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## EFFECTS OF THE MT. PINATUBO ERUPTION ON THE RADIATIVE AND CHEMICAL PROCESSES IN THE TROPOSPHERE AND STRATOSPHERE

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## ABSTRACT

The Lawrence Livermore National Laboratory two-dimensional zonally-averaged chemical-radiative-transport model of the global atmosphere was used to study the effects of the 15 June 1991 eruption of the Mt. Pinatubo volcano on stratospheric processes. SAGE II time-dependent aerosol surface area density and optical extinction data were used as input into the model. By 22 December 1991, a maximum equatorial change of -1.8 % in column ozone was derived from heterogeneous chemical processes that convert  $\text{NO}_x$  into  $\text{HNO}_3$  on sulfuric acid aerosols. Radiative feedbacks from increased aerosol optical thickness independently changes column ozone by approximately -3.5 % for the same period. This occurs from increasing the net heating of the lower stratosphere, which indirectly increases chemical reaction rates via their temperature dependence and from changes in actinic fluxes, which directly modify photodissociation rates. Including both heterogeneous and radiative effects changes column ozone by -5.5 %. The model-derived change overestimates the decrease in column ozone relative to the TOMS instrument on the Nimbus 7 satellite. Maximum local ozone decreases of 12 % were derived in the equatorial region, at 25 km. Model-derived column  $\text{NO}_2$  peaked (-14 %) at 30° S in October 1991. The timing of the  $\text{NO}_2$  peak is consistent with observation, but the model underestimates the magnitude of the decrease. Local concentrations of  $\text{NO}_x$  ( $\text{NO} + \text{NO}_2$ ),  $\text{ClO}_x$  ( $\text{Cl} + \text{ClO}$ ), and  $\text{HO}_x$  ( $\text{OH} + \text{HO}_2$ ), in the lower stratosphere between 30° S and 30° N, were calculated to have changed by -40%, +100 to +160 %, and +120 to +140 % respectively.

## INTRODUCTION

Recent eruptions from Mt. Pinatubo produced a stratospheric aerosol cloud which was observed at altitudes between 12-32 km. Although the latitude distribution of Pinatubo aerosol was initially equatorial, observations suggest that some material has reached northern mid-latitudes, primarily in the lower stratosphere. In a zone about 40° wide straddling the equator, aerosol optical thicknesses have consistently been observed at a factor of 8 to 10 times the expected background values. These perturbations to the ambient background aerosol burden are expected to have produced significant chemical and radiative effects.

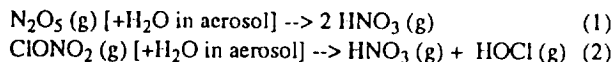
Increases in the background aerosol loading increases the rate of important heterogeneous chemical reactions converting odd nitrogen in both  $\text{ClONO}_2$  and  $\text{N}_2\text{O}_5$  to  $\text{HNO}_3$ . Radiative effects of increased aerosol optical thickness include changes to net radiative heating rates and to actinic fluxes. Changes to heating rates will indirectly change chemical reaction rates via changes in atmospheric temperatures. Changes in actinic fluxes will directly modify photodissociation rates.

## TWO-DIMENSIONAL MODEL DESCRIPTION

The Lawrence Livermore National Laboratory zonally-averaged two-dimensional chemical-radiative-transport model of the troposphere and stratosphere was used in this study. This model currently determines the atmospheric distribution of 50 chemical species and 120 chemical and photochemical reactions. The model domain extends from pole to pole, and from the ground to approximately 60 km. The sine of latitude is used as the horizontal coordinate with intervals of about 10°. The vertical resolution is 1.5 km in the troposphere and 3.0 km in the stratosphere. The circulation is calculated interactively from net radiative and latent heating rates. The net heating rates are determined using accurate solar and infrared radiative models. Reaction rates, solar flux data, temperature dependent absorption cross sections, and quantum yields are based on the latest laboratory measurements. Photodissociation rates, including the effects of multiple scattering, are computed as a function of time at each zone, with optical depths consistent with calculated species distributions. Recent uses of this model include those of Johnston et al., 1989 and Wuebbles et al., 1992.

## HETEROGENEOUS REACTIONS

Recently, laboratory studies suggest that heterogeneous chemical processes may play an important role in lower stratospheric chemistry. Studies indicate that heterogeneous chemistry is important in explaining the Antarctic ozone "hole". In addition, ozone depletion from heterogeneous chemical processes may be important globally. Theoretical studies suggested that including heterogeneous reactions that convert  $\text{N}_2\text{O}_5$  and  $\text{ClONO}_2$  to  $\text{HNO}_3$  on the background sulfuric acid aerosols will both change the partitioning of odd oxygen loss processes between the total odd nitrogen, total odd chlorine, and total odd hydrogen families and change the odd oxygen loss rates in this region. This will change the concentration of ozone (Hofmann and Solomon, 1989; WMO/UNEP, 1992). In this study, we have investigated these issues by adding the following reactions to the LLNL 2-D model chemistry:



Since a complete treatment of these reactions would require a sophisticated aerosol microphysical model, which currently has both theoretical and practical limitations, we treated these reactions using the following relationship to calculate the two rate constants for the above cases.

$$K = (V)(\gamma)(\text{Surface Area Density})$$

Surface area density ( $\text{cm}^2 \text{cm}^{-3}$ ) for the reference atmosphere is based on analysis of SAGE II data by Poole, Thomason, and Yue (WMO/UNEP, 1992). This distribution is representative of an atmosphere that has not been influenced by a major volcanic eruption. The surface area density distribution has altitude (12-32 km), latitude ( $90^\circ \text{N} - 90^\circ \text{S}$ ), and temporal resolution. The effective collision velocity ( $V$ ) is  $5200 \text{ cm s}^{-1}$  for this study. The reaction probability per collision ( $\gamma$ ) is based on laboratory measurements (WMO/UNEP, 1992). For  $\text{N}_2\text{O}_5$  on sulfuric acid aerosols the reaction probability ( $\gamma_1$ ) is set to 0.1 and does not have a temperature dependence. The temperature dependent reaction probability for  $\text{ClONO}_2$  on sulfuric acid aerosols is expressed by:

$$\gamma_2 = 0.006 \exp(-0.15(T-200)).$$

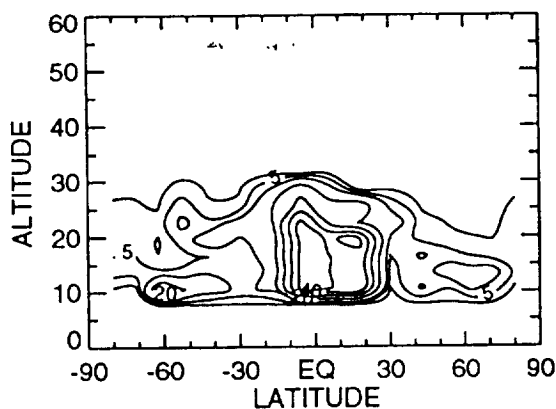


Figure 1. Surface area density ( $\times 10^{-8} \text{ cm}^2 \text{ cm}^{-3}$ ) for the August 23 - September 30 1991 swath retrieved by the SAGE-II satellite.

Time dependent aerosol surface area density data was derived from the SAGE II satellite [Larry Thomason, NASA Langley, private communication]. Seven different swaths were used between 15 June 1991 and 1 January 1992. In Figure 1, an example of one swath (time required for complete latitudinal coverage) for the period of August 23 - September 30, 1991 is shown. In some instances the instrument was saturated and no surface area density retrieval was possible. In these cases the value of  $5.0 \times 10^{-7} \text{ cm}^2 \text{ cm}^{-3}$  was used (this is approximately the upper detection limit of the instrument).

#### AEROSOL EXTINCTION DATA

The primary source of the aerosol extinction data we used for modeling the radiative effects of the Mt. Pinatubo eruption was SAGE II retrievals [McCormick et al., 1992]. These data provided time and latitude varying aerosol extinctions at four wavelengths (385 nm, 483 nm, 525 nm, and 1020 nm) with 1 km vertical resolutions between 9 and 36 km. We first zonally averaged the data by separately averaging sunrise and sunset observations taken during a GMT day (0000 to 2359). Following the Mt. Pinatubo eruption, low latitude retrievals often saturated at altitudes as high as 25 km to 30 km. The result was that high extinction values were reported above that saturation altitude and no data

were reported below. As an initial attempt at treating these data, the extinctions at the two lowest reporting altitudes were averaged. The average was then used to fill in all the lower altitudes. While an admittedly crude estimate, the column optical depths so obtained of up to 0.3 were reasonable (Figure 2). Zonal averages of the NOAA/AVHRR gridded aerosol optical depth product for October to November 1991 contained low latitude peak optical depths varying between approximately 0.32 to 0.38 [Stowe et al., 1992].

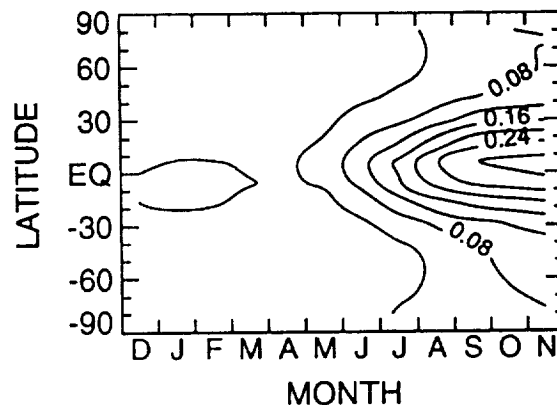


Figure 2. Total aerosol optical depth derived from aerosol extinction data from the SAGE II satellite for 525 nm, during 1991.

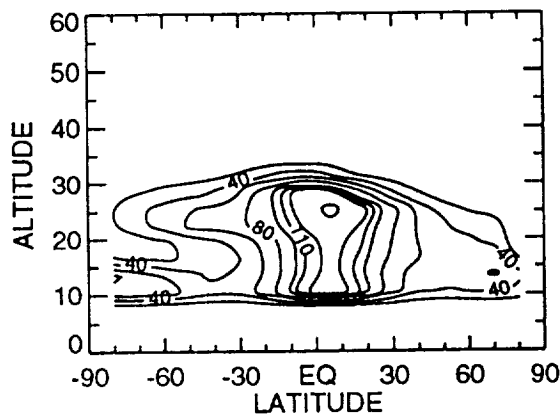


Figure 3. Local extinction ( $\times 10^{-4} \text{ km}^{-1}$ ) data for 525 nm derived from the SAGE II satellite during November 1991.

The data were then gridded by binning and averaging within latitude-time bins. The time bins were for 30 day periods referenced to winter solstice 1990. The time period was chosen to be comparable but not equal to the approximately 35 day "swath" time for the SAGE II latitude coverage. The latitude bins were the LLNL 2-D chemical-radiative-transport model latitude bins. Next a rectangular weighted moving average was passed over the data. The weightings were (1,3,3,1) in time and (1,4,6,4,1) in latitude, resulting in a 16 latitude by 13 time array of smoothed data. This averaging was motivated to minimize the effects of

missing data and striping due to sunrise versus sunset measurement differences. Any grid cells left as zero by the previous binning and averaging process were set to a global average background value. Finally, the data were vertically integrated onto the 2-D model 3 km log-pressure grid. Figure 3 as an example shows the aerosol extinctions derived by this process for a wavelength of 525 nm.

In order to model the full wavelength range used by the 2-D chemical-radiative-transport model, it was necessary to use additional *a priori* information. The model required optical properties from 175 nm to 735 nm in the shortwave. Average aerosol optical properties for the infrared were also needed. We used observed 525 nm to 1020 nm extinction ratios as a basis for extrapolating between extinction versus wavelength models calculated using theoretical aerosol size distributions. The size distributions used were for stratospheric background aerosol, fresh volcanic aerosol, and aged volcanic aerosol.

## DISCUSSION

Model-derived rates for both heterogeneous reactions are substantially increased when the surface area density is increased. These reactions change the odd oxygen loss partitioning between chemical families, increasing the  $\text{HO}_x$  and  $\text{ClO}_x$  odd oxygen loss reactions and decreasing the  $\text{NO}_x$  odd oxygen reactions. The net result is a decrease in ozone in this region (Figure 4). When the radiative feedbacks are included, the increased scattering from increases in the aerosol extinctions causes a increase in temperature which enhances odd oxygen loss. This combined scenario changes the model-derived column ozone by -5.5 % in late December 1991 (Figure 5). The combined scenario over estimates the decrease in column ozone relative to the TOMS instrument on the Nimbus 7 satellite [Chandra and Stolarski, 1992]. This analysis suggests that after the QBO effects are taken into account, the changes in the column ozone attributed to volcanic eruptions may not be more than 2-4 % decrease. By the 15 August 1991, the model-derived ozone maximum

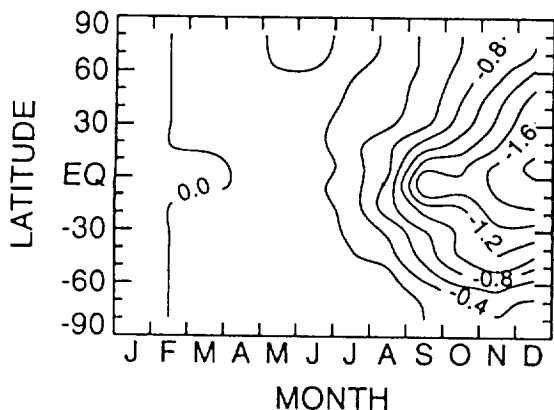


Figure 4. Model-derived percentage change in column ozone including the  $\text{N}_2\text{O}_5$  and  $\text{ClONO}_2$  heterogeneous reactions on the surface of sulfuric acid aerosols (relative to an atmosphere with background surface area density).

reduction decreased by -8 % at 25 km, in the equatorial region. Two months later, the ozone maximum ozone decrease is -10 %; and on 15 December (Figure 6), the maximum decrease is -12 %. At later times, model-derived ozone concentrations decrease by up to 5 % at midlatitudes in both hemispheres. Model-derived  $\text{NO}_x$  decreases by 40 % in the lower stratosphere, between 30° S and 30° N. Concurrent increases in  $\text{ClO}_x$  and  $\text{HO}_x$  are on average between 100-160 % and 120-140 % respectively in the same region.

Observed data collected at 45° S, in Lauder New Zealand measure anomalously low values of slant column  $\text{NO}_2$ . In Lauder, they have measured the column  $\text{NO}_2$  over the last 11 years. During the period after the Mt Pinatubo eruption,  $\text{NO}_2$  column data was observed to decrease by as much as 40 %, peaking in October 1991 [Johnston et al., 1992]. In Figure 7, model-derived column  $\text{NO}_2$  peaked at -14 % at 30° S in October 1991. The period of the peak change in  $\text{NO}_2$  is consistent with observed data, however, the magnitude of the model-derived change underestimates the observed data. It is interesting the model-derived change in column ozone overestimates the change relative to observed data, while the model-derived change in column  $\text{NO}_2$  underestimates the observed data. This would suggest that the model may be missing important processes that limit the odd oxygen destruction, even when changing the  $\text{NO}_2$  column by large amounts.

## CONCLUSIONS

This study has used the LLNL 2-D model of the global atmosphere in an evaluation of the effects on trace gas concentrations from the eruption of the Mt. Pinatubo volcano. We have included observed time dependent surface area density and optical aerosol extinction data from the SAGE II satellite (see Figures 1, 2, and 3). Major findings from this study are:

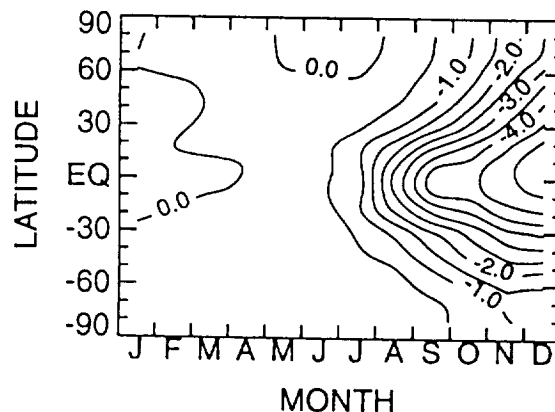
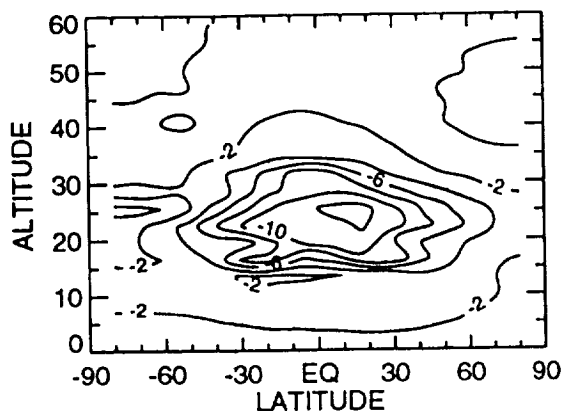


Figure 5. Percentage change in column ozone including both the  $\text{N}_2\text{O}_5$  and  $\text{ClONO}_2$  heterogeneous reactions occurring on sulfuric acid aerosols and the aerosol optical extinctions from the Mt. Pinatubo eruption (relative to an atmosphere with background surface area density and aerosol extinction values).

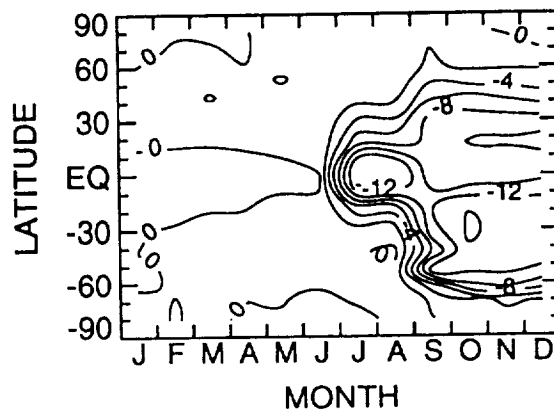


**Figure 6.** Percentage change in local ozone on 15 December 1991, including both the  $N_2O_5$  and  $ClONO_2$  heterogeneous reactions occurring on sulfuric acid aerosols and the aerosol optical extinctions from the Mt. Pinatubo eruption (relative to an atmosphere with background surface area density and aerosol extinction values).

1. Both the  $N_2O_5$  and  $ClONO_2$  heterogeneous reactions rates are increased considerably by the inclusion of observed surface area density from the Mt. Pinatubo eruption.
2. Six months after the eruption on 15 June 1991 model-derived column ozone decreases show a maximum in the equatorial region, with a magnitude of -1.8 % and -5.5 % for including heterogeneous chemical reactions on sulfuric acid aerosols only and with the addition of increased scattering by aerosols respectively (see figures 4 and 5). The model-derived combined scenario is larger than the observed column ozone change derived by the TOMS instrument on the Nimbus 7 satellite.
3. Model-derived local ozone changes on 15 December 1991, including the radiative feedbacks, showed a maximum decrease in the equatorial region of -12 % at 25 km altitude (Figure 6).
4. Column  $NO_2$  peaked at -14 % in the midlatitudes of the Southern Hemisphere in October 1991, which is consistent in period but underestimates the magnitude of the observed data from Lauder, New Zealand (Figure 7).
5. Significant changes in lower stratospheric concentrations of  $NO_x$ ,  $ClO_x$ , and  $HO_x$  species were determined following the eruption.

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**Figure 7.** Percentage change in column  $NO_2$  including both the  $N_2O_5$  and  $ClONO_2$  heterogeneous reactions occurring on sulfuric acid aerosols and the aerosol optical extinctions from the Mt. Pinatubo eruption (relative to an atmosphere with background surface area density and aerosol extinction values).

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