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Quantitative evaluation of the post–Mount Pinatubo NO_2 reduction and recovery, based on 10 years of Fourier transform infrared and UV-visible spectroscopic measurements at Jungfraujoch

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Abstract. The colocation of two technically different instruments for ground-based remote sensing of NO_2 total column amounts at the primary Network for the Detection of Stratospheric Change Alpine station of the Jungfraujoch (46.5°N, 8.0°E) has been exploited for mutual validation of the long-term NO_2 time series from both instruments and for a quantitative evaluation of the impact of the Mount Pinatubo eruption on the NO_2 abundance above this northern midlatitude observatory. The two techniques are high-resolution Fourier transform infrared solar absorption spectrometry and zenith-sky differential optical absorption spectroscopy in the UV visible. The diurnal variation of NO_2 has been simulated by a simple photochemical model that allows a comparison between the data from the two techniques. This model is shown to reproduce the observed morning to evening ratios to 2.3%, on average, which is fully adequate for the needs of this study. From the 1985-1996 combined time series of NO_2 morning and evening abundances, it has been concluded that the enhanced aerosol load injected into the stratosphere by Mount Pinatubo caused a maximum NO_2 reduction above the Jungfraujoch by 45% in early January 1992 that died out quasi-exponentially to zero by the beginning of 1995.

1. Introduction

At the International Scientific Station of the Jungfraujoch (ISSJ) in the Swiss Alps (46.5°N, 8.0°E, 3580 m altitude), the NO_2 total column content has been monitored since 1985 by Fourier transform infrared (FTIR) spectrometry instruments [*Demoulin et al.*, 1996]. Since 1989, when the Jungfraujoch was selected as one of the stations making up the primary Network for the Detection of Stratospheric Change (NDSC) Alpine station at northern midlatitudes [*Delbouille and Roland*, 1995], these measurements have intensified. In the same context and within the framework of European programs such as European Stratospheric Monitoring Stations that started in 1990 [*Simon et al.*, 1990], and Stratospheric Climatology by UV-Visible Spectroscopy a Système d'Analyse par Observations Zénithales (SAOZ) instrument was installed at ISSJ. It automatically performs daily measurements of ozone and NO_2 vertical column amounts at morning and evening twilight [*Van Roozendael et al.*, 1991]. Both FTIR and SAOZ instruments are NDSC qualified for midlatitude use, and their performances have been evaluated and improved in the same context [e.g., *Hofmann et al.*, 1995; *Vaughan et al.*, 1996; *Zander et al.*, 1994].

The FTIR time series shows no apparent long-term change in the NO_2 total column amount over the last 11 years; however, in both time series, the sudden decrease of NO_2 at ISSJ after the eruption of Mount Pinatubo (June 15-16, 1991, 15°N, 120°E) is evident. Such NO_2 reduction has been confirmed at other ground-based observatories, at various latitudes in both hemispheres [*Johnston et al.*, 1992, *Koike et al.*, 1993, *Koike et al.*, 1994; *Goutail et al.*, 1994] and by satellite observations, in particular the Stratospheric Aerosol and Gas Experiment II (SAGE II) (L.R. Poole, and M. P. McCormick, available at http://asd-www.larc.nasa.gov/sage/ASDsage.html, 1997). The latter, together with some balloon measurements, indicate that the impact was largest at relatively high altitude in the stratosphere, namely, around 22 to 24 km [*Webster et al.*, 1994; *Phillips et al.*, 1996].

Observations of NO_2 total abundance decreases and of vertical profile changes had been made after the El Chichon eruption [e.g., *Hofmann and Solomon*, 1989]. The changes in NO_2 after major volcanic eruptions have been qualitatively explained by the enhanced heterogeneous processing of nitrogen- and halogen-bearing species on the volcanic aerosol particles, which strongly modifies the partitioning between the nitrogen compounds; in particular, evidence exists for enhanced conversion of N_2O_5 into HNO_3 [e.g., *Rinsland et al.*, 1994; *Hofmann and Solomon*, 1989; *Brasseur and Granier*, 1992]. A first quantitative evaluation of the post-Mount Pinatubo NO_2 reduction above the Jungfraujoch, supported by two-dimensional model studies, was given by *Van Roozen-*

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dael et al. [1996]. Better understanding and model simulations of the reduction require a more precise estimation of the amount and timing of the NO_2 changes, their decrease and recovery, for which a pre-Mount Pinatubo NO_2 column climatology must first be established. To this end, we combined both ISSJ databases in order to benefit from their individual advantages, of course, after a mutual intercomparison that validates the individual results. This paper discusses the results of the latter intercomparison and the methodology we applied to combine the data sets, taking into account the diurnal variation of NO_2. FTIR data used in the present validation study are limited to the end of 1995. The obtained pre-Mount Pinatubo NO_2 total column climatology is presented, and its changes as observed after the eruption are evaluated quantitatively. The latter evaluation required the use of the entire combined 11-year time series of FTIR and SAOZ data; the latter have been extended until the end of 1996.

The actual study is limited to the investigation of total vertical column abundances. It is known from model calculations and observations that the vertical distribution of NO_2 also is strongly dependent upon the sulfate aerosol content in the lower stratosphere [e.g., *Hofmann and Solomon*, 1989; *Brasseur and Granier*, 1992], but there are still discrepancies between results from box model simulations and observations [*Renard et al.*, 1997]. Additional information about perturbed NO_2 vertical distributions will be investigated in the future to assess how this affects the present findings.

2. NO_2 Time Series at the Jungfraujoch

2.1 Description of Experimental Data

FTIR. The FTIR NO_2 columnar data result from wideband spectra recorded on clear days by one or both of the two spectrometers, a Bruker 120HR and a homemade Fourier transform spectrometer, encompassing the 2914.65 cm^{-1} NO_2 multiplet. The spectra are taken at a spectral resolution of 2.85, 4.00, or 4.96 x 10^{-3} cm^{-1}, depending on instrument and measurement time; they are recorded at various astronomical solar zenith angles (SZA), smaller than about 92°. The mutual consistency of both FTIR instruments is checked regularly (about once a year) through intercomparison of simultaneous measurements; moreover, a mutual consistency check for the NO_2 measurements discussed here has been conducted, as discussed in section 2.2. The analysis of the spectra is performed with the SFIT 1.09 nonlinear least squares fitting algorithm [*Rinsland et al.*, 1984] in the spectral microwindow between 2914.51 and 2914.86 cm^{-1}. In addition to NO_2, H_2O and CH_4 absorptions are also fitted to properly reproduce the local background envelope. The standard SFIT molecular vertical distributions are adopted; daily pressure and temperature profiles provided by the National Centers for Environmental Prediction (NCEP) (formerly the National Meteorological Center) are used up to their minimum pressure level (0.4 hPa), at which altitude they are further extended with the standard SFIT profile. Of importance in this study is the precision of the FTIR NO_2 vertical column abundances, which is estimated to be better than ±10%, based on the observed dispersion among successive measurements and on the impact of typical noise levels with respect to the target absorption features.

The fitting procedure models the radiative transfer through the atmosphere according to the FSCATM algorithm [*Gallery et al.*, 1983] for the solar absorption geometry looking at the sun at a given solar zenith angle. The ray tracing that allows calculation of the conversion factor between vertical and slant column amounts includes the effect of refraction and Earth curvature in a homogeneously layered, spherical atmosphere. The transmission calculation includes only molecular absorptions; aerosol and other particle absorptions, as well as scattering processes, are neglected. The latter effects would be spectrally broadband with respect to the molecular absorption lines. Because the fit procedure is performed over narrow spectral microwindows, in which the molecular absorption depths are evaluated relative to the local continuum that is fitted simultaneously, these approximations should have no impact on the results.

SAOZ. The SAOZ data are derived from zenith-sky observations by the differential optical absorption spectroscopy (DOAS) method in the 408 to 455 nm spectral range, at a resolution of about 1 nm. The instrument's detector was changed from a linear silicon photodiode array of type PCD to one of type NMOS in mid-1991, effectively causing a slightly different instrument function; the period of operation with the first detector is indicated hereinafter as P1. The consequences of this instrumental change as to the NO_2 data are discussed in the next paragraph. Only spectra taken between 87.0° and 91.0° SZA, which is the most reliable range for the SAOZ measurements, are used for the evaluation of mean morning and evening NO_2 column amounts; moreover, data affected by tropospheric pollution are rejected routinely according to a procedure that inspects the change in total vertical column with SZA [*Van Roozendael et al.*, 1994]. The present DOAS analysis uses the NO_2 cross sections provided by *Johnston and Graham* [1974] that are still recognized as an excellent data set [*Harder et al.*, 1997]. The temperature and pressure dependences of the cross sections that have been studied recently [*Sanders*, 1996; *Harder et al.*, 1997; *Vandaele et al.*, 1998] have not been taken into account.

The direct DOAS spectra analysis yields slant column amounts, representative of the absorption along the paths of the light from the source (sun) via the scattering point to the observer. In the visible spectral range, this path is affected by the atmospheric extinction, hence it is a function of the aerosol load and of meteorological conditions such as cloud cover and height, and the absorption is strongly dependent on the absorber's vertical distribution. The conversion factor between effective slant column and vertical column, called the air mass factor, constitutes the major source of uncertainty of the DOAS method. Standard SAOZ air mass factors are used, calculated in a single-scattering scheme, and dependent on SZA only; the uncertainties associated with these approximations are evaluated by *Perliski and Solomon* [1993].These air mass factors adopt an NO_2 vertical distribution from a balloon experiment at midlatitude, which is different from the SFIT profile in the lower stratosphere and troposphere, in that the SFIT profile results in a larger tropospheric contribution to the total amount. During the period after the Mount Pinatubo eruption when the stratosphere was highly loaded with aerosol, the expected change of the NO_2 vertical distribution, as well as a modified scattering geometry, may affect the accuracy of the air mass factor and thus also the NO_2 vertical column data. According to *Johnston et al.* [1992], *Van Roozendael et al.* [1997], and references therein, this effect is small.

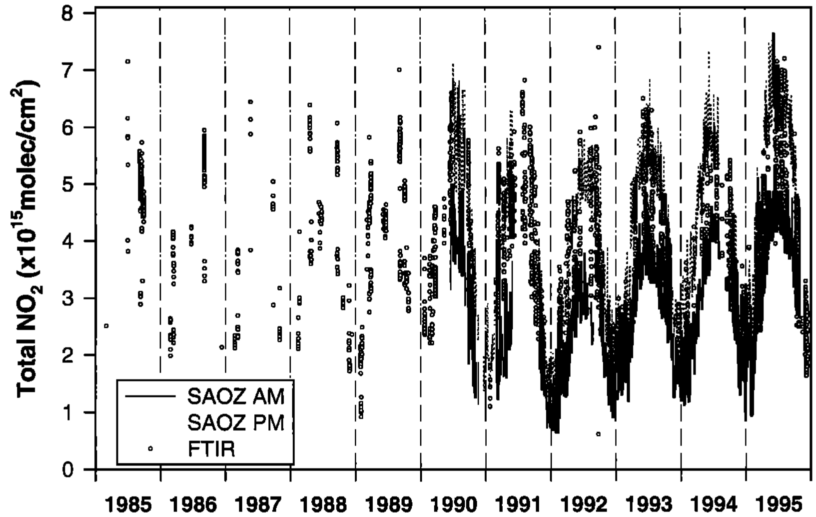

Figure 1. Fourier transform infrared (FTIR) and Système d'Analyse par Observations Zénithales (SAOZ) time series of NO_2 vertical columns at the Jungfraujoch, until the end of 1995. SAOZ data are average morning (AM) and evening (PM) twilight values, from spectra taken in the 87°-91° solar zenith angle (SZA) range. FTIR data are individual measurements taken throughout the day.

The relative precision of the SAOZ NO_2 vertical column data is considered to be better than 10%, except for the small column values; in any case, the absolute error on the vertical column is quasi-constant, of order 0.2 x 10^{15} mol/cm^2 [*Van Roozendael et al.*, 1997]. Because of the somewhat enhanced uncertainties in the period after the eruption of Mount Pinatubo discussed above, this period will be distinguished in the validation exercise reported below and is hereinafter identified as PP. Its delimitation from mid-1991 until the end of 1992 is based on the observation of anomalous SAOZ ozone data [*De Mazière et al.*, 1998]. It is well known indeed that the enhanced aerosol load had a nonnegligible impact on the O_3 air mass factor [*Johnston et al.*, 1992; *Koike et al.*, 1993; *Dahlback et al.*, 1994; *Sarkissian et al.*, 1995].

The SAOZ time series covers nearly all days (twilight values) since mid-1990, except for a few gaps due to instrument failures. The FTIR database covers only about 50% of the days, which is a limitation resulting from weather requirements and the nonautomatic operation of the instruments, but it has the advantage of stretching further back in time to 1985. This paper discusses data until the end of 1995; to complete the NO_2 recovery, SAOZ data until the end of 1996 have been added. Both time series are displayed in Figure 1.

2.2 Mutual Validation

Before combining both SAOZ and FTIR time series, we must validate them. First, we decided to verify the FTIR NO_2 data consistency explicitly, although we know that both FTIR instruments are equally well qualified as explained above. Therefore, initially, the data of both FTIR instruments at ISSJ were distinguished in the intercomparison exercises discussed hereinafter, until their equivalence showed up clearly within the limits of uncertainty of the results. This distinction was then omitted for the derivation of the final conclusions of the validation and for the further studies based on it.

As mentioned above, the sampling time for the SAOZ measurements is identical for all days in terms of SZA, but not for the FTIR data, implying that a direct intercomparison of the NO_2 vertical columns is impossible because of the NO_2 diurnal variation. Therefore two approaches have been adopted for intercomparing observations made on the same day: (1) selecting temporally quasi-coincident observations between 80 and 92° SZA and (2) interpolating the SAOZ mean morning and evening results to the time of the FTIR observations for that day. In the first approach, the SZA range was extended beyond the most reliable range of the SAOZ measurements, for the purpose of increasing the number of overlapping observations. Even so, however, and relaxing the coincidence requirement to be within ± 0.5° SZA, the first approach selects only 53 data from observations over 296 days for which valid SAOZ and FTIR data exist together, whereas the second one exploits 1257 measurements, spread

Table 1. Observed Differences Between the NO_2 Vertical Column Data

Difference	Mean, %	Standard Deviation, %	Number of Data
All	7.5	12.9	1257
P1	22.0	17.7	94
PP	14.8	22.0	141
1993 +	5.1	8.9	1022

Data are from the Fourier transform infrared (FTIR) and Système d'Analyse par Observations Zénithales (SAOZ) at the Jungfraujoch. Differences are calculated as FTIR/SAOZ - 1 and reported as percentage mean differences and their standard deviations. Differences are also distinguished by period; all denotes the whole time series (mid-1990 to 1996), P1 denotes mid-1990 to mid-1991, PP represents the period perturbed by Mount Pinatubo (mid-1991 to the end of 1992), and 1993 + is the period from January 1993 onward.

over 203 days. The latter approach hence has the advantage of better statistics, but the interpolation scheme adds some uncertainty to its results. Between the mean morning and evening values, linear interpolation was chosen because of its simplicity and because the observed diurnal variation between these limits of SZA, i.e., for SZA not higher than 91°, agrees quite well with a linear variation. Recent box model calculations confirm the quasi-linear diurnal variations between these SZA limits at midlatitude (D. Fonteyn, private communication, 1997). Cases for which the standard deviation σ of the individual SAOZ results in the 87° to 91° SZA range show too large a dispersion around their average, which is the mean morning (evening) value, have been rejected in the statistical evaluation. The rejection criterion used is: $\sigma > \sigma_{avg} + 1\,\mathrm{s.d.}_\sigma$. Herein, σ_{avg} is the average value of σ over all days, and $\mathrm{s.d.}_\sigma$ the corresponding standard deviation; the expression has been evaluated and applied separately for the morning and evening values. In the rejected cases, we suspect that too large NO_2 variations throughout the day occur which may invalidate the adopted linear interpolation scheme. Such NO_2 perturbations are detected regularly at the Jungfraujoch; they are believed to originate either in tropospheric pollutions that are not rejected by the filter currently used [*Van Roozendael et al.*, 1994] or in fast meridional transport.

The conclusions drawn from the intercomparison according to the linear interpolation approach are shown in Table 1. The best agreement between FTIR and SAOZ data is obtained in the present configuration that started in 1993, with a systematic difference between the FTIR and SAOZ data of about 5%. This figure may give an indication of the accuracies of the individual measurements. Apparently, the initial SAOZ instrument configuration with the old detector (period P1) caused a systematic, additional, negative offset of SAOZ with respect to FTIR data of 17%; in order to homogenize the SAOZ time series, a correction factor of 1.17 has been applied to the data of period P1. The Mount Pinatubo perturbation (PP) caused mainly a larger uncertainty of the data, reflected as a larger dispersion of the relative differences. The results of the first approach based on quasi-coincident data agree qualitatively with the above findings; quantitatively, they agree within the limits of uncertainty. Because of their limited statistical reliability, they are not tabulated explicitly, and the correction factors that will be used hereinafter for combining both data sets are based on the results of the linear interpolation approach.

2.3 Simulation of NO_2 Morning to Evening Ratio

For the representation and exploitation of the combined FTIR and SAOZ NO_2 total column data sets, we must turn to vertical column data at the same local time because of the different air mass factors involved in the respective slant columns. We opted for morning and evening vertical column (VC) values, corresponding to the SAOZ morning and evening twilight observations. In normal midlatitude conditions, the ratio of the morning to evening columns α_{VC} can be approximated by [*Nevison et al.*, 1996]:

$$\alpha_{VC} = \int dz\, \alpha(z) C_{NO2}(z) / \int dz\, C_{NO2}(z) \qquad (1)$$

where $\alpha(z)$ is the ratio of morning to evening concentrations at altitude z, given by

$$\alpha(z) = \exp\left[-2k1(z) C_{O3}(z) \Delta t_{\mathrm{night}}\right] \qquad (2)$$

Herein, $C_{NO2(z)}$ and $C_{O3(z)}$ are the concentrations at altitude z of NO_2 and O_3, respectively, and $\Delta t_{\mathrm{night}}$ is the duration of the night, in seconds; and $k1$ is the rate-limiting reaction rate for the nighttime conversion of NO_2 to N_2O_5, that is dependent on altitude z through its dependence on temperature $T(z)$ [*Senne et al.*, 1996]:

$$k1(z) = 1.2 \times 10^{-13} \exp\left[-2450\,\mathrm{K} / T(z)\right] \mathrm{cm}^3 / \mathrm{s\,molecule} \qquad (3)$$

In our application, night has been delimited by the 90° SZA times, a choice justified by the SZA dependence of the relevant photochemistry [*Nevison et al.*, 1996] and by the timing of the SAOZ observations. Equations (1) to (3) indicate that α_{VC} depends on latitude and season through $\Delta t_{\mathrm{night}}$ and also on the vertical concentration profile of O_3, on the temperature profile, and on the shape of the vertical distribution of NO_2. For simulating the observed values, we checked the relative impact of each of these parameters on the calculated morning/evening ratio; some quantitative figures are summarized in Table 2. It turns out that the most critical parameters are the

Table 2. Summary of the Sensitivity of the Calculated NO_2 Vertical Column Morning/Evening Ratio to Various Parameters

Temperature Profile,	O_3 column,	O_3 Profile,	NO_2 Profile,	Difference	
NCEP Data	SAOZ Data	Soundings at Payerne	SAGE II Climatology	Mean, %	Standard Deviation, %
S	S	S	S	12.6	21.6
A	S	S	S	7.7	15.8
S	A	S	S	7.3	17.9
A	A	S	S	3.6	14.3
A	A	A	S	4.0	14.5
A	A	A	A	2.3	14.2

Difference indicates the relative difference between the calculated and observed (by SAOZ) morning and evening values over the full SAOZ operational period, except for the mid-1991 to end of 1992 period (PP). NCEP is National Centers for Environmental Prediction; SAGE II is the Stratospheric Aerosol and Gas Experiment II. S and A indicate where U.S. 1976 standard atmosphere or actual profiles/total columns, respectively, were used.

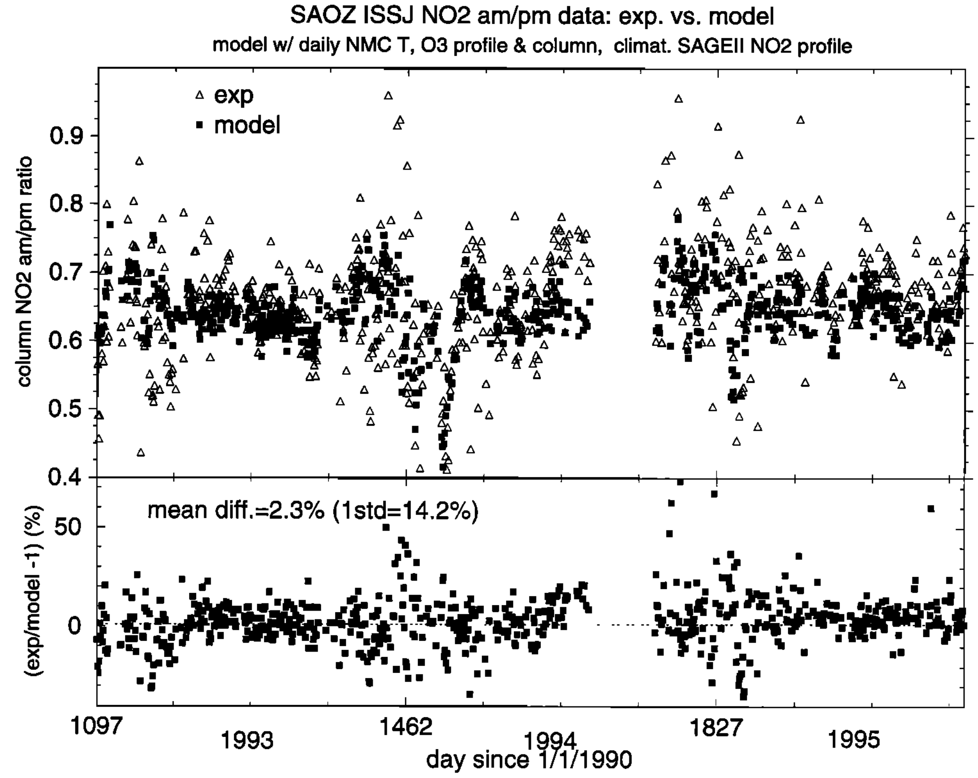

Figure 2. Comparison between observed and modeled morning/evening vertical column ratios at the Jungfraujoch in (top) absolute values and (bottom) as relative percentage differences. The simulation uses actual data for pressure *p*, temperature *T*, ozone and NO$_2$ vertical distributions, whenever available (see text and Table 2).

actual temperature profile and total O$_3$ column, which were obtained from NCEP and on-site SAOZ observations, respectively. The reliability of the SAOZ ozone data has been demonstrated recently; at midlatitude the SAOZ O$_3$ data are of order 2% higher than the Dobson ones, with a random scatter of order 5% [*Van Roozendael et al.*, 1998]. The PP period has been excluded from this simulation exercise, mainly because the SAOZ ozone data are invalid in this period. The use of actual ozone profiles obtained at Payerne (P. Viatte, private communication, 1996) for the period 1993 to the end of 1995, and of NO$_2$ climatological profiles derived from SAGE II for the entire period under discussion (C. Brogniez, private communication, 1996) improved the agreement but to a lesser extent; the dispersion around the mean error (last column in Table 2) is not altered. The latter SAGE II climatology is a set of average profiles over a 10° latitude belt, centered at 45°N, for periods of about 1 month duration; sunrise and sunset profiles were treated separately and gave approximately the same results as the present exploitation. Whenever experimental profiles were used, they were extrapolated, if necessary, to the altitude of the Jungfraujoch and to the higher altitude limit, set to 50 km, by using the U.S. 1976 standard atmosphere profiles [*Anderson et al.,* 1986]; invalid data and data gaps have been replaced and filled by U.S. 1976 standard atmosphere model values. In the case of ozone, the concentration profiles were always scaled such that the integrated amount equalled the total column values as measured by SAOZ. The final simulation is shown in Figure 2; the relative error of the simulation is displayed at bottom, with a mean value of 2.3%.

The largest discrepancies between calculated and observed values generally occur in the winter period, where morning/evening ratios, as well as absolute NO$_2$ column abundances, are smallest and where, in addition, the uncertainties about the vertical ozone and NO$_2$ distributions are probably larger, owing to more frequent dynamical perturbations of the stratosphere in the winter-spring period.

2.4 Combined NO$_2$ Morning and Evening Time Series

On the basis of the assumption of a linear diurnal variation and the prediction of the vertical column morning/evening ratio as demonstrated above, FTIR NO$_2$ vertical column amounts measured at various times *t* throughout the day, VC(t), can be converted to equivalent morning and evening values VC$_{\mathrm{AM}}$ and VC$_{\mathrm{PM}}$, via a linear regression analysis of the following relationship:

$$\mathrm{VC}(t) = \mathrm{VCAM}\left[\frac{t - t_{\mathrm{AM}}}{\Delta t_{\mathrm{day}}}(\alpha_{\mathrm{VC}}^{-1} - 1) + 1\right] \tag{4}$$

where t_{AM} is the time of sunrise 90° SZA and Δt_{day} is the length of day.

Equation (4) has been applied to all FTIR data, starting in 1985; the FTIR data were corrected first for the 5% systematic offset with respect to the SAOZ data (see Table 1). Hereto α_{VC} has been calculated according to (1) to (3), using NCEP temperature profiles, U.S. 1976 standard atmosphere NO$_2$ vertical profiles, and ozone columns from total ozone map-

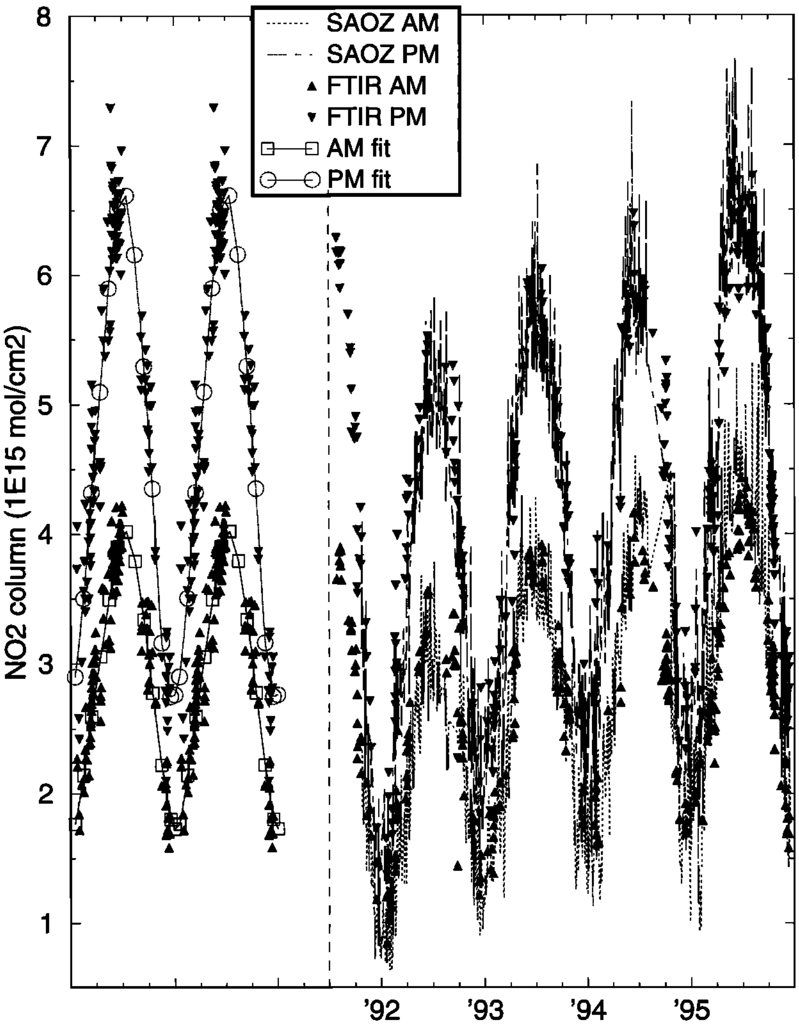

Figure 3. Combined morning and evening NO_2 vertical column time series from SAOZ and FTIR extrapolated (see text) observations at the Jungfraujoch. Data before 1991 are the folded set of pre-Mount Pinatubo FTIR data between 1988 and mid-1991, extrapolated to SAOZ equivalent morning and evening values.

ping spectrometer (TOMS) overpasses over the Jungfraujoch, before May 6, 1993 (end of TOMS/Nimbus 7 operation), or the Dobson data from Arosa beyond that date, if existing. The ozone column values are taken into account in (2) as a scaling factor of a fixed vertical ozone distribution shape, for which the U.S. 1976 standard atmosphere vertical distribution has been adopted. For days where no observational ozone column data were available, the corresponding U.S. 1976 standard ozone column equal to 341.9 Dobson units (DU) (1 DU = 0.001 atm cm) has been assumed; that is, no scaling was applied to the standard profile. The validity of this method for simulating FTIR morning and evening values was tested by verifying the agreement between the thus calculated FTIR values and the observed SAOZ morning and evening values for days from 1993 onward for which valid data from both SAOZ and FTIR instruments are available. On average, the calculated FTIR morning and evening values deviate from the observed SAOZ values by only -1.2 ± 9.8% and +3.4 ± 8.2%, respectively. This validates the method for derivation of FTIR extrapolated morning and evening NO_2 column amounts, also in the period before the Mount Pinatubo eruption; the resulting combined morning and evening NO_2 time series is shown in Figure 3. In this figure, the pre-Mount Pinatubo data derived from the FTIR observations are folded into 1 calendar year because of the scarcity of data per year for the purpose of establishing monthly climatological values; this folded set is reproduced twice for better vizualisation of the winter minimum. The lack of winter data in the early period of the FTIR observations forced us to include data from November and December 1995, which are known to be no more disturbed by the Pinatubo effect; the aerosol level has returned to a background level [*Fiocco and Larsen*, 1997; H. Jäger, private communication, 1997]. The NO_2 data in the period from 1988 to the first half of 1991 have been taken as reference values for the derivation of the climatological monthly mean fitted values displayed in Figure 3. Three very low values in January 1989 and January 1991 that we believe to be related to singular polar vortex air overpasses have been discarded for this derivation. We argue for this choice as follows. Long-term time series of the stratospheric aerosol load at northern midlatitude [*Fiocco and Larsen*, 1997; H. Jäger, private communication, 1997] indicate that low levels can be associated with the periods 1978/1979 and 1988/1991. From 1985 to 1987, the aerosol level was still somewhat higher, as a result of the eruptions of Ruiz (1985) and Nyamuragira (1986) and possibly residues of the El Chichon eruption (1982). Moreover, our FTIR NO_2 data in this period (1985-1987) seem to be systematically lower than in the 1988 to mid-1991 period by almost 10%, which may be related to the difference in aerosol level between both periods. Therefore the data before 1988 have been eliminated from the pre-Pinatubo data plotted in Figure 3. The thus determined climatological morning and evening mean NO_2 levels are evaluated at 2.87 and 4.68 x 10^{15} molecules/cm^2, respectively; the seasonal peak-to-peak variations amount to 79.7% and 82.6% for the morning and evening values, respectively.

3. Impact of Mount Pinatubo's Aerosol Load on NO_2 at the Jungfraujoch

From Figure 3, the reduction and gradual recovery of the morning and evening NO_2 column amounts is clearly apparent. Generally speaking, FTIR and SAOZ data agree very well. As demonstrated above, however (Table 1, period PP), mid-1991 to the end of 1992 is a period where the overall agreement between FTIR and SAOZ data is worse. Moreover, in 1992, the calculations of the FTIR morning and evening values are less reliable, because the model presented above for deriving these values (see (1) to (4)) does not hold in the case of enhanced heterogeneous chemistry; *Nevison et al.* [1996] showed that chemical reactions involving $ClONO_2$ and HNO_3 contribute considerably to the NO_x diurnal variation in the lower to middle stratosphere. We know that the vertical NO_2 distribution was altered after the Mount Pinatubo eruption and that the perturbation extended until 1993 [*Phillips et al.*, 1996]. Only a few reliable experimental profiles seem to be available. The SAGE II data used in the present study often show missing or unreliable values in the lower altitude range (below 25 or even 30 km), especially during the first half of 1992 (C. Brogniez, private communication, 1996). Therefore we decided to base our quantitative evaluation of the NO_2 reduction after the eruption of Mount Pinatubo on the SAOZ data only, up to the end of 1996. The result, reported in terms of monthly mean percentage differences relative to the pre-Mount Pinatubo monthly climatology established above, is displayed in Figure 4. The reduction peaks at the turnover between 1991 and 1992 and amounts to 45% with respect to the pre-Mount Pinatubo 1988 to mid-1991 mean level; no distinct behavior between morning and evening columns is observed. The recovery can be modeled reasonably well by a sum of two exponentials, an initial fast one with an *e*-folding time of 2.7 months, followed by a slower one with an *e*-folding time of 35 months (solid line in Figure 4). We choose this representation of the decay in correspondence with the underlying decay of the aerosol load that is governed by two distinct processes, namely, net northward transport and sedimentation [*Jäger et al.,* 1995]. If we limit the fit to the 24-month period following the maximum impact, for comparison with the decay of the aerosol load measured above the closest lidar station of Garmisch-Partenkirchen [*Jäger et al.,* 1995], we find approximately the same 10-month *e*-folding time, as represented by the dashed line in Figure 4. The tail of the recovery seems to be better fitted by an exponential with *e*-folding time of order 24 months. By mid-1994, both the aerosol load and the NO_2 reduction had decreased to about 10% of their maximum value. The NO_2 abundance observed at the end of 1996 appears to be higher by about 7% than the reference level, which might be related to the fact that the actual aerosol load has come down approximately to the 1978/1979 background level, at least below the 1988/1991 one (H. Jäger, private communication, 1997). Further observations in 1997 are needed to confirm the latter NO_2 value and the long-lasting recovery time.

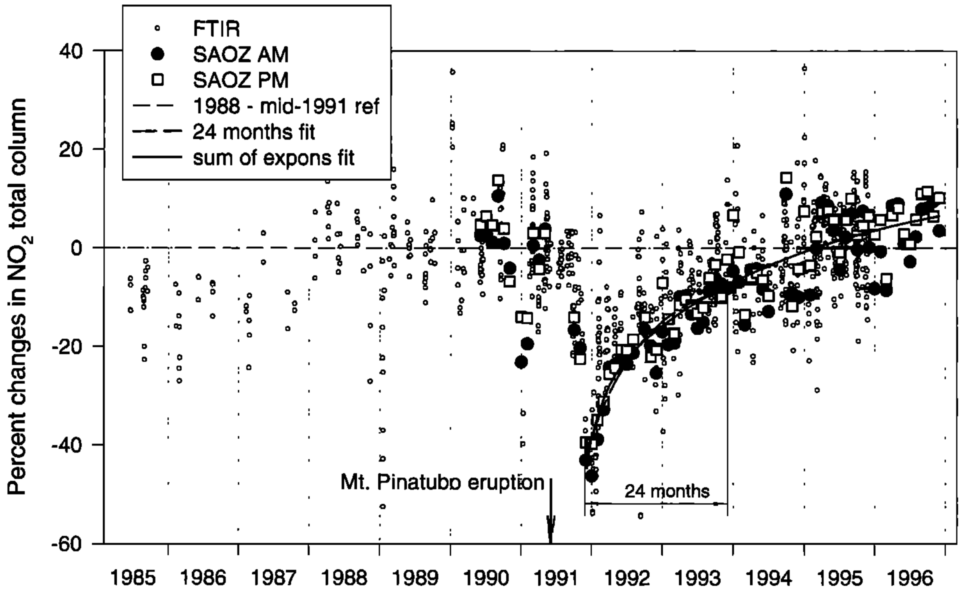

Figure 4. Percentage monthly mean NO_2 vertical column reductions observed at the Jungfraujoch by the SAOZ and FTIR instruments. Reductions are evaluated relative to the 1988 to mid-1991 monthly mean reference values derived from the FTIR observations. SAOZ data (solid circles and open squares) are monthly means for morning and evening vertical column amounts; FTIR (small open circles) are daily values.

In comparison with the observations at Lauder in the southern hemisphere (45°S, 170°E), as reported by *Johnston et al.* [1992] and *Koike et al.* [1994], the reduction in the northern hemisphere was delayed by a few months and peaked at a somewhat larger value of 45% instead of 40%. *Johnston et al.* [1992] argued for a contribution from heterogeneous processing to the NO_2 reduction observed at Lauder of at least 20%. The maximum NO_2 reduction in Japan at 44°N, 142°E [*Koike et al.*, 1993] was observed later, in April 1992, and was of the same order of magnitude (45% to 50%); these results are quite uncertain, however, because the local measurements started only in April 1991, inhibiting the establishment of a reliable NO_2 climatological reference. Contrary to the previously cited observations at Lauder and in Japan, we observe no significant change in the NO_2 morning/evening ratio at the Jungfraujoch. Regarding the NO_2 recovery, *Koike et al.* [1994] were not able to make a good estimate, because the reported time series was still too short. Results obtained during a ship cruise in October/November 1993 as reported by *Senne et al.* [1996] indicate that NO_2 has recovered to its pre-Mount Pinatubo value at northern midlatitudes by that time. The present NO_2 time series at the Jungfraujoch, on the contrary, reveals that by that time (October/November 1993), the NO_2 column abundance was still reduced by about 10% and it had come to complete recovery only by January/February 1995.

No attempt is made here to distinguish real chemical NO_2 destruction from changes due to other effects (radiative, dynamical, etc.). Two-dimensional chemical model simulations of *Van Roozendael et al.* [1997] have shown that at least part of the NO_2 reduction is a direct consequence of heterogeneous processing on the volcanic aerosol. The good overall agreement between FTIR and SAOZ data confirms that the uncertainties in the NO_2 air mass factors associated with the SAOZ measurements are small. The quantitative differences as to the observations of the NO_2 reduction at the different sites mentioned above are related probably to different times of arrival of the Mount Pinatubo aerosol clouds and different characteristics of the aerosol layers, such as, e.g., their distribution with altitude, the particle sizes, etc., that may influence the relative importance of the factors affecting the observed NO_2 total column amounts.

One observes a close resemblance between the time behaviors of the NO_2 reduction and of the aerosol load as observed by ground-based lidar backscattering [*Jäger et al.*, 1995; *Chazette et al.*, 1995; *Osborn et al.*, 1995] or from satellite [*Fussen et al.*, 1998], with *e*-folding times of order 9 to 10 months in the early decay phase. The early 1985 to 1987 inclusive lower NO_2 values from the FTIR observations do not fit with the behavior one would expect on the same grounds from an El Chichon residue only; the aerosol cloud from the latter eruption in April 1982 had about the same decay behavior at northern midlatitudes as the one from Mount Pinatubo [e.g., *Fiocco and Larsen*, 1997, Figure 3.1], thus implying complete NO_2 recovery by the end of 1985. Reductions of NO_2 as a result of the El Chichon eruption have been observed in both hemispheres [e.g., *Johnston and Mc.Kenzie*, 1989; *Roscoe et al.*, 1986; *Coffey and Mankin*, 1993] and confirm the previous statement. So, as mentioned in section 2.4, we believe that it is the other eruptions of Ruiz and Nyamuragira that caused the lower NO_2 values in 1985-1987.

4. Conclusions

The agreement one obtains at the Jungfraujoch observatory between colocated FTIR direct-sun and zenith-sky DOAS UV-visible observations with a SAOZ instrument confirms the relative precisions claimed for the FTIR and SAOZ NO_2 vertical column measurements, and the small systematic offset between both of order 5% is very encouraging as to their accuracies. The SAOZ time series could be homogenized, thanks to the results of the intercomparison with the FTIR time series, proving the benefits of the validation exercise. These results are important for all stations equipped with multiple instrumental techniques, in particular, the NDSC stations, of which the Jungfraujoch is an example.

Some concerns must be raised, however. Recent studies regarding the NO_2 cross sections in the UV-visible spectral range have demonstrated that the latter's temperature and pressure dependences may have a quite important impact on the retrieved column amounts [*Sanders*, 1996; *Harder et al.*, 1997; *Vandaele et al.*, 1998]. In addition, the infrared spectroscopic line parameters of the NO_2 band used in the FTIR analysis have been revised recently (A. Perrin, private communication, 1996). Another concern is the sensitivity of the SAOZ and FTIR column retrievals to the assumed NO_2 vertical distribution and the reliability of observational correlative data from satellite or balloon in the lower stratosphere and troposphere. These issues will be addressed in a future study. In the meantime, the actual results demonstrate the validity of the method for combining the NO_2 data sets from FTIR and SAOZ observations and the enhanced value of the resulting time series.

An important corollary of this validation study is the demonstration of the exploitation of multiple time series for the benefit of geophysical studies. The examples given here are (1) the establishment of a climatology for the pre-Mount Pinatubo NO_2 morning and evening twilight vertical column abundances at the Jungfraujoch site, representative of the past decade at northern midlatitudes, and (2) the quantitative evaluation of the NO_2 vertical column reduction as a consequence of the Mount Pinatubo stratospheric aerosol load with respect to the climatological values. Thus the observed decrease of the NO_2 column abundances amounts to 45% at maximum at the beginning of January 1992, and the subsequent NO_2 recovery fits a double exponential, with initial and subsequent *e*-folding times of 2.7 and 35 months, respectively. The NO_2 abundance above the Jungfraujoch was back to its pre-Mount Pinatubo values by January/February 1995.

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