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Stratospheric NO_2 observations at the Jungfraujoch Station between June 1990 and May 1992

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Abstract. Observations of nitrogen dioxide have been performed at the International Scientific Station at the Jungfraujoch (46.5°N, 8.0°E) during the winters 1990-1991 and 1991-1992. Vertical abundances of NO_2 were obtained by measuring the scattered sunlight at the zenith, during sunset and sunrise, using the differential absorption method in the visible spectrum. The comparison between the two winters shows a NO_2 reduction of 15% in March-May 1992, following the eruption of Mt. Pinatubo. This decrease is likely to be due to heterogeneous reactions on the volcanic aerosols converting N_2O_5 to HNO_3. Radiative interferences on ground-based visible absorption measurements of NO_2 caused by the enhanced aerosol layer are considered to be negligible (*Perliski and Solomon*, 1992). The results are discussed with respect to measurements made at Lauder, New Zealand (45°S, 170°E) and published by Johnston et al. (1992).

Introduction

The role of nitrogen dioxide in stratospheric chemistry is of fundamental importance in the control of the ozone budget in the stratosphere. The diurnal and seasonal variations of NO_x are well explained by the gas phase chemistry in which the photodissociation of N_2O_5 and its temperature dependence plays an important role. However the seasonal behaviour of HNO_3 at mid- and high latitudes cannot be reproduced by the current photochemical/dyn-amical models (*Austin et al.*, 1986). The partitioning of nitrogen compounds is modified by heterogeneous chemistry on ice particles at high latitudes during polar night and on sulfuric acid aerosols at all latitudes, leading to NO_2 and ozone reductions (*Hofmann and Solomon*, 1989; *Brasseur et al.*, 1990). The conversion of N_2O_5 to HNO_3 is the most likely process responsible for the reduction of NO_2 after a major volcanic eruption like El Chichon in 1982 (*Roscoe et al.*, 1986) and Mt. Pinatubo in 1991 (*Rodriguez et al.*, 1991).

Ground-based measurements of NO_2 were initiated in the 1970s by *Brewer et al.* (1973) and *Noxon* (1975) by measuring its absorption around 450 nm in scattered sunlight observed at the zenith during twilight. This method has been used during the 1980s by several groups (e.g. *Mount et al.*, 1987; *Pommereau and Goutail*, 1988; *Johnston and McKenzie*, 1989) for stratospheric monitoring.

Similar observations were initiated in 1990 at the International Scientific Station at the Jungfraujoch (ISSJ) which is, with the "Observatoire de Haute Provence" (OHP), the Northern mid-latitude NDSC (Network for the Detection of Stratospheric Change) station. This work presents the results obtained for NO_2 total abundances before and after the Mt. Pinatubo eruption to determine the possible effects of aerosol loading in the stratosphere. The observations from November 1991 to March 1992 were performed in the frame of the European Arctic Stratospheric Ozone Experiment (EASOE).

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Experimental and Retrieval Methods

Nearly continuous measurements of nitrogen dioxide column abundances were performed during the winter 1990-1991 and 1991-1992 at the International Scientific Station at the Jungfraujoch (ISSJ) situated in the Swiss Alps (46.5°N, 8.0°E) at an altitude of 3580 m. A "Système d'Analyse par Observations Zénithales" (SAOZ, *Pommereau and Goutail*, 1988) was installed in June 1990. It has been replaced by a new version of the same instrument at the end of October 1991. No data were obtained from June to October 1991 due to the request for the first instrument at another site in summertime and the delivery time of the second one.

The SAOZ instrument, made by Atmos Equipment, is based on a photodiode array spectrometer Jobin-Yvon (model CP 200) coupled to a 512-elements Hamamatsu PCD detector. The dimensions of each pixel are 2.5 mm x 25 µm. The improved characteristics of the new Hamamatsu NMOS array used in the new SAOZ result in a better signal-to-noise ratio of the spectra. This improved the precision of the NO_2 measurements by approximately a factor 2, resulting in an average precision of the vertical column of 2×10^{14} molec/cm^2. The entrance slit width is 25 µm. Direct sunlight and scattered sunlight at the zenith can be observed in two wavelength ranges, in the UV (290-400 nm) and in the visible (400-590 nm). The instrument is mounted in a watertight container and operates outside. Its field of view, through the quartz window on the top, is 30°. It is driven by a Hewlett-Packard 9000 computer which also stores and automatically analyses the data. Observations of scattered sunlight are performed at large solar zenith angles (SZA) with an exposure time between 0.1 and 150 s depending upon the intensity levels to be measured. Narrow absorption features due to the absorption by O_3, NO_2, O_4 and H_2O are detected by the differential absorption method in the visible range.

NO_2 abundances are determined from absorption spectra between 405 and 485 nm. Interfering absorption features from O_4 and H_2O need to be removed. Daily measurements at sunrise and sunset result from an average over a few spectra (between 3 and 6, depending on weather conditions) obtained for SZA between 87 and 91°.

An improved algorithm for NO_2 retrieval has been made available for the SAOZ instruments in 1991. All the NO_2 data obtained at the ISSJ have been reanalysed in order to produce a coherent set retrieved with a common reference spectrum.

Vertical column abundances are deduced from slant column amounts by using an identical airmass factor (*Solomon et al.*, 1987) for the two winters despite the presence of an enhanced sulfuric acid aerosol layer around 20 km altitude in winter 1991-1992 in the Northern Hemisphere. Following the calculations by *Perliski and Solomon* (1992), its impact on the scattering geometry is considered to be negligible for NO_2 retrieval.

Results of Observations

The time series of NO_2 daily measurements obtained at the ISSJ presents the usual diurnal and seasonal variabilities. Important peaks are observed for some days due to dynamical effects related with pollution events.

Although the bulk of the NO_2 column is between 20 and 30 km altitude at mid-latitudes, its measurement from the ground can be perturbed. In particular two types of tropospheric events can introduce large errors in the determination of the stratospheric NO_2 :

1- the transport, from industrialized areas to the Jungfraujoch observatory, of polluted airmasses containing high NO_2 concentrations,

2- the occurrence of snow showers or heavy fogs enhancing the scattering efficiency and increasing the light path in the lower troposphere.

Pollution episodes and snowfalls, thick clouds or fogs increase the absorption in the lower part of the atmosphere. Slant column densities measured as a function of the SZA in perturbed conditions are thus offset upward compared to unpolluted clear-sky conditions. The greater the perturbation, the larger the offset.

Snowfall, fog and thick clouds lead to intense absorption peaks due to O_4 and, if the atmosphere is humid, to H_2O. Because H_2O has an absorption band interfering with NO_2 around 430 nm, additional errors in the NO_2 slant column amount determination can be introduced.

A careful inspection of the O_4 and H_2O data has been made to detect the occurrence of tropospheric perturbations. In addition, plots of the slant column against airmass factor ("Langley plots") have been drawn for each day of measurement for a limited range of SZA in order to minimize the influence of the diurnal variation. For clear sky conditions the intercept at zero airmass (offset) in these plots gives a negative value whose magnitude is approximately equal to the total amount in the reference spectrum (*Roscoe et al.*, 1993). Tropospheric perturbations cause the offsets to be increased by a quantity related to the tropospheric slant amount in the measured spectra, giving, for large perturbations, positive values of the offset. The offsets have been systematically calculated and compared with O_4 and H_2O data. A strong departure from the mean value of the offsets indicates tropospheric perturbations. When correlated with H_2O and/or O_4, the offset should originate from a multiple scattering effect; if not, it must be attributed to a pollution event. These criteria have been used to remove from the time series daily values of NO_2 for which the tropospheric conditions have perturbed the stratospheric measurements. Further details on the Langley plot analysis are given in *Van Roozendael et al.* (1993).

The validated time series is presented in figure 1 with respect to the day of year, with the same scale for 1990, 1991 and 1992 for comparison purposes. Monthly mean NO_2 column for the two winters have also been calculated and are presented in figure 2 with the standard deviation at 1 sigma for each average. A systematic decrease of about 15% in NO_2 amounts can be observed in March, April and May 1992, after the Pinatubo eruption, compared to 1991, before the eruption. The observed decrease is slightly smaller for sunrise data (13% in average) than for sunset data (15.7% in average). However this difference is not significant considering that the mean day-to-day variability (1 sigma) is close to 10% during this period of the year. No reduction is observed in the January and February morning data for which the uncertainties are comparable to the day-to-day variability. The relative uncertainties are less than the day-to-day variability for the larger vertical amounts measured at sunset and at sunrise in March, April and May.

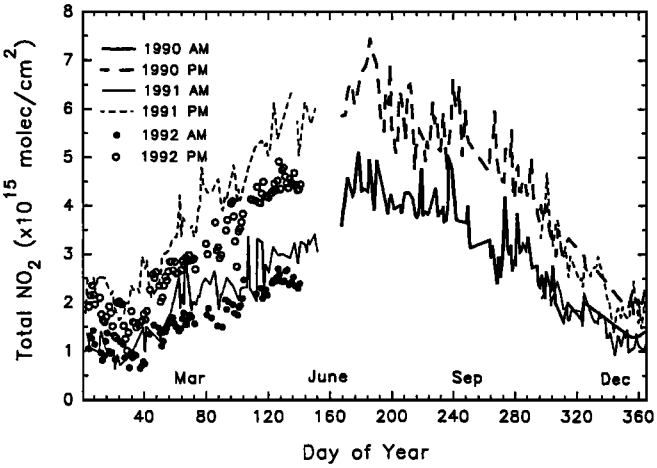

Fig. 1 Daily observations of NO_2 vertical columns in 1990, 1991 and 1992 made at the Jungfraujoch after removing the values obtained for days with perturbed tropospheric conditions (see text).

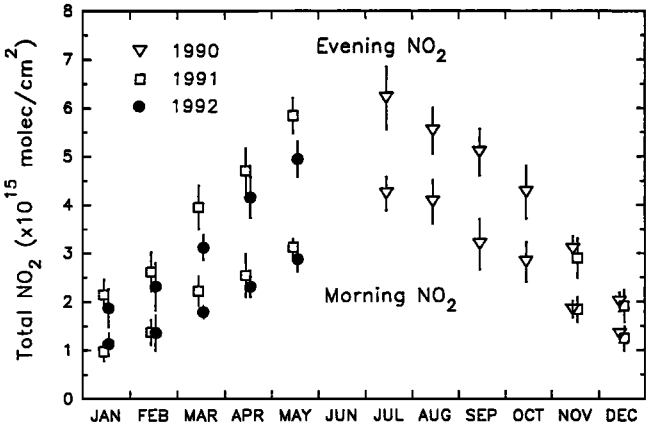

Fig. 2 Comparison of monthly mean NO_2 vertical abundances from measurements obtained at the Jungfraujoch (figure 1). The vertical bar represents the 1 sigma variability of the data during the considered month.

Discussion

NO_2 depletion after the El Chichon eruption in April 1982 (17.3°N, 93.2°W) was reported by *Roscoe et al.* (1986) and by *Johnston and McKenzie* (1989). The reduction observed in Lauder New Zealand (45°S, 170°E) started in mid 1982 and reached a maximum reduction of 20% in March 1983. During the Austral spring following the Mt. Pinatubo eruption in June 1991 (14°N, 122°E) *Johnston et al.* (1992) found a reduction of slant column abundances of NO_2 during the Austral spring between 30 to 40% for the evening twilight and between 35 to 45% for dawn. These reductions exceed the El Chichon effects on NO_2 by more than a factor of 2. The observations made in the Northern Hemisphere at the ISSJ six months later lead to a reduction of NO_2 abundances of only 15% in March and April 1992.

The impact of stratospheric aerosols on ozone and on the partitioning of NO_2 has been investigated by several authors (*Hofmann and Solomon*, 1989; *Rodriguez et al.*, 1991). The aforementioned measurements support the theory of heterogeneous mechanisms on sulfuric acid aerosol decreasing both ozone and NO_2. However, the presence of significant aerosol loading in the stratosphere could also introduce errors in ground-based observations of NO_2 in the visible. Two factors related to changes in radiative processes have been studied by *Perliski and Solomon* (1992). For the effective optical path, as already mentioned, they concluded that changes in scattering properties due to an aerosol layer below 25 km altitude can be neglected when measuring an absorber located around 30 km altitude. They also demonstrated, taking an aerosol extinction coefficient from SAGE II observations made above Lauder, that the effect of Pinatubo aerosol on the diurnal variations of NO and NO_2 due to changes in photolysis rates in pure gas-phase photochemistry are negligible. The alteration of the radiation field by aerosols and its impact on photochemistry were proposed by *Michelangeli et al.* (1989). The quantification by *Perliski and Solomon* (1992) of these two radiative factors leads to the conclusions that depleted NO_2 observed at Lauder after the Mt. Pinatubo eruption is mainly caused by heterogeneous chemistry on volcanic aerosols. This conclusion can be extended to the observations from the ISSJ six months later.

The significant difference in the NO_2 decrease in spring between the two hemispheres can be explained by the differences in the altitude distribution of the Pinatubo aerosol layer. According to SAGE II observations reported by *Perliski and Solomon* (1992) the maximum aerosol extinction coefficient above Lauder was located at 22 km altitude during November 1991 while it was around 18 km in the Alps during the first half of 1992 as estimated from backscatter Lidar observations made at Garmisch Partenkirchen (Germany) by Jäger (private communication).

Ozone measurements were performed at the same time at four different sites in the Alps including the SAOZ observations at the ISSJ. They all found low ozone values during the winter 1991-1992 with respect to the average of Dobson time series obtained close to the Jungfraujoch (~ 200 km) at Arosa since 1931. The interpretation of these observations in terms of dynamical and/or chemical effects is still in progress. Ozone reductions after the Mt. Pinatubo eruption have been reported by *Gleason et al.* (1992) in the tropical stratosphere.

Conclusions

Systematic measurements of NO_2 abundances covering the last two winters have been made by a SAOZ instrument at the ISSJ (45°N). The data have been carefully analyzed to eliminate values perturbed by unusual tropospheric conditions. The monthly mean values indicate a NO_2 reduction of 15% at morning and evening in March-May 1992, after the Mt. Pinatubo eruption, compared with the results obtained in 1991. Considering that the measurements by visible absorption of NO_2 in the scattered sunlight are not affected by the changes in the radiative processes induced by the volcanic aerosols, this reduction is likely to be related to heterogeneous reactions converting N_2O_5 to HNO_3 on the sulfuric acid aerosol surface. These results obtained in the Northern Hemisphere confirm qualitatively those reported by Johnston et al. (1992) at Lauder (45°S) in the Southern Hemisphere. The larger reduction (30-40% at sunset) obtained at Lauder is explained by the higher altitude of the volcanic aerosol layer above Lauder (22 km) with respect to the aerosol altitudes observed in the Alps (18 km) during the NO_2 depletion.

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References

Austin J., R. R. Garcia, J. M. Russell, S. Solomon, and A. F. Tuck, On the atmospheric photochemistry of nitric acid, *J. Geophys. Res., 91*, 5477-5485, 1986.

Brasseur, G. P., C. Granier and S. Walters, Future changes in stratospheric ozone and the role of heterogeneous chemistry, *Nature, 348*, 626-628, 1990.

Brewer, A. W., C. T. McElroy and J. B. Kerr, Nitrogen dioxide concentrations in the atmosphere, *Nature, 246*, 129-133, 1973.

Gleason, J. F., P. K. Bhartia, J. R. Herman, R. Mc Peters, P. Newman, R. S. Stolarski, L. Flynn, G. Labow, D. Larko, C. Seftor, C. Wellemeyer, W. D. Komhyr, A. J. Miller and W. Planet, Record Low Global Ozone in 1992, *Science, 260*, 523-526, 1993

Hofmann, D. J. and S. Solomon, Ozone destruction through heterogeneous chemistry following the eruption of El Chichon, *J. Geophys. Res., 94*, 5029-5041, 1989.

Johnston, P. V. and R. L. McKenzie, NO_2 observations at 45°S during the decreasing 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 NO_2 following the Pinatubo volcanic eruption, *Geophys. Res. Lett.*, 19, 211-213, 1992.

Michelangeli, D. V., M. Allen and Y. Yung, El Chichon volcanic aerosols : impact of radiative, thermal and chemical perturbations, *J. Geophys. Res., 94*, 18429-18443, 1989.

Mount, G. H., R. W. Sanders, A. L. Schmeltekopf and S. Solomon, Visible spectroscopy at McMurdo Station, Antarctica, 1, Overview and daily variations of NO_2 and O_3 during austral spring, 1986, *J. Geophys. Res., 92*, 8320, 1987.

Noxon, J. F., Nitrogen dioxide in the stratosphere and troposphere measured by ground-based absorption spectroscopy, *Science, 189*, 547-549, 1975.

Perliski, L. M. and S. Solomon, Radiative influences of Pinatubo volcanic eruption aerosols on twilight observations of NO_2 column abundances, *Geophys. Res. Lett., 19*, 1923-1926, 1992.

Pommereau, J.-P. and F. Goutail, Stratospheric O_3 and NO_2 observations at the southern polar circle in summer and fall 1988, *Geophys. Res. Lett., 15*, 895, 1988.

Rodriguez, J. M., M. K. W. Ko and N. D. Sze, Role of heterogeneous conversion of N_2O_5 on sulfate aerosols in global ozone losses, *Nature, 352*, 134-137, 1991.

Roscoe, H. K., B. J. Kerridge, L. J. Gray, R. J. Wells and J. A. Pyle, Simultaneous measurements of stratospheric NO and NO_2 and their comparison with model predictions, *J. Geophys. Res., 91*, 5405-5419, 1986.

Roscoe, H. K., J. A. C. Squires, D. J. Oldham, A. Sarkissian, J.P. Pommereau, F. Goutail, Improvements to the accuracy of zenith-sky measurements of total ozone by visible spectrometers, submitted to *J. Geophys. Res.*

Solomon, S., A. L. Schmeltekopf and R. W. Sanders, On the interpretation of Zenith Sky Absorption Measurements, *J. Geophys. Res., 97*, 8311-8319, 1987.

Van Roozendael, M., C. Hermans, M. De Mazière, P. C. Simon, Stratospheric NO_2 observations at the Jungfraujoch Station before and after the Pinatubo eruption, Proceedings of the 11th ESA Symposium on European Rocket and Balloon Programmes and Related Research, Montreux, in press.

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