, 333(6044), 866–870,

499   doi:10.1126/science.1206027.

500   Solomon, S. D. Kinnison, J. Bandoro, and R. R. Garcia, (2015), Polar ozone depletion:

501   An update, *J. Geophys. Res*. 120, doi:10.1002/ 2015JD023365.

502   Stolarski, R. S., D. W. Waugh, L. Wang, ☐L. D. Oman, A. R. Douglass, and P. A.

503   Newman (2014), Seasonal variation of ozone in the tropical lower stratosphere:

504   Southern tropics are different from northern tropics, *J. Geophys. Res*., 119,

505   doi:10.1002/2013JD021294. ☐

506   Thornton, B. F., Toohey, D. W., Tuck, A. F., Elkins, J. W., Kelly, K. K., Hovde, S. J.,

507   Richard E. C., Rosenlof, K. H., Thompson, T. L., Mahoney, M. J., Wilson, J. C.,

508   (2007) Chlorine activation near the midlatitude tropopause, *J. Geophys. Res*., 112,

509   D18306, doi:10.1029/2006JD007640.

510   Toon, G. C., C. B. Farmer, L. L. Lowes, P. W. Schaper, J.-F. Blavier, and R. H. Norton

511   (1989), Infrared Aircraft Measurements of Stratospheric Composition Over

512   Antarctica During September 1987, *J. Geophys. Res*., 94, 16,571–16,596, doi:

513   10.1029/JD094iD14p16571.

514   Vernier, J.-P., L. W. Thomason, and J. Kar (2011), CALIPSO detection of an Asian

515   tropopause aerosol layer, *Geophys. Res. Lett*., 38, L07804,

516   doi:10.1029/2010GL046614.

517   Vernier, J.-P., T. D. Fairlie, M. Natarajan, F. G. Wienhold, J. Bian, B. G. Martinsson, S.

518   Crumeyrolle, L. W. Thomason, and☐K. M. Bedka (2015), Increase in upper

519   tropospheric and lower stratospheric aerosol levels and its potential connection

520   with Asian pollution,☐*J. Geophys. Res*., 120, 1608–1619,

521   doi:10.1002/2014JD022372. ☐

522 Volkamer, R., et al. (2015), Aircraft measurements of BrO, IO, glyoxal, NO_2, H_2O, O_2-

523   O2, and aerosol extinction profiles in the tropics: comparison with aircraft- and

524   ship-based in situ and lidar measurements, *Atm. Meas. Tech.*, 8, 2121-2148.

525 Von Hobe, M. et al. (2011), Evidence for heterogeneous chlorine activation in the

526   tropical UTLS, *Atm. Chem. Phys.*, 11, 241-256, doi:10.5194/acp-11-241-2011.

527 Wang, S., et al. (2015), Active and widespread halogen chemistry in the tropical and

528   subtropical free troposphere, *Proc. Nat. Acad. Sci.*, 112, 9281-9286.

529 WMO/UNEP (2014), *Scientific assessment of ozone depletion: 2014*, World

530   Meterorological Organization Global Ozone Research and Monitoring Project,

531   Report 55, Geneva, Switzerland.

532

533 Figure Captions

534

535 Figure 1. Distributions of HCl from MLS satellite data for the channel centered at 100

536 hPa (top) and at 100 and 85 hPa in SD-WACCM simulations for July 2011. Wind

537 vectors and temperatures from SD-WACCM are superimposed.

538

539

540 Figure 2.   Model calculated monthly mean distributions of ClO (pptv, top panel),

541 $ClONO_2$ (pptv, bottom panel) for July 2011 at 17 km, with superimposed wind vectors.

542

543

544

545   Figure 3. Zonally averaged $ClONO_2$ abundances (pptv) in July 2011 versus latitude and

546   altitude in SD-WACCM model calculations with (top) and without (bottom) low-latitude

547   heterogeneous chlorine chemistry, including volcanic inputs.   The location of the

548   meteorological tropopause has been indicated with a dashed green line, and the red box

549   highlights the region discussed.

550

551   Figure 4. Model-calculated chemical constituents (pptv) averaged over the latitude band

552   14-20°N versus month at 17 km, for simulations with and without volcanic inputs, and

553   without low-latitude heterogeneous chlorine chemistry, for 2009-2012 for ClO (top), and

554    $ClONO_2$ (second from top).   The time series of extinction at 532 nm measured by

555   satellite lidar, averaged over the monsoon region (15-45°N, 5-105°E, adapted from

556   Figure 2 of Vernier et al., 2015), compared to the model values at 15, 16, and 17 km

557   (third from top). Aerosol backscatter integrated over 15-20 km (bottom) at Mauna Loa

558   (per steradian) from observations (right axis) and from the model, assuming an

559   extinction-to-backscatter conversion factor of 40 (left axis). Note change in scale of the

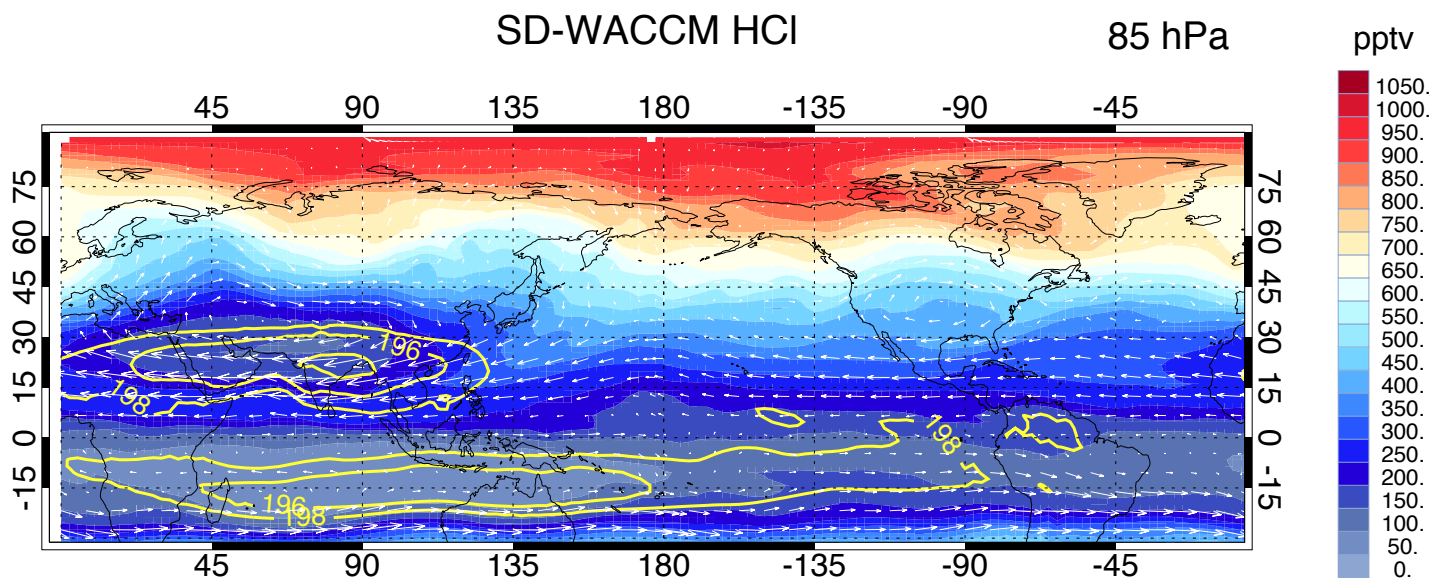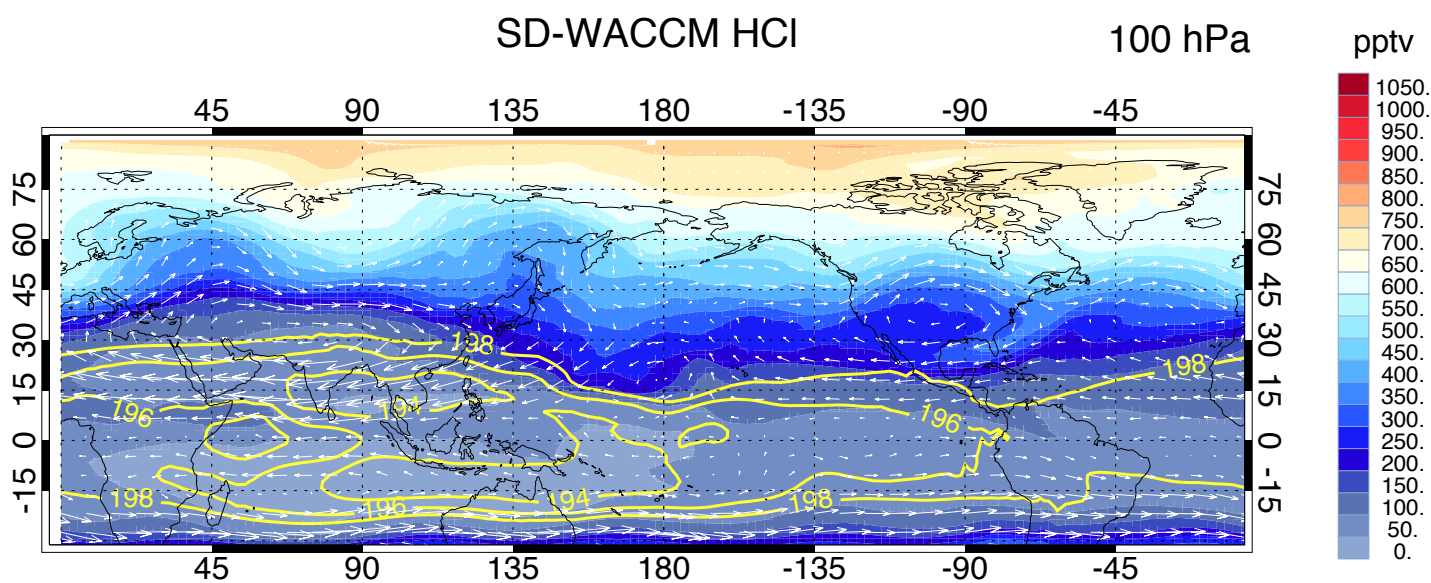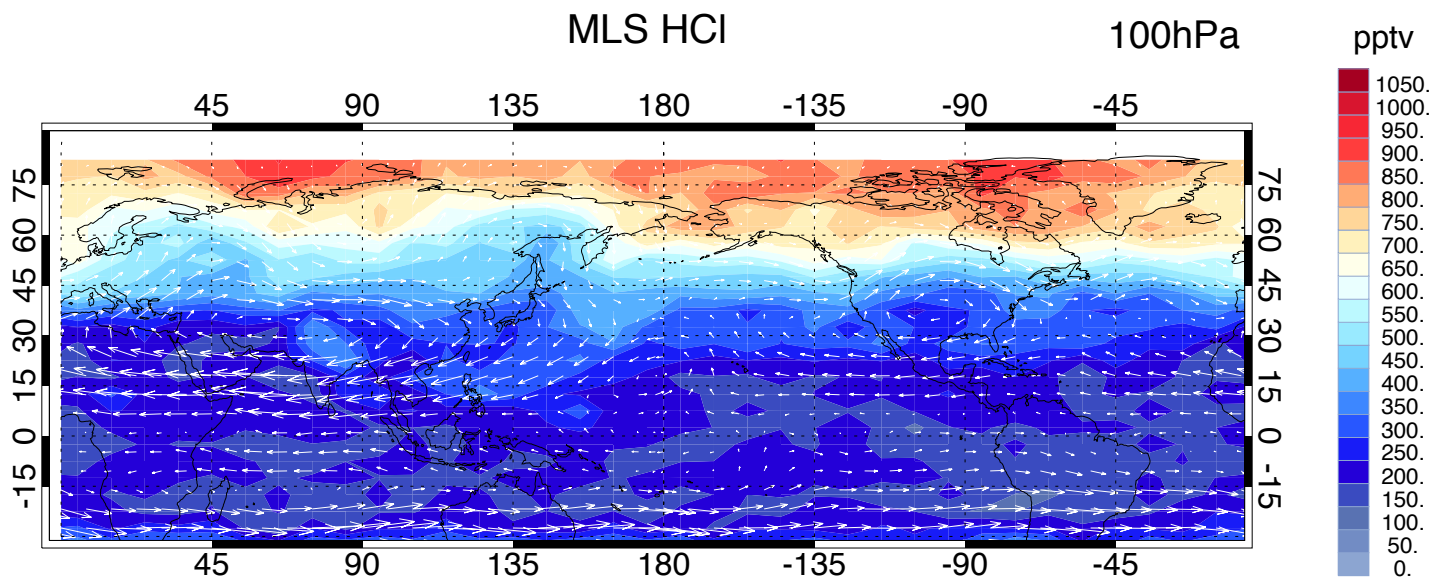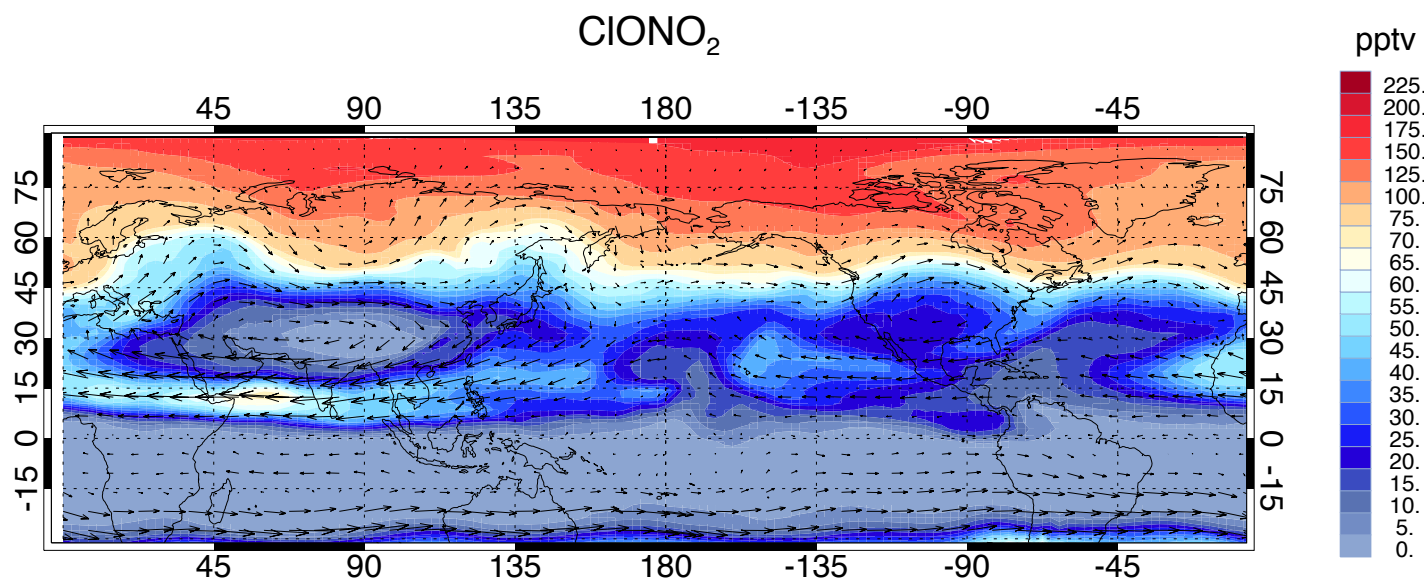560   two y-axes in the bottom panel.

561

562

Figure 1.

Figure 2.
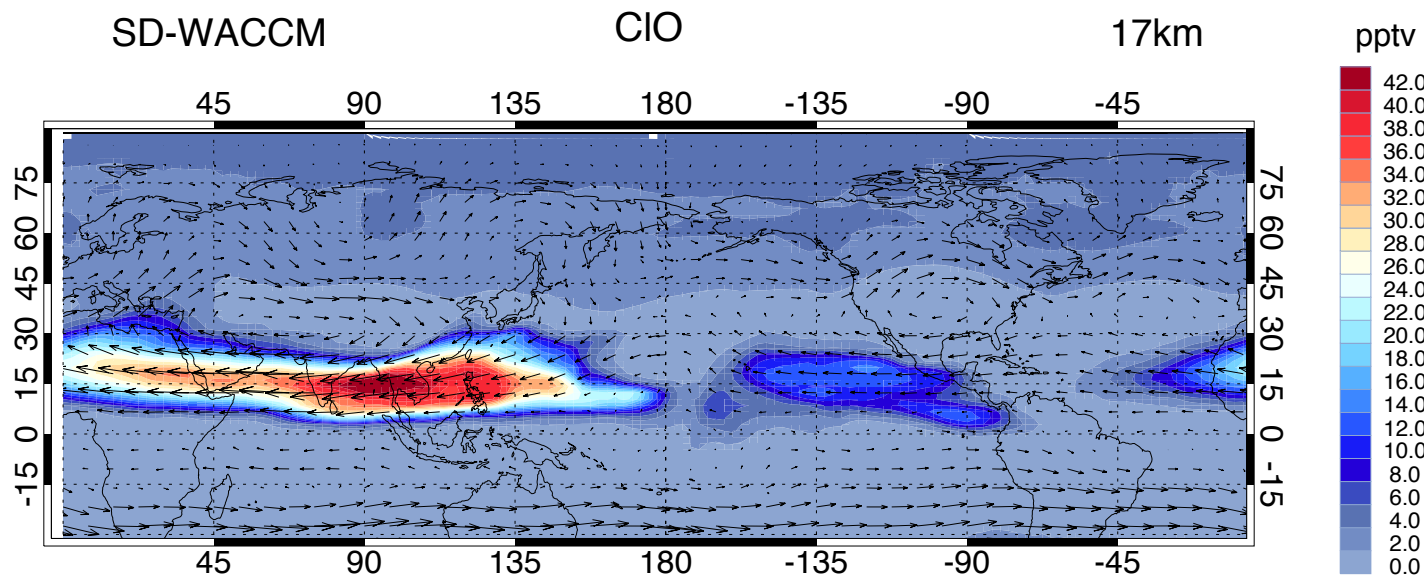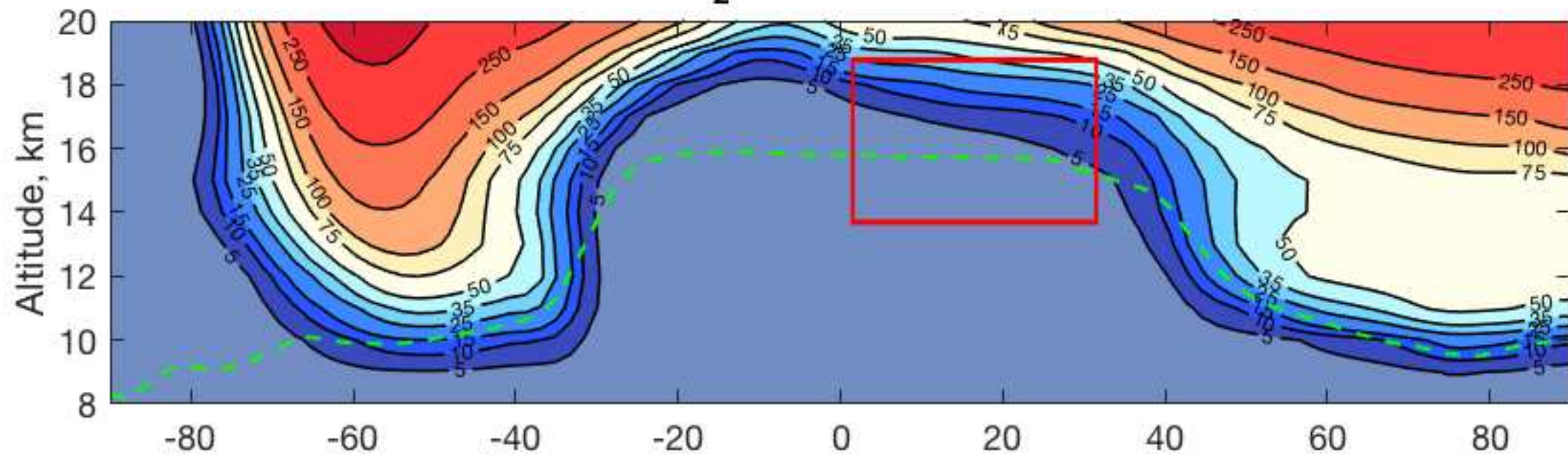
SD-WACCM ClO 17km

ClONO₂

Figure 3.

July 2011 Model ClONO$_2$ no tropical heterogeneous chemistry

July 2011 Model ClONO$_2$ heterogeneous chemistry included

Figure 4.