GEOPHYSICAL RESEARCH LETTERS, VOL. 40, 5553–5558, doi:10.1002/2013GL056563, 2013

Tropospheric ozone decrease due to the Mount Pinatubo eruption: Reduced stratospheric influx

Qi Tang,[1,2] Peter G. Hess,[1] Benjamin Brown-Steiner,[1] and Douglas E. Kinnison[3]

Received 25 July 2013; revised 4 October 2013; accepted 10 October 2013; published 28 October 2013.

[1] We quantify the relationship between Mount Pinatubo eruption in June 1991 and tropospheric ozone abundances. The ozone reduction in the stratosphere and troposphere following the eruption is simulated by the Whole Atmosphere Community Climate Model and is in good agreement with the ozonesonde observations. Simulated anomalies in the global stratosphere-troposphere flux of ozone following the eruption are well correlated with those in the tropospheric ozone column. Both are at their minimum in late 1992 to early 1993 ($-70\,\mathrm{Tg\,yr^{-1}}$ in January 1993 for the flux and –1.9 Dobson Unit in November 1992 for tropospheric ozone) and recover after 1995. Therefore, this study identifies the reduced stratosphere-to-troposphere ozone flux as an important driver of the ozone decline in the troposphere following the eruption. A large fraction (67%) of the decrease in the flux is compensated by an increase in tropospheric photochemical ozone production. While both the strength of the residual circulation and the decrease in stratospheric ozone reduce the stratospheric ozone flux, the ozone reduction is identified as the dominant cause.
Citation: Tang, Q., P. G. Hess, B. Brown-Steiner, and D. E. Kinnison (2013), Tropospheric ozone decrease due to the Mount Pinatubo eruption: Reduced stratospheric influx, *Geophys. Res. Lett.*, *40*, 5553–5558, doi:10.1002/2013GL056563.

1. Introduction

[2] The Mount (Mt) Pinatubo (15°N, 120°E) eruption on 15 June 1991 injected a large amount of gaseous sulfur dioxide (SO_2), water vapor, as well as particulate matter into the lower stratosphere. The SO_2 was converted into sulfuric acid (H_2SO_4) through reaction with the hydroxyl radical [*McKeen et al.*, 1984] and formed H_2SO_4/H_2O aerosol in about 30 days (e-folding time scale). The peak aerosol loading produced by the Pinatubo eruption is estimated to be 30 Tg [*McCormick and Veiga*, 1992]. This eruption is considered to be the largest perturbation to stratospheric aerosol in the 20th century [*McCormick et al.*, 1995].

[3] Significant ozone (O_3) depletion in total columns [e.g., *Schoeberl et al.*, 1993] and in the lower stratosphere [e.g., *Grant et al.*, 1994] was observed by ozonesondes after the Mt Pinatubo eruption. Previous studies have attributed this ozone decrease to heterogeneous chemistry [*Prather*, 1992; *Kinnison et al.*, 1994], as the sulfate aerosols provide extra effective surface area for heterogeneous chemistry to occur, and dynamic processes [*Kinne et al.*, 1992; *Kinnison et al.*, 1994], as the lofting of the aerosol layer by solar and infrared heating brings O_3-poor air into the tropical O_3-rich region.

[4] Stratospheric ozone influences tropospheric ozone abundances through stratosphere-troposphere exchange (STE) and changes in the photolysis rates. Decreases in tropospheric ozone following Mt Pinatubo were observed at middle and high latitudes in the Northern Hemisphere (NH) [*Fusco and Logan*, 2003; *Oltmans et al.*, 1998; *Hess and Zbinden*, 2013]. The association between the ozone decreases in the troposphere and those in the stratosphere after the Pinatubo eruption has been noted [*Fusco and Logan*, 2003; *Oltmans et al.*, 1998], but never quantified. In this study, we quantify the change in the cross-tropopause ozone flux due to the Pinatubo eruption and show that the tropospheric ozone decrease is consistent with the impact of Pinatubo. To our knowledge, this is the first study quantifying the relationship between the Pinatubo eruption and tropospheric ozone.

2. Methodology

[5] The ozonesonde data are downloaded from the World Ozone and Ultraviolet Radiation Data Centre (WOUDC) (http://www.woudc.org). We select 12 stations with good data quality in terms of sampling frequency, time coverage, and consistency for Canada, Northern Europe, the United States, and Lauder in New Zealand (see supporting information for details). We apply the Free-Running (FR) version of the Whole Atmosphere Community Climate Model (WACCM) [*Marsh et al.*, 2013] of the NCAR Community Earth System Model (CESM1) to perform simulations for the Mt Pinatubo period. Results using the Specified Dynamics (SD) version of the model (nudged WACCM) and the off-line Community Atmospheric Model with chemistry (CAM-chem) are given in the supporting information. The meteorology fields of FR WACCM are generated online using observed sea surface temperature (SST) data set HadISST1 [*Rayner et al.*, 2003] and respond to the aerosol heating in the stratosphere. The stratospheric aerosol distribution is derived using a prescribed surface area density (SAD) field based on Chemistry-Climate Model Initiative [*Eyring et al.*, 2013] (see supporting information for model details). The STE ozone flux is diagnosed as a residual term

Additional supporting information may be found in the online version of this article.

[1]Department of Biological and Environmental Engineering, Cornell University, Ithaca, New York, USA.
[2]Lawrence Livermore National Laboratory, Livermore, California, USA.
[3]Atmospheric Chemistry Division, National Center for Atmospheric Research, Boulder, Colorado, USA.

Corresponding author: Q. Tang, Department of Biological and Environmental Engineering, Cornell University, Ithaca, NY 14853, USA. (tang30@llnl.gov)

0094-8276/13/10.1002/2013GL056563

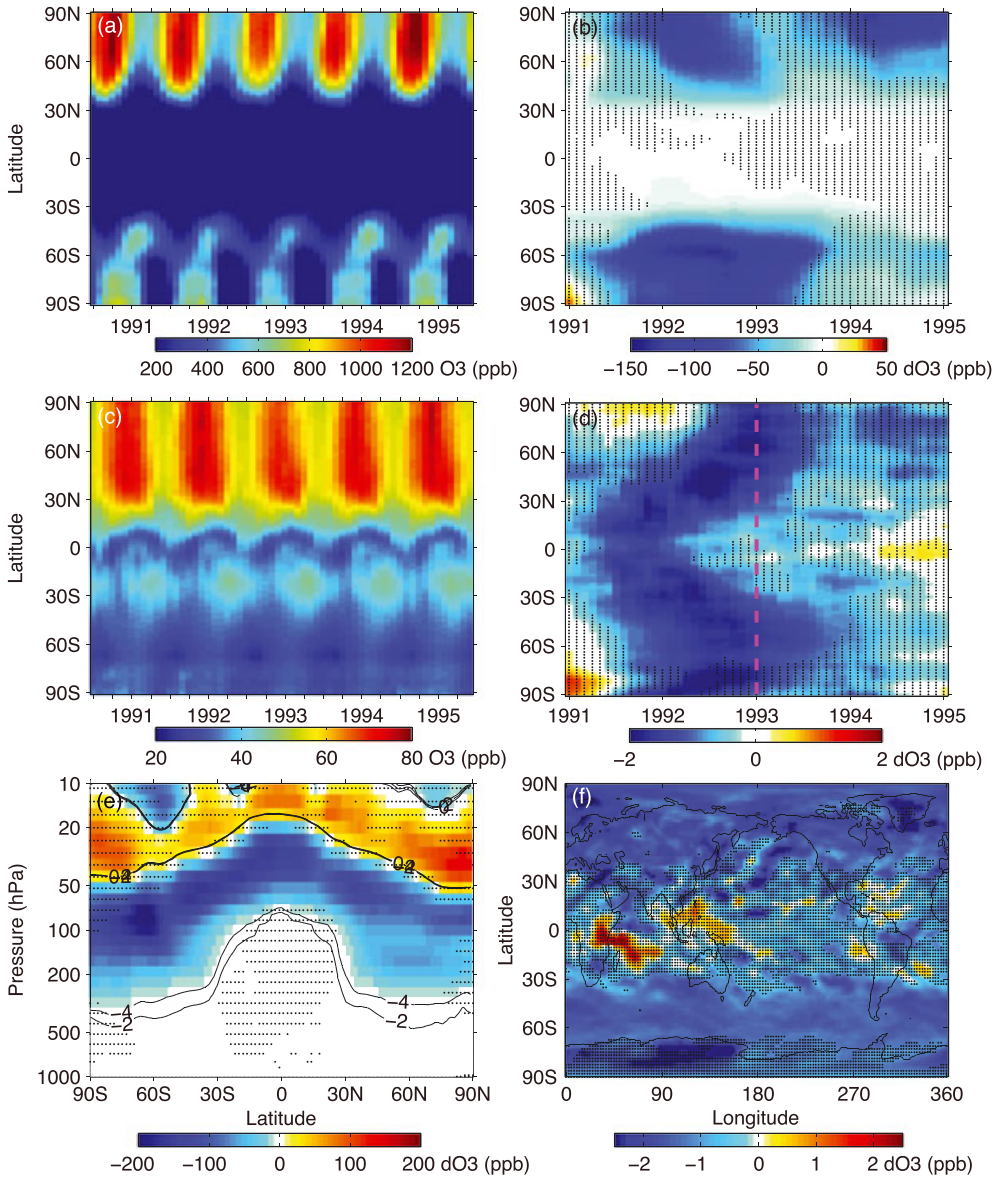

Figure 1. Monthly ensemble mean O_3 (unit: ppb) from the FR WACCM (1991–1995) for the Vol case (a) at 150 hPa, and (c) at 500 hPa; and for the mean differences (Vol–NoVol) (b) at 150 hPa and (d) at 500 hPa. The (e) pressure-latitude and (f) 500 hPa latitude-longitude cross sections of the differences for June 1993 are denoted by the dashed magenta line in Figure 1d. A 12 month running mean is applied to the difference plots (see Figure S2 in the supporting information for results without smoothing). The mean differences which are not significant at 90% level of *t* test are shaded by black dots.

in the tropospheric ozone budget following *Hsu et al.* [2005], while the air mass and ozone flux at 100 hPa are estimated using the monthly mean transformed Eulerian mean (TEM) residual vertical velocity (w^*) [*Rosenlof*, 1995].

[6] In this paper, the conclusions are based on the monthly mean results from two 5 year (1991–1995) FR WACCM ensemble simulations, each of which consists of four ensemble members. The control simulations (Vol) explicitly include the impacts of the Mt Pinatubo eruption as derived from the observed stratospheric aerosol distribution. In the perturbed simulation (NoVol), we use a stratospheric aerosol distribution without significant volcanic influence (i.e., we use the average distribution from 1998 to 1999). The only difference in the external forcing between these two runs is their stratospheric aerosol distribution. Therefore, the differences from these two ensembles can be attributed to the differences in their stratospheric aerosol chemical process and the associated forced dynamical fields due to stratospheric aerosol heating process caused by the Mt Pinatubo eruption. Large differences of over 10 $\mu m^2\,cm^{-3}$ appear between the two SAD fields at 16–27 km (20–100 hPa) from June 1991 through January 1993 (see Figure S1 in the supporting information). Note that Cerro Hudson (46°S, 73°W) erupted in August 1991, but its stratospheric SAD perturbation was one magnitude smaller than Mt Pinatubo's [*McCormick et al.*, 1995]. Therefore, Mt Pinatubo dominates the differences in the two ensemble simulations.

3. Results

[7] Shortly after the Pinatubo eruption in June 1991, a significant reduction of ozone appears at middle to high

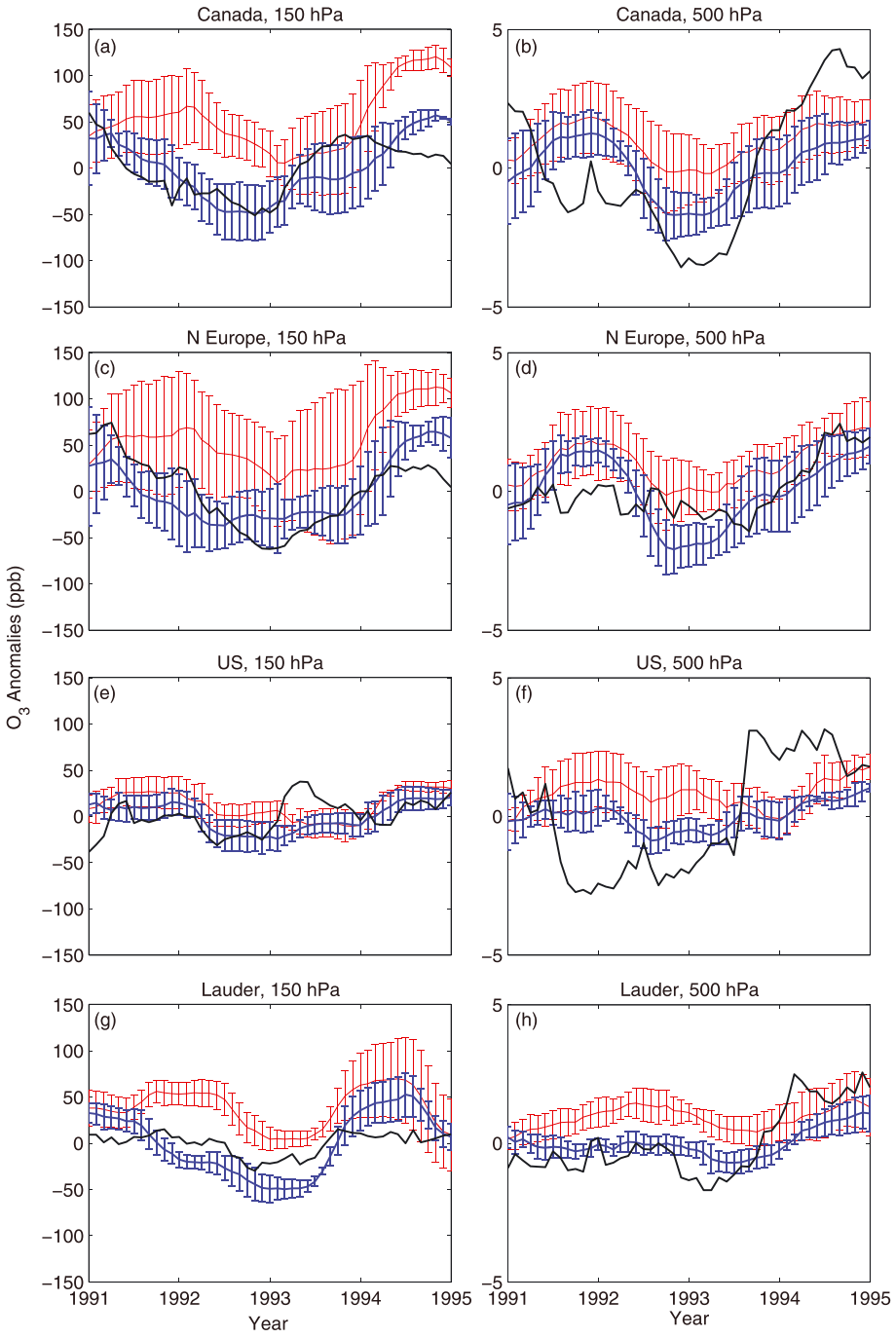

Figure 2. The 12 month running mean of regionally averaged ozone anomalies (unit: ppb) for (a, b) Canada, (c, d) Northern Europe, (e, f) United States, and (g, h) Lauder (45°S, 170°E), New Zealand at 150 hPa (left column) and 500 hPa (right column) for each month of 1991–1995. Black lines: sonde; blue lines: Vol mean; red lines: NoVol mean; error bars: $\pm 1\sigma$ of the ensemble. The O_3 anomalies (blue and red lines) are calculated relative to the means of the Vol time series. Model results are averaged for the grid boxes containing the sonde locations.

latitudes in the lower stratosphere in both hemispheres at 150 hPa (Figures 1a and 1b). This ozone decreasing trend persists and reaches a minimum in 1993, in agreement with observations [*Froidevaux et al.*, 1994] and previous modeling studies [*Hadjinicolaou et al.*, 1997; *Rosenfield et al.*, 1997]. Ozone starts recovering in 1994 and recovers back to the pre-eruption levels after 1995 as the SAD anomaly decreases after 1993 (see supporting information Figure S1). The ozone decrease following Pinatubo eruption is caused by the combination of heterogeneous chemical processes and the circulation change [*Hadjinicolaou et al.*, 1997; *Rosenfield et al.*, 1997]. Other notable features are the inter-hemispheric asymmetry in the ozone anomaly and the Antarctic ozone hole pattern in the stratosphere in austral winter-spring time (Figure 1a). The ozone difference in the raw monthly data at 150 hPa (Figure S2a) is noisy and reaches 300 ppb in both hemispheres at high latitudes in springtime 1992 and 1993. The loss is greater in high

latitudes than in middle latitudes, which is consistent with the total ozone measurement from the total ozone mapping spectrometer (TOMS) [*Herman and Larko*, 1994]. The difference fields are smoothed with a 12 month running mean (Figure 1b) as we focus on the interannual variations. The smoothed ozone decreases reach 150 ppb and occur at middle to high latitudes during most months from 1992 to 1993. Over the tropics, the ozone loss is small and mostly insignificant at this level, as the Pinatubo aerosols are initially concentrated in the tropics at higher altitudes (20–25 km) [*McCormick and Veiga*, 1992].

[8] The ozone reduction at 500 hPa after the Mt Pinatubo eruption propagates from the tropics to the poles through late 1993 (Figure 1d). The maximum decrease is 2 ppb on interannual time scale, whereas 5 ppb reductions occur in monthly averages (Figure S2b). A large decrease in zonal mean ozone occurs below 20–50 hPa (Figure 1e) in June 1993. The largest decrease is found in the stratosphere between 50 and 200 hPa due to chemical and dynamical responses [*McCormick et al.*, 1995], in agreement with the SAD differences (see Figure S1). The differences switch sign above 50 hPa in the extra-tropics and 20 hPa in the tropics, which is consistent with ozonesonde measurements [*Hofmann et al.*, 1993, 1994] and is attributed to the reduction of ozone loss through reactive nitrogen chemistry [*Granier and Brasseur*, 1992]. The latitude-longitude pattern at 500 hPa also shows significant widespread ozone reduction, which is up to ∼2 ppb in the extra-tropics on an interannual time scale (Figure 1f) and up to 12 ppb in the NH on a monthly time scale. The ozone increases over some tropical areas are largely caused by increased ozone production and can be attributed to a decrease in the overhead stratospheric column and the subsequent increase in solar radiation.

[9] FR simulations are not expected to reproduce the exact timing and location of measured interannual variability unless the variability is strongly forced (e.g., by Mt Pinatubo or by El Niño–Southern Oscillation (ENSO)). Figure 2 compares the 12 month running mean of monthly ozone anomalies from ozonesondes, the Vol simulations, and the NoVol simulations for 1991–1995.

[10] At 150 hPa, the simulations accounting for Mt Pinatubo (blue lines) generally match the sonde observations quite well (see Figure 2, left column). The 1993 ozone minimum is captured at all locations within $\pm 1\sigma$. The ozone depletion signal at Lauder does not emerge until about 1 year (middle 1992) after the Pinatubo eruption (Figure 2g), as the stratospheric dynamic response dominates the ozone change at southern middle latitudes in the first 6 months after the eruption [*Aquila et al.*, 2013]. However, the mean of Vol simulations at Lauder shows the significant decrease as early as 1992. Since the simulated meteorology is only forced by the observed SST, it is expected that the timing of some stratospheric dynamic features will not be exact, which is also reflected by the large error bars around the ensemble means. These results suggest that the simulated decline in stratospheric ozone in the Pinatubo period is robust and close to reality. When the volcano-related heterogeneous chemistry and dynamical response are removed (red lines) by using a volcanically clean stratospheric aerosol distribution, the ozone abundances become large compared to the Vol case (blue lines). The mean of NoVol simulations have an ozone minimum in 1993 in all locations except the U.S.

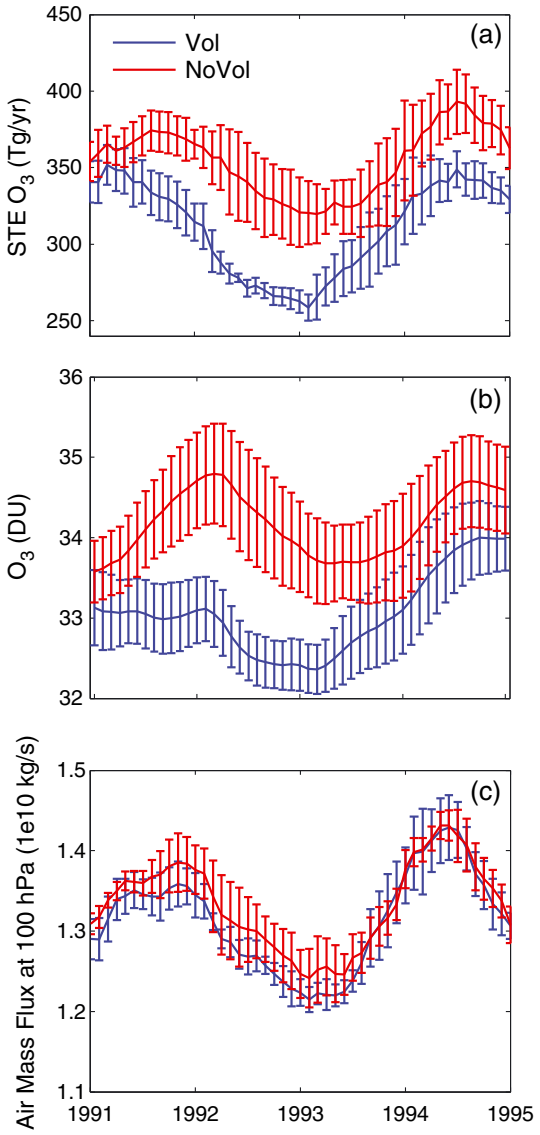

Figure 3. The 12 month running means of global (a) STE O_3 fluxes (unit: Tg yr^{-1}), (b) tropospheric ozone columns (unit: DU), and (c) downward air mass fluxes at 100 hPa (unit: 10^{10} kg s^{-1}) for 1991–1995. Figures 3a and 3b use the WMO thermal tropopause. Blue and red lines represent Vol and NoVol simulations, respectively. Error bars denote the $\pm 1\sigma$ of the ensemble.

At 500 hPa, the model-sonde comparisons (Figure 2, right column) are slightly less satisfying than those at 150 hPa. Ozone decreases occur in all locations between 1991 and 1993 in observations and Vol simulations. The magnitude of observed interannual variation is again well-captured at all locations examined here.

[11] The monthly 12 month running mean global STE fluxes of O_3, tropospheric O_3 columns, and downward air mass fluxes at 100 hPa for both ensembles from 1991 to 1995 are shown in Figure 3. The mean and standard deviation of STE O_3 fluxes for this time period are 314 ± 33 Tg yr^{-1} and 353 ± 38 Tg yr^{-1} for Vol and NoVol runs. These results are smaller than *Tang et al.* [2011, Figure 3], where a mean STE flux of 481 Tg yr^{-1} is calculated for 2004–2006 using the 120-ppb O_3 surface to determine the

tropopause and the European Centre for Medium-Range Weather Forecasts (ECMWF) meteorological fields.

[12] The largest difference in STE O_3 fluxes reaches –70 Tg yr^{-1} (–20%) in January 1993 (see Figure 3a). The decline in global mean tropospheric O_3 column reaches the peak of 1.9 Dobson Unit in November 1992 (see Figure 3b). The mean differences (Vol-NoVol) of FR WACCM for the annual mean tropospheric budget terms during the Pinatubo period (July 1991 to December 1994) are –46 ± 17 Tg yr^{-1} (mean±1σ) for the STE O_3 flux; –3±2 Tg yr^{-1} for the tropospheric abundance change; +31 ± 16 Tg yr^{-1} for the net tropospheric chemical production; and –12±2 Tg yr^{-1} for the surface deposition (Table S5). A large fraction (67%) of the decrease in STE O_3 flux is compensated by increases in tropospheric ozone production, as the photochemistry shifts in favor of producing ozone. A small fraction (26%) is buffered by the surface deposition change, since the tropospheric ozone abundance decreases.

[13] The global downward air mass fluxes at 100 hPa are also smaller in the Vol runs than in the NoVol runs (Figure 3c), but the mean differences are not statistically significant. The air mass flux reaches a minimum in 1993 without the volcano. The difference in the air mass flux between the two ensembles is less than its interannual variability. These results suggest that the interannual variability in the air mass flux is externally forced (e.g., by SST). The mean O_3 flux at 100 hPa reduces by 7.9% during the Pinatubo period (July 1991 to December 1994). Of this decrease, 95% can be attributed to the decrease in stratospheric O_3, while 5% is due to the decrease in w*. These results indicate that the chemical reduction of stratospheric O_3 is the main cause of the STE O_3 flux decrease following Pinatubo.

4. Conclusions

[14] Ozone changes in response to the stratospheric heterogeneous chemical processes and the aerosol heating induced dynamical changes after the Mount Pinatubo eruption in June 1991 are simulated in this study. Simulated ozone decreases throughout the lower stratosphere and troposphere. The reduction is prolonged in 1992–1993, and ozone recovers to the pre-eruption levels after 1995. These results are consistent across the models we have examined (see supporting information for results using SD WACCM and CAM-chem). These results give us some confidence in the FR WACCM's ability in mimicking the O_3 changes in the stratosphere and troposphere (e.g., Figure 1bdef). The diagnosed reduction of the cross-tropopause ozone flux (FR WACCM: –46 Tg yr^{-1}) clearly links the decrease signals in the stratosphere to those in the troposphere and identifies the reduced stratospheric influx as an important driver of the decline in the tropospheric ozone abundance following the Pinatubo eruption.

[15] In addition, we estimate the net global ozone flux at lower stratosphere (100 hPa) using the monthly mean transformed Eulerian mean residual vertical velocity (w*). The reduced ozone influx at 100 hPa is primarily caused by the reduction of stratospheric ozone due to heterogeneous chemical reactions rather than the dynamical response triggered by the Pinatubo eruption. These results suggest that the decrease in STE ozone flux is mainly caused by stratospheric ozone reduction.

[16] **Acknowledgments.** We acknowledge anonymous reviewers and the science team producing the World Ozone and Ultraviolet Radiation Data Centre (WOUDC) ozonesonde data. This work is funded by NSF grant (AGS-1042787) to Cornell University. The National Center for Atmospheric Research is operated by the University Corporation for Atmospheric Research under sponsorship of the National Science Foundation. Work at LLNL was performed under the auspices of the U.S. Department of Energy (DOE), Office of Science, Office of Biological and Environmental Research by Lawrence Livermore National Laboratory under contract DE-AC52-07NA27344 and supported by the Atmospheric Radiation Measurement Program of the Office of Science at the U.S. Department of Energy.

[17] The Editor thanks two anonymous reviewers for their assistance in evaluating this paper.

References

Aquila, V., L. D. Oman, R. Stolarski, A. R. Douglass, and P. A. Newman (2013), The response of ozone and nitrogen dioxide to the eruption of Mt. Pinatubo at Southern and Northern midlatitudes, *J. Atmos. Sci.*, *70*(3), 894–900, doi:10.1175/JAS-D-12-0143.1.

Eyring, V., et al. (2013), Overview of IGAC/SPARC Chemistry-Climate Model Initiative (CCMI) community simulations in support of upcoming ozone and climate assessments, *SPARC Newsletter*, *40*, 48–66.

Froidevaux, L., J. W. Waters, W. G. Read, L. S. Elson, D. A. Flower, and R. F. Jarnot (1994), Global ozone observations from the UARS MLS: An overview of zonal-mean results, *J. Atmos. Sci.*, *51*(20), 2846–2866.

Fusco, A. C., and J. A. Logan (2003), Analysis of 1970–1995 trends in tropospheric ozone at Northern Hemisphere midlatitudes with the GEOS-CHEM model, *J. Geophys. Res.*, *108*(D15), 4449, doi:10.1029/2002JD002742.

Granier, C., and G. Brasseur (1992), Impact of heterogeneous chemistry on model predictions of ozone changes, *J. Geophys. Res.*, *97*(D16), 18,015–18,033.

Grant, W. B., et al. (1994), Aerosol-associated changes in tropical stratospheric ozone following the eruption of Mount Pinatubo, *J. Geophys. Res.*, *99*(D4), 8197–8211, doi:10.1029/93JD03314.

Hadjinicolaou, P., J. A. Pyle, M. P. Chipperfield, and J. A. Kettleborough (1997), Effect of interannual meteorological variability on mid-latitude O_3, *Geophys. Res. Lett.*, *24*(23), 2993–2996.

Herman, J. R., and D. Larko (1994), Low ozone amounts during 1992–1993 from Nimbus 7 and Meteor 3 total ozone mapping spectrometers, *J. Geophys. Res.*, *99*(D2), 3483–3496, doi:10.1029/93JD02594.

Hess, P. G., and R. Zbinden (2013), Stratospheric impact on tropospheric ozone variability and trends: 1990–2009, *Atmos. Chem. Phys.*, *13*(2), 649–674, doi:10.5194/acp-13-649-2013.

Hofmann, D. J., S. J. Oltmans, J. M. Harris, W. D. Komhyr, J. A. Lathrop, T. DeFoor, and D. Kuniyuki (1993), Ozonesonde measurements at Hilo, Hawaii following the eruption of Pinatubo, *Geophys. Res. Lett.*, *20*(15), 1555–1558, doi:10.1029/93GL01585.

Hofmann, D. J., et al. (1994), Ozone loss in the lower stratosphere over the United States in 1992–1993: Evidence for heterogeneous chemistry on the Pinatubo aerosol, *Geophys. Res. Lett.*, *21*(1), 65–68, doi:10.1029/93GL02526.

Hsu, J., M. J. Prather, and O. Wild (2005), Diagnosing the stratosphere-to-troposphere flux of ozone in a chemistry transport model, *J. Geophys. Res.*, *110*, D19305, doi:10.1029/2005JD006045.

Kinne, S., O. Toon, and M. J. Prather (1992), Buffering of stratospheric circulation by changing amounts of tropical ozone: A Pinatubo case study, *Geophys. Res. Lett.*, *19*(19), 1927–1930.

Kinnison, D. E., K. E. Grant, P. S. Connell, D. A. Rotman, and D. J. Wuebbles (1994), The chemical and radiative effects of the Mount Pinatubo eruption, *J. Geophys. Res.*, *99*(D12), 25,705–25,731, doi:10.1029/94JD02318.

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

McCormick, M. P., and R. E. Veiga (1992), SAGE II measurements of early Pinatubo aerosols, *Geophys. Res. Lett.*, *19*(2), 155–158.

McCormick, M. P., L. W. Thomason, and C. R. Trepte (1995), Atmospheric effects of the Mt Pinatubo eruption, *Nature*, *373*, 399–404.

McKeen, S. A., S. C. Liu, and C. S. Kiang (1984), On the chemistry of stratospheric SO_2 from volcanic eruptions, *J. Geophys. Res.*, *89*(D3), 4873–4881, doi:10.1029/JD089iD03p04873.

Oltmans, S. J., et al. (1998), Trends of ozone in the troposphere, *Geophys. Res. Lett.*, *25*(2), 139–142, doi:10.1029/97GL03505.

Prather, M. (1992), Catastrophic loss of stratospheric ozone in dense volcanic clouds, *J. Geophys. Res.*, *97*(D9), 10,187–10,191, doi:10.1029/92JD00845.

Rayner, N. A., D. E. Parker, E. B. Horton, C. K. Folland, L. V. Alexander, D. P. Rowell, E. C. Kent, and A. Kaplan (2003), Global analyses of sea surface temperature, sea ice, and night marine air temperature

since the late nineteenth century, *J. Geophys. Res.*, *108* (D14), 4407, doi:10.1029/2002JD002670.

Rosenfield, J. E., D. B. Considine, P. E. Meade, J. T. Bacmeister, C. H. Jackman, and M. R. Schoeberl (1997), Stratospheric effects of Mount Pinatubo aerosol studied with a coupled two-dimensional model, *J. Geophys. Res.*, *102*(D3), 3649–3670.

Rosenlof, K. H. (1995), The seasonal cycle of the residual mean meridional circulation in the stratosphere, *J. Geophys. Res.*, *100*, 5173–5191.

Schoeberl, M. R., P. K. Bhartia, E. Hilsenrath, O. Torres, and H. S. T. X. Corp (1993), Tropical ozone loss following the eruption of Mt. Pinatubo, *Geophys. Res. Lett.*, *20*(1), 29–32.

Tang, Q., M. J. Prather, and J. Hsu (2011), Stratosphere-troposphere exchange ozone flux related to deep convection, *Geophys. Res. Lett.*, *38*, L03806, doi:10.1029/2010GL046039.