

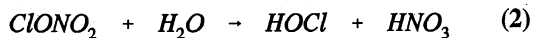
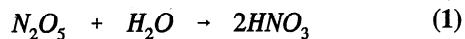
Impact of Pinatubo aerosols on the partitioning between NO₂ and HNO₃

M Koike¹, N. B. Jones², W. A. Matthews², P. V. Johnston², R. L. McKenzie², D. Kinnison³, and J. Rodriguez⁴

Abstract. Ground based infrared observations of HNO₃ column amount at Lauder, New Zealand (45°S, 170°E), show significant increases in HNO₃ following the arrival of Pinatubo volcanic aerosols. The increase first became apparent in September 1991 when the HNO₃ amount was higher than that expected from the regular seasonal variation by $2.3 \times 10^{15} \text{ cm}^{-2}$, which corresponds to 16 % of the unperturbed value. Between September 1991 and May 1993, the observed HNO₃ amounts were systematically higher, typically by 1.5 to $3.5 \times 10^{15} \text{ cm}^{-2}$ or 10 to 30 %. After June 1993, the observed HNO₃ amounts were close to the unperturbed values. The decrease in stratospheric NO₂ due to the volcanic aerosols was observed at Lauder after August 1991 [Johnston *et al.*, 1992, 1993]. The start of the HNO₃ increase and the general trend are in agreement with those expected from the NO₂ decrease when heterogeneous reactions on the sulfate aerosols are considered. Model calculations, in which observed aerosol fields have been used, qualitatively agree with these observed trends, although the magnitude of the changes have been underestimated. These results provide further understanding of the impact of heterogeneous chemistry on the partitioning between NO₂ and HNO₃.

Introduction

Laboratory studies have suggested that the heterogeneous reactions,



on the surface of the sulfate aerosols can convert reactive nitrogen into HNO₃ efficiently [Tolbert *et al.*, 1988; Hanson and Ravishankara, 1991]. Since reaction (2) becomes

important only at temperatures below about 210 K, it plays a minor role in the in situ reduction of reactive nitrogen at mid-latitudes. In contrast, since reaction (1) is fairly insensitive to temperature, it has the potential to greatly reduce reactive nitrogen globally, even under background aerosol conditions [Hofmann and Solomon, 1989; Rodriguez *et al.*, 1991; Prather, 1992; Granier and Brasseur, 1992]. The reduction of reactive nitrogen (NO_x) leads to an increase in active chlorine (Cl_x) and odd hydrogen (HO_x). Prather, 1992]. With this higher contribution of Cl_x catalyzed ozone loss, the known growth in anthropogenic chlorine is considered to be a plausible explanation for the observed. Consequently, the relative importance of Cl_x and HO_x catalyzed ozone destruction increases while that of NO_x catalyzed destruction decreases [McElroy *et al.*, 1992; downward ozone trend, especially at mid-latitudes [Brasseur *et al.*, 1990; Rodriguez *et al.*, 1991; Toumi *et al.*, 1993].

The increase in surface area of sulfate aerosols in the stratosphere due to the Pinatubo volcanic eruption provides an excellent opportunity to test our understanding of these heterogeneous reactions and in turn, their role on background aerosols. Following the arrival of the Pinatubo volcanic aerosols, a large decrease in stratospheric NO₂ was observed at mid-latitudes in both hemispheres, providing evidence for heterogeneous reactions on sulfate aerosols [Johnston *et al.*, 1992, 1993; Koike *et al.*, 1993; Mills *et al.*, 1993]. In situ measurements also have confirmed the reduction in the NO_x/NO_y ratio due to heterogeneous reactions [Fahey *et al.*, 1993]. Since the HNO₃ produced by reactions (1) and (2) is believed to return to the gas phase [Reihs *et al.*, 1990], an increase in gas phase HNO₃ should be observed following an eruption. Prior to the Pinatubo volcanic eruption, a seasonal increase in HNO₃ was observed in the Austral autumn being consistent with the heterogeneous reactions on the background sulfate aerosols [Keys *et al.*, 1993]. However, clear evidence of increased HNO₃ at mid-latitudes after the Pinatubo eruption has not yet been reported.

Regular measurements of the total column HNO₃ amount, using a ground based Fourier transform infrared spectrometer (FTS), started at Lauder, New Zealand (45°S, 170°E, altitude 0.3 km) in October 1990. The seasonal variation observed prior to the volcanic aerosol arrival has been described in a companion paper by Jones *et al.* [this issue]. In this paper, we focus on the effect of volcanic aerosols on the HNO₃ amount and its relationship with NO₂ measurements.

Measurements

The measurements, retrieval, and error analysis of HNO₃ column amounts have been described in detail in Jones *et al.* [this issue]. The data used in the present analysis were obtained at solar zenith angles (SZA) less than 85 degrees,

¹Solar-Terrestrial Environment Laboratory, Nagoya University

²National Institute of Water and Atmospheric Research, NIWA Climate, Lauder

³Lawrence Livermore National Laboratory, University of California

⁴Atmospheric and Environmental Research, Inc.

both in the morning and the evening. In general, 1 to 5 spectra were obtained on the same day and 2 to 15 days data were available for each month. In total 525 spectra obtained for three year period have been analyzed and used in this study. When more than one measurement is made on a single day, a standard deviation within a day is smaller than 3 % for 78 % of the days, indicating very high repeatability of the measurement. The standard deviation of daily averages within a month is typically 5 to 15 %. These variabilities are considered to be dominated by the actual day to day variation in the atmosphere; i.e. change in the tropopause height and transport. NO₂ column amounts obtained by the visible spectrometer at Lauder [Johnston and McKenzie, 1989; Johnston *et al.*, 1992] are also used in this study. The monthly averages for the retrieved vertical column obtained at a solar zenith angle of 90 degrees at sunrise and sunset are used. To calculate the vertical column amount from the slant column, an airmass factor of 16 has been used. The absolute accuracy of the NO₂ vertical column amount is estimated to be +0 to -15 % due to error in the NO₂ absorption cross section and ± 10 % due to error in the airmass factor.

Results

In Figure 1, the monthly averages of observed HNO₃ column amount between October 1990 and October 1993 are shown. A standard deviation within a month is also shown as a vertical bar for every second month. The volcanic eruption of Mt. Pinatubo occurred in June 1991 and volcanic aerosols were visually seen at Lauder as a regular feature from the middle of August 1991. A clear decrease in stratospheric NO₂ was observed after August 1991 [Johnston *et al.*, 1992]. Considering these results, the seasonal variation of HNO₃, without the presence of the volcanic aerosols, has been established and characterized by using the ten months of data between October 1990 and July 1991 [Jones *et al.*, this issue]. It has been found that a sinusoidal curve represents this unperturbed seasonal variation very well. The best fit

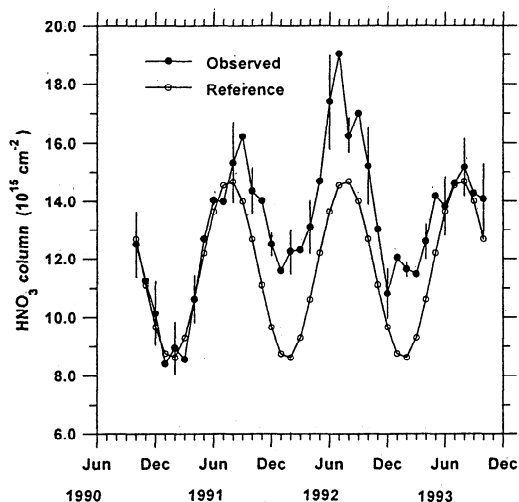


Figure 1. Monthly average of HNO₃ column amounts observed at Lauder (closed circles). One standard deviation of the daily values within a month are shown as vertical bars or every second month. Reference values established from the data, which are free from the volcanic effect (i.e. data between October 1990 and July 1991), are also shown (open circles).

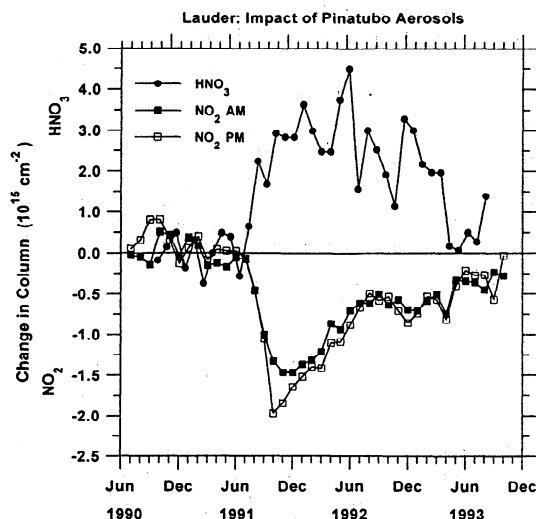


Figure 2. Deviation of observed HNO₃ column amount from the reference monthly mean values (closed circles). Deviation of observed NO₂ vertical column amount from the reference climatology at sunrise (closed squares) and at sunset (open squares) at SZA of 90 degrees are also shown. Note that the vertical scale for HNO₃ is different from that for NO₂.

relation for the monthly mean values for this period obtained by a least-squares calculation, [Jones *et al.*, this issue], gives an rms residual of $0.46 \times 10^{15} \text{ cm}^{-2}$, which corresponds to about 4 % of the annual average of $11.6 \times 10^{15} \text{ cm}^{-2}$.

The monthly values calculated from this relation are plotted in Figure 1 as reference values. It can be clearly seen in this figure that the observed HNO₃ column amounts are systematically higher than the reference values after September 1991. The seasonal minima at the beginning of 1992 and 1993 are clearly higher than that at the beginning of 1991, and the seasonal maximum in 1992 is also higher than in the other years. Deviations of the monthly values from the reference values are shown in Figure 2. Deviations from zero in the period between October 1990 and July 1991 correspond to residuals from the sinusoidal curve fitting described above. A clear increase in the HNO₃ column amount is seen after September 1991, when the HNO₃ value was larger by $2.3 \times 10^{15} \text{ cm}^{-2}$, or 16 % of the reference value. Between September 1991 and May 1993, the HNO₃ values are systematically higher than the reference values typically by 1.5 to $3.5 \times 10^{15} \text{ cm}^{-2}$ or 10 to 30 %. The increase appears to be largest from the end of 1991 to the beginning of 1992 and it gradually decreases after this. The observed values after June 1993 are close to the reference values. Large month to month variations in the HNO₃ increase in Figure 2 is probably due to statistical fluctuations caused by the large day to day variations as mentioned above. Including the uncertainty in the reference values, the overall uncertainty in the HNO₃ column change shown in Figure 2 is less than $1.5 \times 10^{15} \text{ cm}^{-2}$. The systematic increase in the column after September 1991 is therefore statistically significant.

Discussion

Possible effects on HNO₃ measurements caused by a change in instrumental conditions and/or the radiational effect of volcanic aerosols have been examined. Ozone

column amounts have been calculated from the absorption features near 764 cm⁻¹ in the same spectra as used for HNO₃ retrieval. The retrieved ozone amounts have been compared with Dobson ozone data observed simultaneously at Lauder and found to be reasonably consistent throughout the whole period. Therefore, we consider that any instrument artifact and any radiation effects of the volcanic aerosols, will have a small effect on the retrieval of HNO₃ used in this study.

It is likely that the usual vertical profile of HNO₃ will be perturbed to larger values in the region where heterogeneous reactions occur after the arrival of volcanic aerosols. Sensitivity tests have been made to see how changes in the shape of the HNO₃ vertical profile used as the initial guess would affect the retrieved columns. The spectra obtained after the eruption have been retrieved using a perturbed HNO₃ vertical profile, in which the volume mixing ratios in every 5 km interval between 15 and 30 km were scaled by 1.7 to 2.4 so that most of the observed increase in the column after the eruption was accounted for by each of these perturbations. With these perturbations in the shape of the initial guess profile, the retrieved HNO₃ column changed by no more than 3%. Therefore, even if heterogeneous reactions perturb the HNO₃ vertical profile in the stratosphere, errors in the retrieved column amount appear to be small.

The absolute change in monthly averaged NO₂ vertical column amounts at sunrise and sunset observed at Lauder after the arrival of the Pinatubo volcanic aerosols is shown in Figure 2. The percent changes for sunrise NO₂ values are also shown in Figure 3. For the reference NO₂ values, the averaged amounts for 1981, 1989, and 1990 have been used, in which solar activity was similar and the atmospheric aerosol loading was essentially at background levels. The observed change in NO₂ amounts until April 1992 has been described in *Johnston et al.* [1992, 1993]. The clear decrease in NO₂ at Lauder started in August 1991. The largest decrease of about 40% was observed in October 1991 and the decrease declined after this. Relatively large percent decreases were apparent in May and June 1992, as can be seen in Figure 3. However, since the NO₂ column amount has a minimum value in winter months, this feature cannot

be seen in the absolute NO₂ decrease in Figure 2. The percent NO₂ decrease recovered quickly from June 1992 to October 1992. After November 1992, percent deviations from the reference values changed little, however the NO₂ values were still systematically smaller than the reference values by about 7 to 15%. This deviation could be partly due to the declining phase of the solar activity [*Johnston and McKenzie, 1989*], however the NO₂ still seems to be affected by the volcanic aerosols. These observed features will be discussed in more detail in a paper under preparation.

Figure 2 shows clearly that the start of the increase in HNO₃ is consistent with the start of the decrease in NO₂. Both HNO₃ and NO₂ changed sharply with the arrival of volcanic aerosol and the largest change in column amounts appeared around the end of 1991. The general trend in HNO₃ is in agreement with that expected from the NO₂ decrease. Aerosol surface area densities compiled from SAGE II aerosol data at 47°S [*L.Thomason private communication*] show that changes in the surface area densities at altitudes between 25 and 32 km generally match the observed changes in NO₂ and HNO₃. This is reasonable because the peak concentration of NO₂ is likely to be located between 25 and 30 km and background aerosol concentration is very small at these altitudes. *Mills et al.* [1993] have found that at altitudes around 30 km, heterogeneous reactions saturated with aerosol surface area density at value of approximately 1 × 10⁻⁸ cm²/cm³. The aerosol surface area at 29 km was approximately at this level in June 1992 and it decreased by more than a factor of 5 by September 1992. This period generally corresponds with the timing of the quick recovery in NO₂ as seen in Figure 3. Under the presence of volcanic aerosols, the HNO₃/NO₂ column ratios were a factor of 1.6 to 1.8 larger than those of the reference values between October 1991 and July 1992, and a factor of 1.25 to 1.55 larger between August 1992 and May 1993.

In Figure 3, the observed percent changes in HNO₃ and sunrise NO₂ column amounts have been compared with two numerical two-dimensional model calculations; LLNL model for 42.5°S [e.g. *Wuebbles et al., 1991*] and AER model for 47°S [e.g. *Rodriguez et al., 1991, 1993*]. Both the models include heterogeneous reactions (1) and (2) but do not include radiative changes caused by the aerosols. Observed zonally averaged aerosol fields from the SAGE II experiment have been used in both the models, although the compiled surface area densities given in each model were not identical. Further, the LLNL model is diurnally averaged, while the AER model includes diurnal variations. In both the model results, the increase in HNO₃ and the decrease in NO₂ start in August to September 1991 and the largest changes appear in October to November 1991. These results qualitatively agree with the observations and the observed features are generally reproduced by these models, however the magnitude of the changes have been underestimated. The AER modelled NO₂ sunset percent decreases are closer to the observed values than the sunrise case. However larger decreases were found for the sunset in the model, while the observed decreases are larger for sunrise. There are number of factors that could cause differences between the observations and model results. The models are two-dimensional and do not include the interannual variation of air circulation, and some important mechanism may still be missing. Therefore further investigation is required to understand these differences.

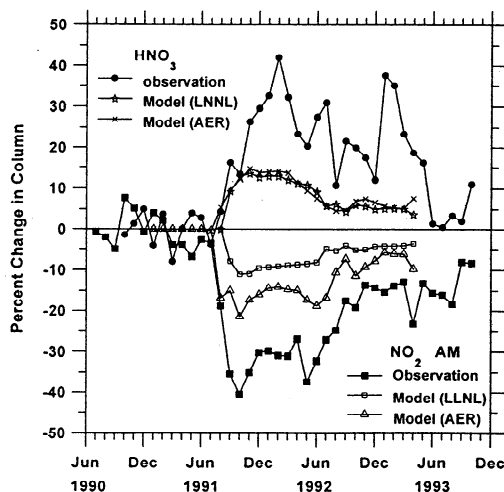


Figure 3. Percent change of observed HNO₃ amount and sunrise NO₂ amount. The LLNL model results for 42.5°S and the AER model results for 47°S (sunrise results for NO₂) are also shown. In these model calculations, heterogeneous chemistry is included and observed aerosol field from SAGE II is used as input.

Summary

After the arrival of Pinatubo volcanic aerosols, a significant increase in column HNO₃ was observed at Lauder, New Zealand, from ground based FTS infrared measurements. The increase appear to start in September 1991 and the maximum increase was around the end of 1991. Between September 1991 to May 1993, the HNO₃ amounts were systematically higher than those expected from the regular seasonal variation by about 1.5 to 3.5×10^{15} cm⁻² or 10 to 30 %. After June 1993, the HNO₃ amounts were close to the unperturbed value. The start of the HNO₃ increase and the general trend are in agreement with those expected from the NO₂ decrease observed at Lauder. The aerosol surface area especially at altitudes between 25 and 32 km generally corresponds to the observed changes in both species.

Model calculations qualitatively agree with the observations when heterogeneous reactions on the observed volcanic aerosols are included, although the magnitude of the changes have been underestimated. These results are considered as strong evidence for the impact of heterogeneous chemistry on the partitioning between NO₂ and HNO₃ and that the HNO₃ produced generally returns to the gas phase.

Acknowledgments. We thank B.McNamara for the FTS measurements. We also thank J.G.Keys, NIWA Atmosphere, and Y.Kondo, Nagoya University for useful comments and discussions. We are grateful to C.P.Rinsland, NASA Langley for the use of his spectral fitting software and to L.Thomason, NASA Langley for providing SAGE II aerosol data. This work was funded by the New Zealand Foundation for Research, Science and Technology (Contract number CO 1221). The support of the Japanese Ministry of Education, Science and Culture (for M.K.) is gratefully acknowledged as is the support of the Japan Society for the Promotion of Science.

References

- Brasseur, G. P., C. Granier, and S. Walters, Future changes in stratospheric ozone and the role of heterogeneous chemistry, *Nature*, 348, 626-628, 1990.
- Fahey, D. W., *et al.*, In Situ measurements constraining the role of sulphate aerosols in mid-latitude ozone depletion, *Nature*, 363, 509-514, 1993.
- Granier, C., and G. Brasseur, Impact of heterogeneous chemistry on model predictions of ozone changes, *J. Geophys. Res.*, 97, 18015-18033, 1992.
- Hanson, D. R., and A. R. Ravishankara, The reaction probabilities of ClONO₂ and N₂O₅ on 40 to 75 % sulfuric acid solutions, *J. Geophys. Res.*, 96, 17307-17314, 1991.
- Hofmann, D. J., and S. Solomon, Ozone destruction through heterogeneous chemistry following the eruption of El Chicón, *J. Geophys. Res.*, 94, 5029-5041, 1989.
- Johnston, P. V., and R. L. McKenzie, NO₂ observation at 45°S during the decrease phase of solar cycle 21, from 1980 to 1987, *J. Geophys. Res.*, 94, 3473-3486, 1989.
- Johnston, P. V., R. L. McKenzie, J. G. Keys, and W. A. Matthews Observations of depleted stratospheric NO₂ following the Pinatubo volcanic eruption, *Geophys. Res. Lett.*, 19, 211-213, 1992.
- Johnston, P. V., R. L. McKenzie, and J. G. Keys, NO₂ column changes induced by volcanic eruptions, proceedings of the 1992 Quadrennial Ozone Symposium, in press, 1993.
- Keys, J. G., P. V. Johnston, R. D. Blatherwick, and F. J. Murcray, Evidence for heterogeneous reactions in the Antarctic autumn stratosphere, *Nature*, 361, 49-51, 1993.
- Koike, M., Y. Kondo, W. A. Matthews, P. V. Johnston, K. Yamazaki, Decrease of stratospheric NO₂ at 44°N caused by Pinatubo volcanic aerosols, *Geophys. Res. Lett.*, 20, 1975-1978, 1993.
- McElroy, M. B., and R. J. Salawitch and K. Minschwaner, The changing stratosphere, *Planet. Space Sci.*, 40, 373-401, 1992.
- Mills, M. J., A. O. Langford, T. J. O'Leary, K. Arpag, H. L. Miller, M. H. Proffitt, R. W. Sanders, and S. Solomon, On the relationship between stratospheric aerosols and nitrogen dioxide, *Geophys. Res. Lett.*, 20, 1187-1190, 1993.
- Prather, M., Catastrophic loss of stratospheric ozone in dense volcanic clouds, *J. Geophys. Res.*, 97, 10187-10191, 1992.
- Reihs, C. M., D. M. Golden, and M. A. Tolbert, Nitric acid uptake by sulfuric acid solutions under stratospheric conditions: Determination of Henry's law solubility, *J. Geophys. Res.*, 95, 16545-16550, 1990.
- Rinsland, C. P., R. Zander, and P. Demoulin, Ground-based infrared measurements of HNO₃ total column abundances: Long-term trend and variability, *J. Geophys. Res.*, 96, 9379-9389, 1991.
- Rodriguez, J. M., M. K. W. Ko, and N. D. Sze, Role of heterogeneous conversion of N₂O₅ on sulphate aerosols in global ozone losses, *Nature*, 352, 134-137, 1991.
- Rodriguez, J. M., M. K. W. Ko, N. D. Sze, C. W. Heisey, G. K. Yue, and M. P. McCormick, Ozone response to enhanced heterogeneous processing after the eruption of Mt. Pinatubo, *Geophys. Res. Lett.*, in press, 1993.
- Russell III, J. M., C. B. Farmer, C. P. Rinsland, R. Zander, L. Froidevaux, G. C. Toon, B. Gao, J. Shaw, and M. Guson, Measurements of odd nitrogen compounds in the stratosphere by the ATMOS experiment on Spacelab 3, *J. Geophys. Res.*, 93, 1718-1736, 1988.
- Tolbert, M. A., M. J. Rossi, and D. M. Golden, Heterogeneous interactions of ClONO₂, HCl, and HNO₃ with sulfuric acid surfaces at stratospheric temperature, *Geophys. Res. Lett.*, 15, 851-854, 1988.
- Toumi, R., R. L. Jones, and J. A. Pyle, Stratospheric ozone depletion by ClONO₂ photolysis, *Nature* 365, 37-39, 1993.
- Wuebbles, D. J., D. E. Kinnison, and J. Lean, Solar variations and trace gas emissions on recent trends in stratospheric ozone and temperature, *J. Geomag. Geoelectr.*, 43, 709-718, 1991.

M. Koike, Solar-Terrestrial Environmental Laboratory, Nagoya University, Toyokawa, Aichi, Japan. (e-mail: koike@stelab.nagoya-u.ac.jp)

P.V. Johnston, N.B. Jones, W.A. Matthews, and R.L. McKenzie, National Institute of Water and Atmospheric Research, NIWA - Atmosphere, Lauder, Central Otago, New Zealand. (e-mail: nicholas@wao.greta.cri.nz)

D. Kinnison, Lawrence Livermore National Laboratory, University of California, P.O. Box 808, L-262, Livermore, CA 94550, USA

J. Rodriguez, Atmospheric and Environmental Research, Inc., 840 Memorial Drive, Cambridge, MA 02139, USA

(Received December 22, 1993; accepted February 3, 1994)