Ground-based observations of stratospheric NO₂ at high and midlatitudes in Europe after the Mount Pinatubo eruption

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Abstract. Nitrogen dioxide has been monitored at the International Scientific Station at the Jungfraujoch (46°N, 8°E) since June 1990 and at Sodankyla (67°N, 27°E) since January 1990. NO₂ 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 NO₂ starting in winter 1992, after the eruption of the Mount 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 NO₂ column until August 1995. These results are compared with two-dimensional chemical model calculations, including the effect of heterogeneous reactions on observed Pinatubo aerosols. In general, the modeled NO₂ columns agree qualitatively with the observations although the amplitude of the seasonal variation is underestimated, possibly due to internal limitations of the model which, for example, does not include diurnal changes. The observed and calculated NO₂ percent changes are in good agreement, which confirms quantitatively the impact of the heterogeneous chemistry on stratospheric NO₂.

1. Introduction

Strong evidence exists on the basis of comparisons between model simulations and observations that heterogeneous processes occurring on the surface of stratospheric sulfuric acid aerosols (SSAs) are responsible for stratospheric ozone losses at midlatitudes. These heterogeneous processes lead to ozone depletion by converting halogens from reservoir forms to active forms, hence feeding halogen-based ozone-destroying catalytic cycles [*Solomon et al.*, 1996, and references therein].

The key chemical reactions are the hydrolysis of N_2O_5 and $ClONO_2$:

$$N_2O_5 + H_2O \xrightarrow{\text{Aer.}} 2HNO_3 \tag{1}$$

$$ClONO_2 + H_2O \xrightarrow{\text{Aer.}} HNO_3 + HOCl \tag{2}$$

The conversion of nitrogen oxide into nitric acid is more efficient at high latitude during winter because the lack of solar radiation in those conditions reduces the efficiency of nitric acid photodissociation. In addition, the conversion of chlorine nitrate is strongly temperature dependent and efficient only at low temperature. Therefore reaction (2) can generally be neglected at midlatitude [*Tie et al.*, 1994].

As both N_2O_5 and $ClONO_2$ are produced by reactions involving NO_2 ($NO_2 + NO_3$ and $NO_2 + ClO$, respectively) and HNO_3 is the long-lived sink for reactive nitrogen NO_x ($NO +$

NO_2), both reactions (1) and (2) decrease NO_x. Hence they were already proposed as possible mechanisms for the significant NO_x reduction observed between 30 and 35 km from balloon measurements performed before and after the El Chichon eruption in April 1982 [*Roscoe et al.*, 1986].

Following the major eruption of Mount Pinatubo in June 1991 which injected 20 megaton of SO_2 in the stratosphere [*Bluth et al.*, 1993; *McCormick et al.*, 1995] several observations have confirmed the chemical changes of the midlatitude stratosphere. *Johnston et al.* [1992] have reported 35% reduction of NO_2 total amount based on the longest time series of stratospheric NO_2 reported so far, beginning in the 1980s in Lauder (New Zealand). A similar reduction has been reported for the winter 1991-1992 by *Van Roozendael et al.* [1994] from measurements made at the International Scientific Station of the Jungfraujoch (ISSJ) in the Alps (46°N). *Mills et al.* [1993] confirmed the strong anticorrelation between the NO_2 total amount above Colorado and the SSAs. They also confirmed experimentally that NO_2 perturbation tends to saturate with increasing surface area of SSA as indicated by *Prather* [1992]. In situ measurements published by *Fahey et al.* [1993], including reactive nitrogen and chlorine species, confirmed the importance of SSA surface area in the production of the inactive nitrogen reservoir HNO_3. Changing the partitioning between reservoir halogenated compounds and active ozone-destroying species, SSAs and associated heterogeneous reactions modify the relative importance of the destroying catalytic cycles of ozone. In addition to NO_2 total amount reduction, changes in nitrogen reservoirs resulting from reactions (1) and (2) have been measured. *Koike et al.* [1994] reported measured HNO_3 total amounts anticorrelated with NO_2 above Lauder (New Zealand) over the period 1992-1993. However, these observations are not confirmed by aircraft measurements at northern midlatitudes by *Coffey and Mankin* [1993] although they report a NO_2 total amount reduction of about 50% after both El Chichon and Mount Pinatubo eruptions.

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Profile measurements of N_2O_5 and HNO_3 obtained by ATMOS between 25°N and 53°S in March-April 1992 during the ATLAS 1 mission confirmed the perturbed vertical distribution of those species, especially in the tropics [*Rinsland et al.*, 1994]. These measurements confirm the role of reaction (1) in altering the odd nitrogen partitioning after the Mount Pinatubo eruption.

Several model calculations have been performed which support the experimental results. Regarding NO_2 total amounts, the most significant comparison has been published by *Bekki and Pyle* [1994] based on a coupled two-dimensional chemical-microphysical model and on measurements performed at Sodankyla (67°N) one year before and one year after the Mt. Pinatubo eruption.

This work reports on time series of ground-based visible measurements of NO_2 total columns covering pre- and post-Pinatubo eruption conditions at two latitudes (46°N and 67°N). The experimental results obtained over 6 years with identical instruments at both sites are compared with 2-D model simulations, including the heterogeneous processes already mentioned. The aerosol climatology used in the calculations is based on lidar measurements above the Alps (47°N) from which surface area of SSAs have been calculated [*Jäger*, 1995].

2. Instrument and Data Analysis

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 a Système d'Analyse par Observations Zénithales (SAOZ) [*Pommereau and Goutail*, 1988]. The SAOZ spectrometer and the data analysis method were described in details in previous papers [*Goutail et al*, 1994; *Van Roozendael et al*, 1994a]. After participating in the Network for Detection of Stratospheric Changes (NDSC) intercomparison of UV-visible instruments (May 1992, Lauder, New Zealand [*Hofmann et al.*, 1995]), this instrument has been qualified for inclusion in the NDSC.

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° solar zenith angle (SZA). The conversion from slant to vertical column amounts is obtained using air mass factors (AMFs) calculated according to *Solomon et al.* [1987]. These calculations use a NO_2 vertical distribution measured from balloon experiment at midlatitude. It is assumed that the AMF depends on the SZA only; that is, the same set of AMFs is used throughout the year at both sites. Comparisons with integrated profiles measured with the SAOZ balloon-borne version in France and Scandinavia [*Pommereau and Piquard*, 1994] have shown that the uncertainty on the NO_2 vertical column due to this approximation is less than 10% [*Goutail et al.*, 1994]. The seasonal dependence of the error due to seasonal changes in the NO_2 profile is estimated less than 5% from calculations based on SAGE II data (unpublished results). Other sources of uncertainties, discussed by *Van Roozendael et al.* [1994b], are (1) the absorption cross-sections, (2) the calculation of the residual amount in the reference spectrum and (3) the meas-

urement 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 (relative error less than 10%) and by the measurement noise for small NO_2 columns (absolute error of about 2×10^{14} molecules/cm²). Much larger errors can be encountered due to contamination of the site by tropospheric 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 the 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.

3. Results

Daily sunrise and sunset NO_2 total column measurements were carried out from January 1990 to August 1995 at Sodankyla (67°N) and at the Jungfraujoch Station (46°N). The 5-year NO_2 time series from Sodankyla is complete, but some data are missing at the Jungfraujoch, as listed below. During winter 1990/1991, morning values could not be reliably retrieved due to noise at the detector level. In October 1991 the SAOZ spectrometer was replaced by a new version of the same instrument. No data were obtained between June and October 1991 due to the first instrument being requested at another site and the delivery time of the second one. Other gaps in summer 1992 and 1994 resulted from damages to the instrument's electronics due to thunderstorms.

Figure 1 shows monthly averaged morning and evening NO_2 column amounts calculated at both stations in order to smooth out the day-to-day variability. Instead of using arithmetic means, monthly means were obtained by fitting a re-
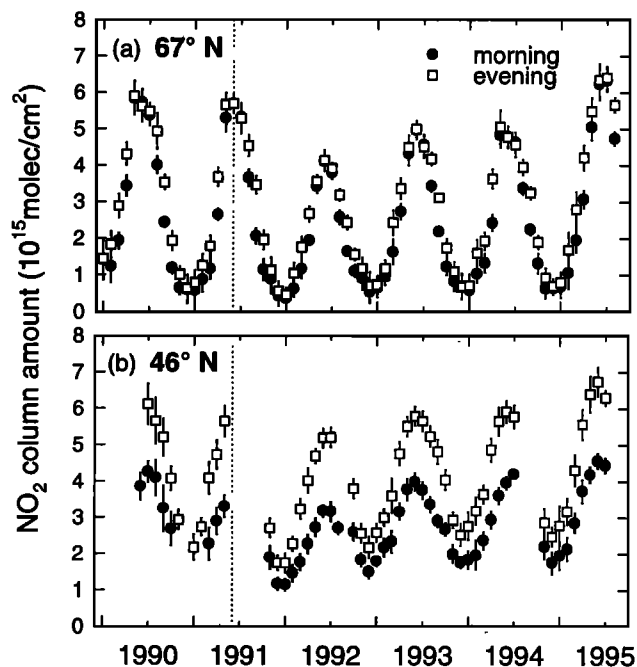

Figure 1. Time series of monthly averaged NO_2 data available at (a) Sodankyla and (b) the Jungfraujoch Station. For each month an average morning and evening twilight value is plotted. The vertical dotted line indicates the day of the Mount Pinatubo eruption.

gression line to the daily columns within a month and calculating the value of this line on the 15th of the month. This method minimizes the error on the monthly averages that might arise because of missing NO₂ values. The error bars shown together with the monthly means represent the variability of the NO₂ columns within a month (1 σ standard deviation). Except for winter data at 67°N, these variabilities are larger than the uncertainties on the measurements.

The observed NO₂ columns follow the known latitudinal distribution of stratospheric NO₂ [e.g., *Noxon et al.*, 1979, 1980]. Midlatitude data are characterized by larger diurnal changes, while the NO₂ winter minimum is significantly lower at high than at midlatitude. 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 NO₂ 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 midlatitude [*Koike et al.*, 1993; *Elokhov and Gruzdev*, 1993] as well as at southern middle [*Johnston et al.*, 1992] and high latitudes [*Solomon et al.*, 1994]. The progressive recovery of the NO₂ column amounts between 1992 and 1995 can be easily followed in the data of Figure 1. In 1995 the NO₂ level is similar (even slightly larger) to the one measured in 1990.

From these results the monthly NO₂ column amounts in the absence of volcanic aerosols were determined, for Sodankyla, using observations before the Pinatubo eruption (i.e., from January 1990 to June 1991). In the case of Jungfraujoch data, the NO₂ reference was obtained from a combination of pre-Pinatubo and 1995 column measurements, the latter year being considered as free of Pinatubo aerosols (H. Jäger, private communication, 1995). The percentage deviation calculated from these reference values are shown in Figure 2 for morning and evening observations. The uncertainties on these calculated percent changes are related to the natural variability of the NO₂ column which limits both the precision on the NO₂ monthly averages and the precision in the determination of the NO₂ reference. Given the standard deviation of the NO₂ 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 2 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 NO₂ column in winter at high latitude (typically 50%). Part of this variability results from measurement noise, larger for small NO₂ columns, but also from the location of the station alternatively outside and inside the cold polar vortex where the NO₂ abundance is reduced due to (1) conversion of NO$_x$ into HNO₃ on Polar Stratospheric Clouds (PSCs), (2) the temperature dependence of the gas phase NO$_x$ chemistry, and (3) possible denitrification known to have occurred at several occasions in the Arctic winter. Within these uncertainties, the maximum NO₂ 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 1992/1993 and 1993/1994 due to the larger uncertainties on the measurements. As reported by *Koike et al.* [1993] and *Johnston et al.* [1992], NO₂ percent changes seem to be larger for morning
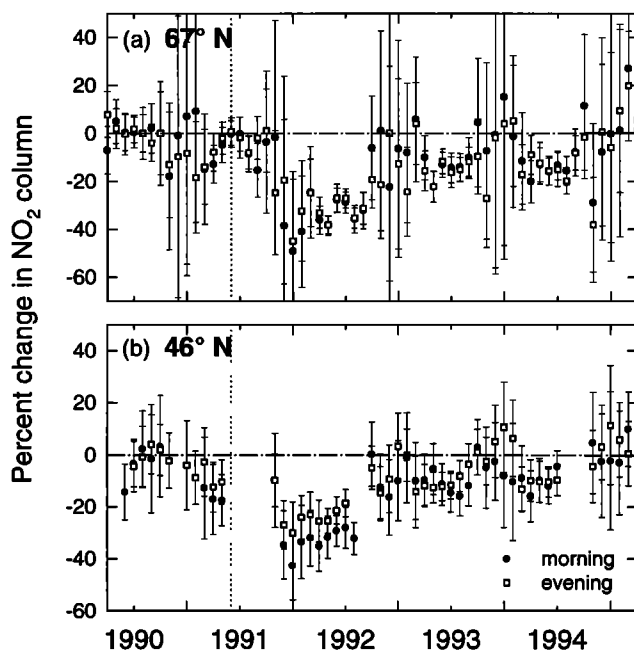

Figure 2. Relative change of the monthly averaged morning and evening NO₂ columns, relative to the respective unperturbed pre-Pinatubo reference value (see text), observed at (a) Sodankyla and (b) the Jungfraujoch Station. The vertical dotted line indicates the day of the Mt. Pinatubo eruption.

data than for evening ones at the midlatitude station. However, this difference might be insignificant considering the error bars. There is no difference between morning and evening percent changes measured at Sodankyla, but the amplitude of the diurnal variation is also considerably smaller than at midlatitude.

4. Discussion

The observation of significant reductions of the NO₂ column amount was reported after the eruption of El Chichon in April 1982 [*Roscoe et al.*, 1986; *Johnston and McKenzie*, 1989, *Coffey et al.*, 1993] and after the eruption of Mount Pinatubo in June 1991 [*Johnston et al.*, 1992; *Koike et al.*, 1993; *Elokhov and Gruzdev*, 1993; *Mills et al.*, 1993; *Goutail et al.*, 1994; *Solomon et al.*, 1994; *Van Roozendael et al.*, 1994]. Most of these observations were obtained from ground-based UV-visible measurements. Two possible causes of alteration of these measurements were investigated by *Perliski and Solomon* [1992]. First, the dependence of air mass factors on the presence of volcanic aerosols was studied using a spherical Monte Carlo radiative transfer model. It was shown that NO₂ AMFs were almost insensitive to changes in scattering geometry induced by Pinatubo aerosols. Secondly, the changes in NO₂ photolysis rates due to changes in the radiation field, which might affect NO₂ vertical distribution through a modification of the partitioning between NO and NO₂ [e.g., *Michelangeli et al.*, 1989], were shown to have only a small effect.

The impact of stratospheric aerosols on ozone and NO₂ was investigated by several authors [e.g., *Hofmann and Solomon*, 1989; *Granier and Brasseur*, 1992; *Bekki and Pyle*, 1994; *Tie et al.*, 1994]. The measurements mentioned above

support the theory of NO_2 depletion due to heterogeneous conversion of N_2O_5 to HNO_3 on the surface of the volcanic aerosol. This interpretation has been confirmed by HNO_3 measurements carried out at Lauder, New Zealand, showing a HNO_3 increase occurring in phase with a NO_2 decrease after the Pinatubo eruption [Koike et al., 1994].

In Figure 3 the measured monthly averaged NO_2 column amounts are compared with calculations at 65° and 45°N obtained from a two-dimensional chemical model [Granier and Brasseur, 1992]. The aerosol climatology used in the model for midlatitudes was constrained by aerosol lidar measurements from Garmisch-Partenkirchen provided by H. Jäger (private communication, 1995). For high latitudes the same climatology was adjusted in phase with a simulation of the Mount Pinatubo aerosol evolution as a function of the latitude and time [Tie et al., 1994]. The 2-D model does not include diurnal variations, therefore morning and evening observed values were averaged in order to facilitate the comparison. Although the mean NO_2 level is rather well reproduced by the calculations, the amplitude of the seasonal variation is largely underestimated, especially at midlatitude. Part of the discrepancy between model and observations can be accounted for by the temperature dependence of the NO_2 absorption cross sections that were measured for the SAOZ instrument at room temperature instead of stratospheric temperature. This could lead to a systematic overestimation of the NO_2 column by 20% [Harwood and Jones, 1994]. It is clear however that the observations does not always exceed the calculations and therefore other factors have to be searched. We believe that one other important reason for the differences between the model and the observations may be due to the fact that the
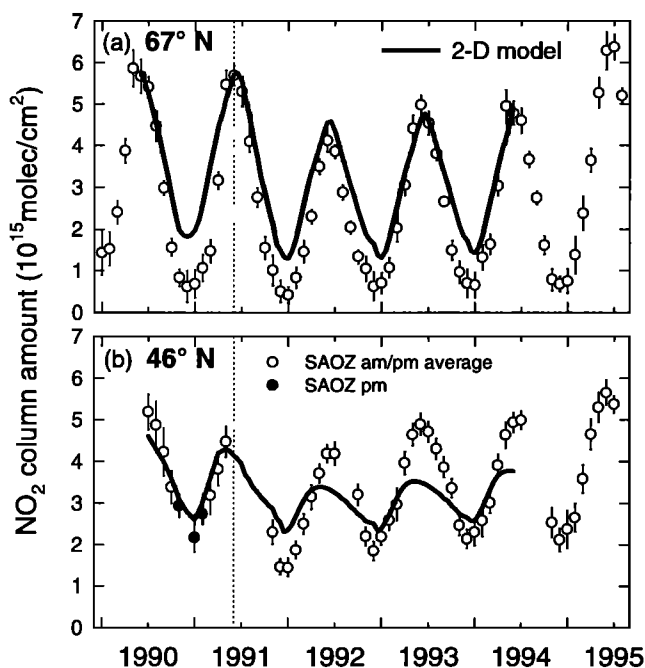
model does not include the diurnal cycle. The diurnally averaged model used in this work will produce at least two differences with respect to the observations. First, the morning/evening mean values determined from the measurements may not represent the diurnal averaged values calculated in the model over the full day. Second, the diurnal averaged model uses approximations that may have important effects. For example, the real loss rate for NO_2 by reacting with OH should be

$$\int_{day-night} [OH][NO_2].dt \tag{3}$$

while the model uses

$$[\overline{OH}]_{diurnal\,average} \cdot [\overline{NO_2}]_{diurnal\,average} \tag{4}$$

Figure 4 shows a comparison between the observed percent changes in NO_2 column amounts (again diurnally averaged) and the calculated ones. These latter were derived using a model calculation including background aerosol only as pre-Pinatubo reference. 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 middle and high latitudes. These results match quite well the observations both in time and in magnitude. The recovery of the NO_2 column is also captured by the model but, however, at a slower rate, particularly at 46°N. The agreement with the observations is better in 1992, when the aerosol layer extended up to 26 km and the aerosol density was large, than during the following years when the aerosol had partly sedimented. This may indicate a tendency of the model to better simulate conditions of high aerosol loading when the NO_x reduction process is largely saturated; that is, the production of N_2O_5 becomes the rate-limiting step in the conversion of NO_x to HNO_3. On the contrary, the model appears to overestimate the NO_x reduction at low aerosol loading. Another disagreement, again more significant at 46°N, is the marked minimum in winter in the simulations of the NO_2 percent changes at the opposite of what is observed. This might relate with the overestimation of the column by the model in winter (Figure 3), possibly due, as discussed above, to the fact that the model does not include the diurnal cycle. The dip in the model results is particularly important at 67°N. However, profile measurements from balloon in Scandinavia in the winter have shown that the NO_2 concentration is dramatically reduced below 20 km just because of the lack of sunlight [Lateltin et al., 1994], and therefore it is difficult to understand how aerosol located below 20 km in 1993 and 1994 could have reduced significantly the column.

Finally, it must be mentioned that the model results also indicate that although the NO_2 column change is not significantly sensitive to the heterogeneous reaction rates, it is much more sensitive to the aerosol surface area used in the calculations. Some discrepancies between observations and calculated values may be due to uncertainties in the sulfate aerosol surface areas applied in the model. To illustrate this, Figure 5 displays the results of a sensitivity study of sulfate aerosol loading on the calculation. It shows that if the aerosol loading after the eruption of Mt. Pinatubo is reduced by a factor of 2, the NO_2 reduction becomes less important, and at 45°N, the
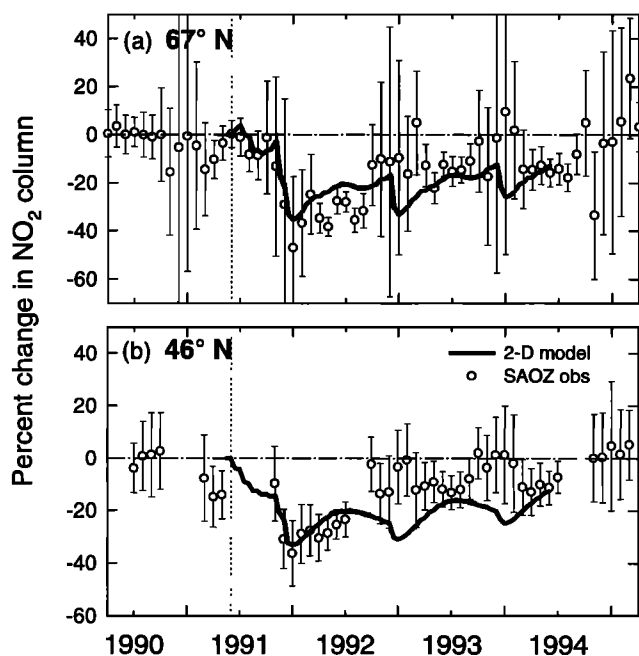

Figure 3. Comparison between experimental and modeled monthly averaged NO_2 column data at (a) Sodankyla and (b) the Jungfraujoch Station. The experimental data considered are the average between morning and evening twilight values except when only reliable evening data are available. The vertical dotted line indicates the day of the Mount Pinatubo eruption.

Figure 4. Comparison between experimental and modeled results for the monthly averaged relative NO_2 column change at (a) Sodankyla and (b) the Jungfraujoch Station. The experimental data considered are the same as in Figure 3. The vertical dotted line indicates the day of the Mount Pinatubo eruption.
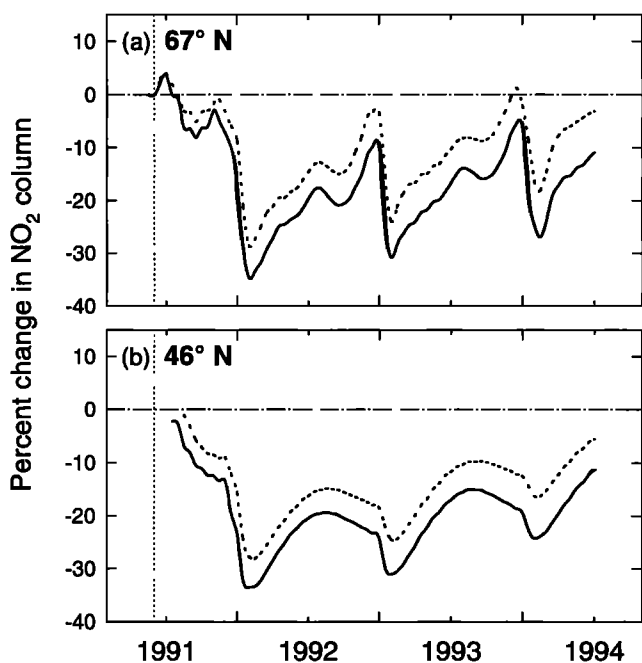

Figure 5. Sensitivity study showing the variation in calculated relative NO_2 column change at (a) 67°N and (b) 46°N, when reducing by a factor of 2 the aerosol loading after the Mount Pinatubo eruption. Dotted curves in both plots were obtained with half the amount of sulfate aerosols used to calculate solid curves.

calculation is in better agreement with the observations, indicating that uncertainties in the aerosol loading could significantly affect the model results.

The maximum reduction in the NO_2 column determined from Sodankyla and Jungfraujoch data for the northern hemisphere is delayed by three months compared with the reduction of similar amplitude observed at southern midlatitude [*Johnston et al.*, 1992]. This delay is consistent with the different arrival times of the Pinatubo aerosols in the two hemispheres. SAGE II measurements [*Trepte et al.*, 1993] show that by the end of September 1991 the volcanic aerosol had spread to southern midlatitudes at an altitude of about 30 km. At northern midlatitudes, the aerosol cloud reached altitudes above 25 km by the end of December. These satellite observations are in agreement with ground-based lidar measurements reported at northern hemisphere sites [*Jäger et al.*, 1995].

Koike et al. [1993] report the largest NO_2 reduction occurring in April 1992 at the northern hemisphere midlatitude station of Moshiri, Japan (44°N). According to these measurements, the maximum NO_2 reduction above Japan appears to be delayed by three months with respect to European midlatitudes. However, the uncertainty in the NO_2 percent changes determined from Moshiri data might be larger because the Pinatubo-free NO_2 values used at that site were deduced from data obtained at 45°S (shifted by six months in order to account for the interhemispheric difference in the phase of the NO_2 seasonal variation). Moreover, anomalously low NO_2 values might have been observed in April 1992 above Japan due to transport of air masses originating in the periphery of the polar vortex [see *Koike et al.*, 1993].

5. 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 behavior at 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.

Measured NO_2 column amounts are qualitatively well reproduced by the 2-D model calculations, including heterogeneous reactions on the observed volcanic aerosols, although somewhat underestimated by the model mainly at midlatitudes. There is a good quantitative agreement between modeled and observed percent changes in NO_2 column. These results confirm the important effect of stratospheric sulfuric acid aerosols on the composition of the stratosphere.

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