Nitrogen Dioxide Column Amounts Measurements at 45° and 65° N Following Mt Pinatubo Eruption and Comparison With 2-D Model Calculations

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INTRODUCTION

Nitrogen dioxide column amounts have been monitored both at the International Scientific Station at the Jungfraujoch (46°N, 8°E) and at Sodankyla (67°N, 27°E) for several years. Vertical column abundances are measured during the morning and evening twilights by application of the differential absorption method using the sunlight scattered at zenith in the visible range. The available time series shows a significant reduction of NO_2 starting in winter 1992, after the eruption of the Mt Pinatubo volcano. A maximum decrease of about 35% is observed in January 1992 at both stations. The continued series of observations shows the recovery of the NO_2 column until August 1995. These results are compared with 2-D chemical model calculations including the effect of heterogeneous reactions on observed Pinatubo aerosols. In general the modelled NO_2 columns agree qualitatively with the observations although the amplitude of the seasonal variation is underestimated, possibly due to internal limitations of the model which e.g. does not include diurnal changes. The observed and calculated NO_2 percent changes are in good agreement which confirms quantitatively the impact of the heterogeneous chemistry on stratospheric NO_2.

MEASUREMENTS

Measurements of the NO_2 vertical column amount have been performed since June 1990 at the International Scientific Station at the Jungfraujoch (46°N, 8°E) and since January 1990 at the Sodankyla observatory (67°N, 26°E) using SAOZ spectrometers ("Système d'Analyse par Observations Zénithales", Pommereau and Goutail, 1988). The SAOZ spectrometr has been qualified for stratospheric NO_2 measurements in the frame of the Network for Detection of Stratospheric Changes (NDSC) after participation to the NDSC intercomparison of UV-visible instruments held at Lauder, New-Zeland in May 1992 (Hofmann et al., in press).

Daily observations of the zenith-scattered sunlight are carried out at sunrise and sunset twilights in the visible region. The NO_2 column amounts are retrieved by the differential absorption method between 400 and 455 nm. Twilight measurements result from an average over a few spectra (between 4 and 8) recorded between 87 and 91° SZA. The conversion from slant to vertical column amounts is obtained using airmass factors (AMFs) calculated according to Solomon et al. (1987). The NO_2 vertical distribution used in these calculations was measured from balloon experiment at mid latitude. It is assumed that the AMF depends on the SZA only, i.e. the same set of AMFs is used throughout the year at both sites. The uncertainty on the NO_2 vertical column due to this approximation is estimated to be less than

10%. Other sources of uncertainties, discussed in Van Roozendael et al. (1994b), are (i) the absorption cross-sections, (ii) the calculation of the residual amount in the reference spectrum and (iii) the measurement noise. At 90° SZA, the overall precision of the NO_2 measurements by the SAOZ instrument is limited by the AMF for large NO_2 columns (error less than 10%) and by the measurement noise for small NO_2 columns (absolute uncertainty of about 2 10^{14} molec/cm^2). Much larger errors can be encountered due to contamination of the site by troposheric NO_2. Very large NO_2 enhancements are observed regularly at both sites mostly due to a combination of surface pollution and tropospheric multiple scattering in presence of rain or snow showers. In the case of Jungfraujoch data, a systematic method has been developed to detect and reject pollution events (Van Roozendael et al., 1994b). The Sodankyla data set was cleaned from the largest pollution peaks by simple observation of the time series. The dependence of airmass factors on the presence of volcanic aerosols was studied by Perliski and Solomon (1992) using a spherical Monte Carlo radiative transfer model. It was shown that NO_2 AMFs were almost insensitive to changes in scattering geometry induced by Pinatubo aerosols. The changes in NO_2 photolysis rates due to changes in the radiation field, that might affect NO_2 vertical distribution through a modification of the partitioning between NO and NO_2, were also shown to have a negligible effect.

RESULTS AND DISCUSSION

Daily sunrise and sunset NO_2 total column measurements carried out from January 1990 to August 1995 at Sodankyla (67°N) and at the Jungfraujoch station (46°N) are shown in Fig. 1, after elimination of the data affected by tropospheric pollution. The observed NO_2 columns follow the known latitudinal distribution of stratospheric NO_2 (e.g. Noxon et al., 1979, 1980).

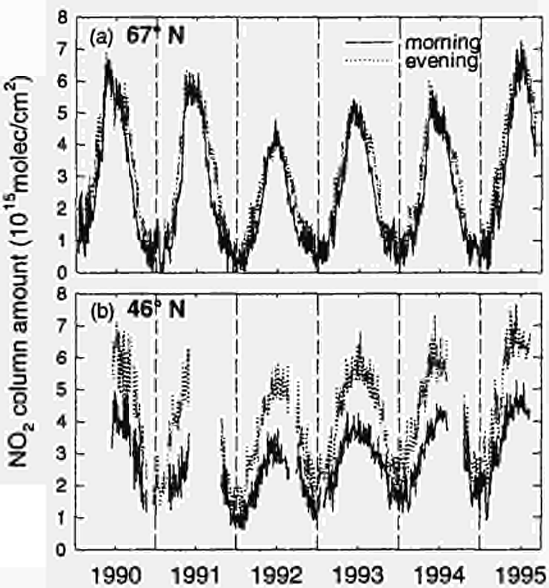

Fig. 1 Time series of daily morning and evening NO_2 column amounts measured by ground-based UV-visible spectroscopy at Sodankyla(a) and Jungfraujoch(b) from 1990 to 1995.

Mid-latitude data are characterized by larger diurnal changes, while the NO_2 winter minimum is significantly lower at high than at mid-latitude. The winter minima and summer maxima in 1990 and 1995 at both sites are in reasonable agreement with other authors at northern latitudes (e.g. Coffey et al., 1981). As already reported (Van Roozendael et al., 1994; Goutail et al., 1994), a significant reduction of the NO_2 column amount starting after the eruption of Mt Pinatubo in June 1991 and reaching a maximum during winter 1991/1992 is observed at both latitudes. Similar reductions were reported at northern mid-latitude (Koike et al., 1993) as well as at southern mid- (Johnston et al., 1992) and high latitudes (Solomon et al., 1994).

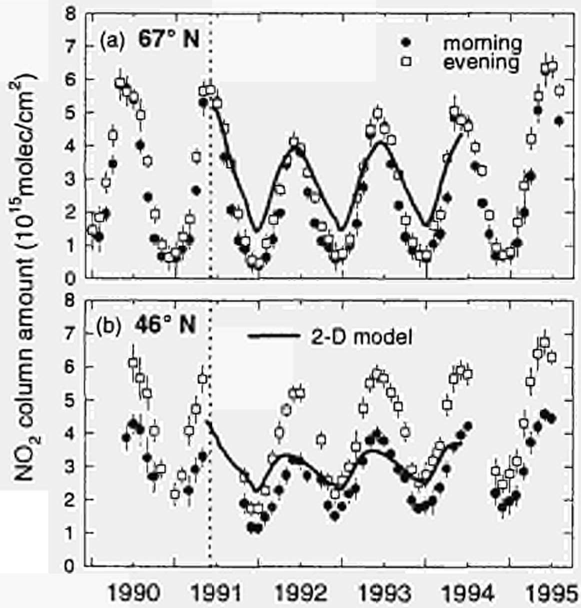

Fig. 2 Comparison between measured NO_2 monthly averaged column amounts and results of 2-D model calculations including heterogeneous reactions on the Pinatubo aerosols. The Mt Pinatubo eruption is indicated by the dotted lines.

In order to smooth out the day-to-day variability, monthly averaged morning and evening NO_2 column amounts were calculated in Fig. 2. The error bars shown together with the monthly means represent the variability of the NO_2 columns within a month (1σ standard deviation). Except for winter data at 67°N, these variabilities are larger than the uncertainties on the measurements. The progressive recovery of the NO_2 column amounts between 1992 and 1995 can be easily followed. In 1995, the NO_2 level is similar (even slightly larger) to the one measured in 1990.

In the same figure, the measured monthly averaged NO_2 column amounts are compared with calculations at 65° and 45° N obtained from a two-dimensional chemical model including heterogeneous reactions on the Pinatubo aerosol (Granier and Brasseur, 1992). The aerosol climatology used in the model for mid-latitudes was constrained by aerosol lidar measurements from Garmish-Partenkirchen provided by H. Jager (private communication). For high latitudes, the same climatology was adjusted in phase with a simulation of the Pinatubo aerosol evolution (Tie et al., 1994). Although the mean NO_2 level is rather well reproduced by the calculations, the amplitude of the seasonal variation is largely underestimated, especially at mid-latitude. Part of this discrepency can be accounted by the temperature dependence of the NO_2 absorption cross-sections which were measured for the SAOZ instrument at room temperature instead of stratospheric temperature. This could lead to a systematic overestimation of the measured NO_2 column by 20% (Harwood and Jones, 1994). The remaining discrepency might be due to the fact that the 2-D model does not include the diurnal changes in its computation scheme.

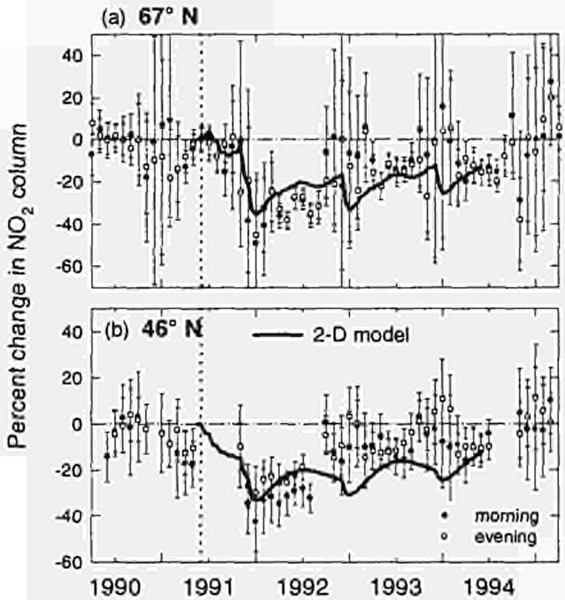

Fig. 3 Comparison between percent changes in NO_2 column amounts determined from UV-visible observations and from 2-D model calculations.

From the monthly averaged NO_2 columns shown in Fig. 2, the NO_2 column amounts in the absence of volcanic aerosols were determined using observations before the Pinatubo eruption (i.e. from January 1990 to June 1991). In the case of Jungfraujoch data, the NO_2 reference was obtained from a combination of pre-Pinatubo and 1995 column measurements, the latter year being considered as free of Pinatubo aerosols (Jäger, private communication). The percentage deviation calcultated from these reference values are shown in figure 3 for morning and evening observations. The uncertainties on these calculated percent changes are related to the natural variability of the NO_2 column which limits both the precision on the NO_2 monthly averages and the precision in the determination of the NO_2 reference. Given the standard deviation of the NO_2 data within a month and assuming a standard deviation of the interannual variations of the same magnitude (Johnston and McKenzie, 1989), error bars shown in figure 3 were calculated. There is a large uncertainty on the percent changes at 67°N during winter periods which is due to the large variability of the NO_2 column in winter at high latitude (typically 50%). Part of this variability results from measurement noise (larger for small NO_2 values). Within these uncertainties, the maximum NO_2 reduction of about 35% is obtained in January 1992 at both latitudes. It is followed by a progressive recovery lasting until summer 1994. There is no significant reduction measured during winters 1992/93 and 1993/94 due to the larger uncertainties on the measurements.

These NO_2 percent changes were compared to 2-D model calculations. In the model results, the main NO_2 decrease starts in November 1991. The largest reduction of about 35% is obtained in January 1992 at mid- and high latitudes. In this case, the calculations match quite well the observations both in time and magnitude. The recovery of the NO_2 column is also well reproduced, except during winter periods where calculated percent changes are characterized by local minima not seen in the observations. However this discrepency appears to be significant only for results at 46° N. At 67°N, the differences are within the error bars of the measurements. These results add a confirmation to the theory of NO_2 depletion due to heterogeneous conversion of N_2O_5 to HNO_3 at the surface of the volcanic aerosol (e.g., Hofmann and Solomon, 1989; Granier and Brasseur, 1992; Tie et al., 1994).

CONCLUSION

Ground-based visible measurements of NO_2 abundances covering one year before and four years after the Pinatubo eruption have been carried out at the Jungfraujoch station (46°N) and at Sodankyla (67°N). The data display a similar behaviour a both latitudes, i.e. a reduction of the NO_2 column starting at the end of 1991, reaching a maximum of about 35% in January 1992 and then followed by a progressive recovery until summer 1994. In 1995 the NO_2 abundances appear to be similar to those measured before the eruption.

2-D model calculations including heterogeneous reactions on the observed volcanic aerosols agree qualitatively with measured NO_2 column amounts, although the model results have been underestimated mainly at mid-latitudes. There is a good quantitative agreement between modelled and observed percent changes in NO_2 column. These results confirm the important effect of stratospheric sulphuric acid aerosols on the composition of the stratosphere.

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