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SPECTROSCOPIC MEASUREMENTS OF ATMOSPHERIC CHANGES (SMAC)

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Abstract

Observations of ozone and 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 these constituents 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 low ozone values with respect to the average of Dobson time series obtained in Arosa since 1931. In addition, NO_2 reductions of 15% in March-May 1992 and of 30% in the summer have been observed after 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 factors which might affect ground-based visible absorption measurements because of the presence of the enhanced aerosol layer are considered as negligible for NO2 according to recent radiative transfer calculations.

Similar measurements have been performed by ground-based visible spectrometry at Keflavik, Iceland (64.0°N, 22.6°W) during EASOE. NO_2 column amounts below $1x10^{15}$ molec/cm^2 are measured between December 1991 and mid-February 1992, the lowest values being reached inside the polar vortex during the coldest period of the campaign. The usual correlation between sunset NO_2 total columns and 20 hPa temperatures was not observed during the warming of the stratosphere in February. This indicates low N_2O_5 amounts outside the vortex, possibly related to heterogeneous reactions on Pinatubo aerosol. However the low NO_2 amounts observed could be attributed partly to the advection of air masses from the polar night region.

I. INTRODUCTION

Over the last three decades, ground-based spectroscopic observations which use the Sun and/or the zenith sky as a source of radiation have provided a large amount of information on the composition and the structure of the stratosphere. The UV range of the solar spectrum has been used for remote sensing of stratospheric ozone since the 1930s. Very significant results have been obtained for example with the Dobson network which have been used to determine trends in ozone total content from 1957.

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 improved during the 1980s by several groups (e.g. Mount et al., 1987; Pommereau and Goutail, 1988a,b; Johnston and McKenzie, 1989) by using photodiode array spectrometers for stratospheric monitoring of both O_3 and NO_2.

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

mid-latitudes NDSC (Network for the Detection of Stratospheric Change) station in the Northern Hemisphere. This work presents the results obtained for O_3 and 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).

In addition, it also reports ground-based observations of O_3 and NO_2 total amounts made at Keflavik, Iceland (64.0°N, 22.6°W) during EASOE from November 15, 1991 to March 30, 1992.

These scientific studies contribute to several international programmes, namely :

- The Network for the Detection of Stratospheric Change (NDSC);
- The Stratospheric Processes and their Role in Climate (SPARC), a project of the World Climate Research Programme (WCRP);
- The Environment Programme of the Commission of the European Communities, DGXII;
- The correlative measurement programme of the Upper Atmosphere Research Satellite (UARS).

II. STRATOSPHERIC OBSERVATIONS AT THE JUNGFRAUJOCH BY ULTRAVIOLET-VISIBLE ABSORPTION SPECTROSCOPY

II.1. Introduction

Nearly continuous measurements of ozone and nitrogen dioxide column abundances were performed since 3 years at the International Scientific Station at the Jungfraujoch (ISSJ) situated in the Swiss Alps (46.5°N, 8°E) at an altitude of 3580 m. Therefore, they covered the winters 1990-1991 and 1991-1992. In addition to the O_3 and NO_2 total amount, line-of-sight amounts of O_4 and H_2O are systematically recorded. As these two molecules are mainly tropospheric constituents, their line-of-sight amounts indicates anomalies of the optical path trough the lower atmosphere.

A "Système d'Analyse par Observations Zénithales" (SAOZ, Pommereau and Goutail, 1988a) was installed in June 1990. It has been replaced by a new version of the same instrument at the end of October 1991 and no data were obtained from June to October 1991. In addition, simultaneous ozone and NO_2 measurements have been obtained occasionally by the University of Liège, using FTIR spectroscopy.

II.2. Experimental and Retrieval Methods

Slant column abundances of ozone and nitrogen dioxide can be determined by measuring the absorption in the ultraviolet and the visible of scattered and/or direct sunlight or the incoming light reflected by the Moon. Vertical column abundances are deduced from those measurements by calculation

of the optical path or airmass factor according to the description published by Solomon et al. (1987). The number of absorbing molecules in the light path is deduced by using the Beer-Bouguer-Lambert law.

Very recently, differential absorption in the Chappuis bands was developed thanks to new detectors like the photodiode arrays which allow to record at once a complete spectrum over a broad wavelength range if the instrumental bandpass is set around 1 nm. This range is sufficient to bring out the narrow features present in the Chappuis bands which have the advantage with respect to the Huggins bands to be temperature independent.

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 after an appropriate analysis. Indeed, the solar spectrum (direct and diffuse) is characterized in the UV-visible range by Fraunhofer lines usually masking absorption features of terrestrial trace species (with the exception of ozone in some wavelength ranges). This problem is overcome by dividing the observed spectrum by a reference spectrum, then by smoothing with a broad bandpass moving average to remove the background attenuation due to molecular (Rayleigh) and aerosol (Mie) scattering and the instrumental characteristics. The so-called differential absorption spectrum is then obtained, where the signature of the various absorbing constituents can be clearly identified.

Ozone abundances are determined in the spectral range 400 - 520 nm and NO_2 abundances from absorption spectra between 405 and 485 nm. In both cases, absorption features from O_4 and H_2O are interfering and need to be removed. Corrections for the Ring effect are made using pseudo cross sections generated by detrending the reference spectrum (J.P. Pommereau, private communication). Daily measurements at sunrise and sunset result from an average on a few spectra (between 3 and 6, depending on weather conditions) obtained for SZA between 88 and 91°.

Vertical column abundances were deduced from slant column amounts by using an identical airmass factor (Solomon et al., 1987) for the whole time series despite the presence of an enhanced sulfuric acid aerosol layer around 20 km altitude in the 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 very low for NO_2 retrieval. The aerosols effects on the airmass factor appear only for SZA larger than 91° if the NO_2 absorption is confined between 20 and 25 km altitude. They become negligible when the bulk of the NO_2 column is taking place between 30 and 35 km.

II.3. Results of observations

The time series of ozone and NO_2 daily measurements obtained at Jungfraujoch are presented in figure 1. The lower

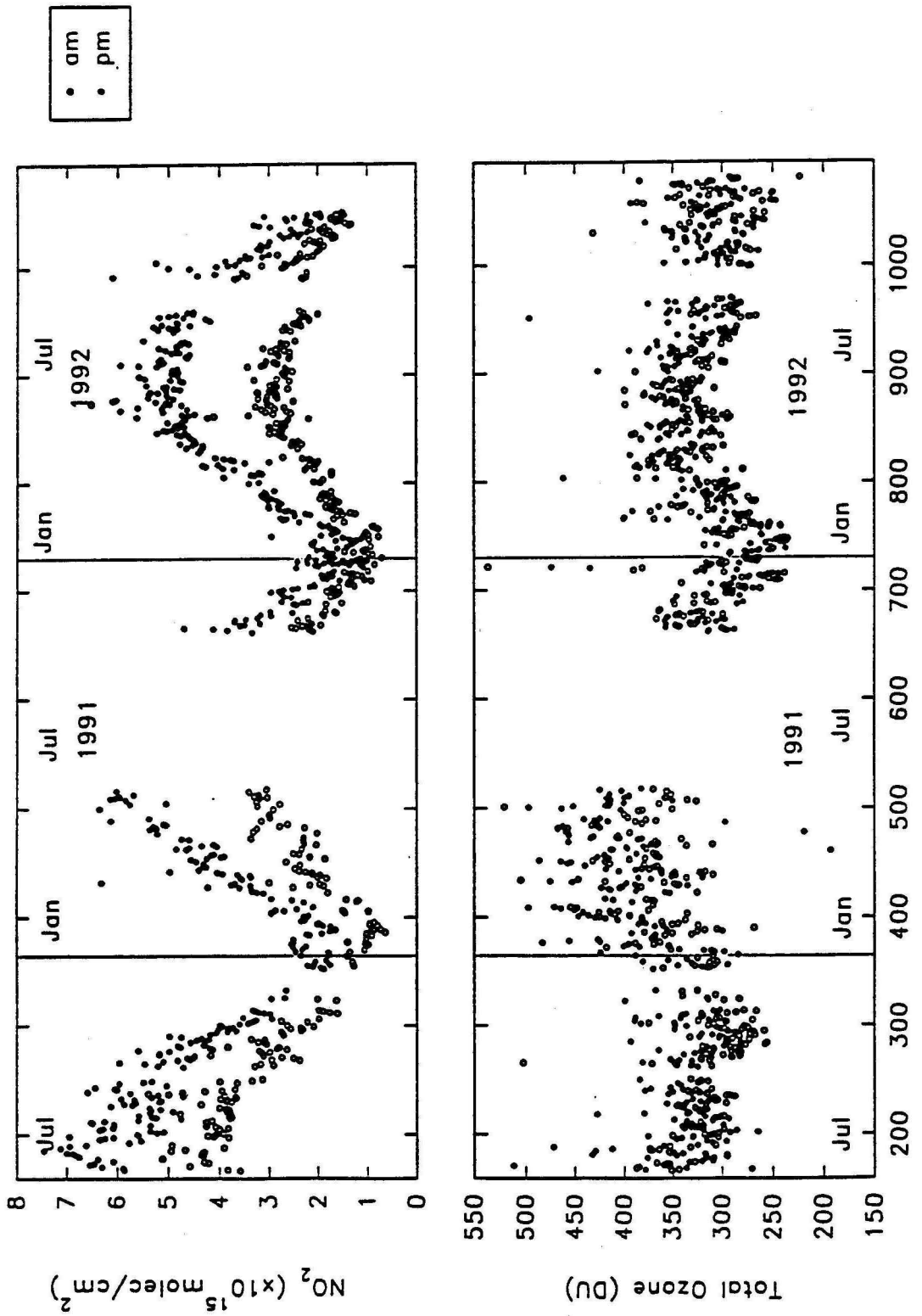

Figure 1 : Time series of O_3 and NO_2 total amounts obtained at the ISSJ.

values for the standard deviations of the fits in the results of the 1992 winter as compared to 1991 are shown in figure 2.

II.3.1. Nitrogen dioxide

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 located in the stratosphere, around 30 km altitude at mid-latitudes, its measurement from the ground can be perturbed by the conditions in the troposphere. In particular two types of tropospheric events can introduce large errors in the determination of the NO_2 total contents :
1. the transportation, from industrialized areas to the Jungfraujoch observatory, of airmasses containing high NO_2 concentrations due to pollution.
2. the occurrence of snowfalls, thick clouds or fogs enhancing the scattering efficiency and increasing the light path in the lower troposphere.

These tropospheric conditions increase the absorption in the lower part of the atmosphere. In case of enhanced tropospheric multiple scattering, this excess remains approximately constant during the twilight period because geometrical enhancement in zenith sky measurements affects only the stratospheric part of the column (Solomon et al, 1987). Slant column densities measured as a function of the SZA in perturbed conditions are thus offset upward as compared to clear-sky conditions. The more important the perturbation is, 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.

In order to detect the occurrence of tropospheric perturbations, a careful inspection of the O_4 and H_2O data has been made. 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. The intercepts at zero airmass in those plots are the total amount in the reference spectrum minus the tropospheric slant amount in the measured spectra (Roscoe et al, 1993). They 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 (see figure 3). When correlated with H_2O and/or O_4, the offset should originate from 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.

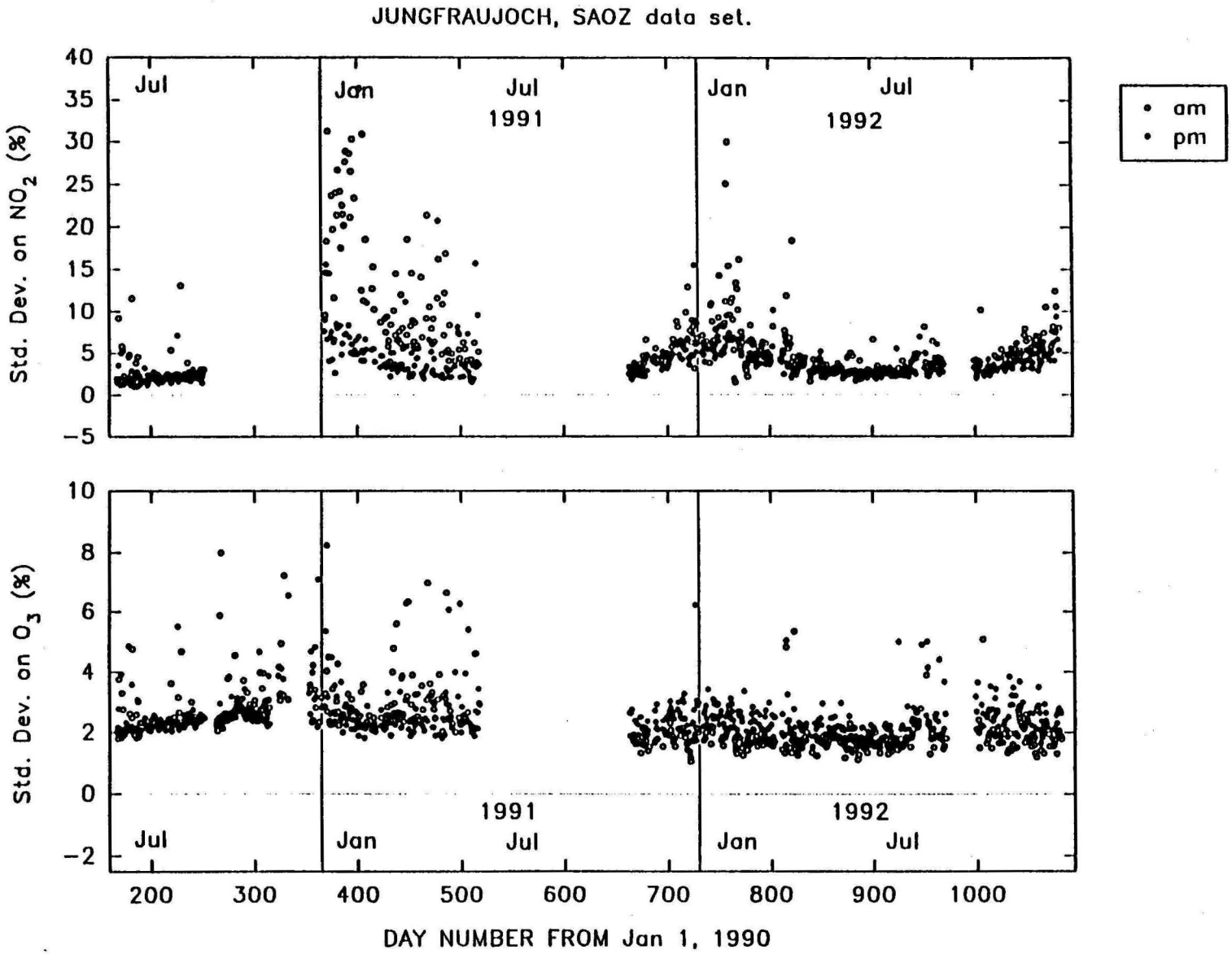

Figure 2 : Standard deviation in percent on the fits corresponding to the results presented in fig. 1.

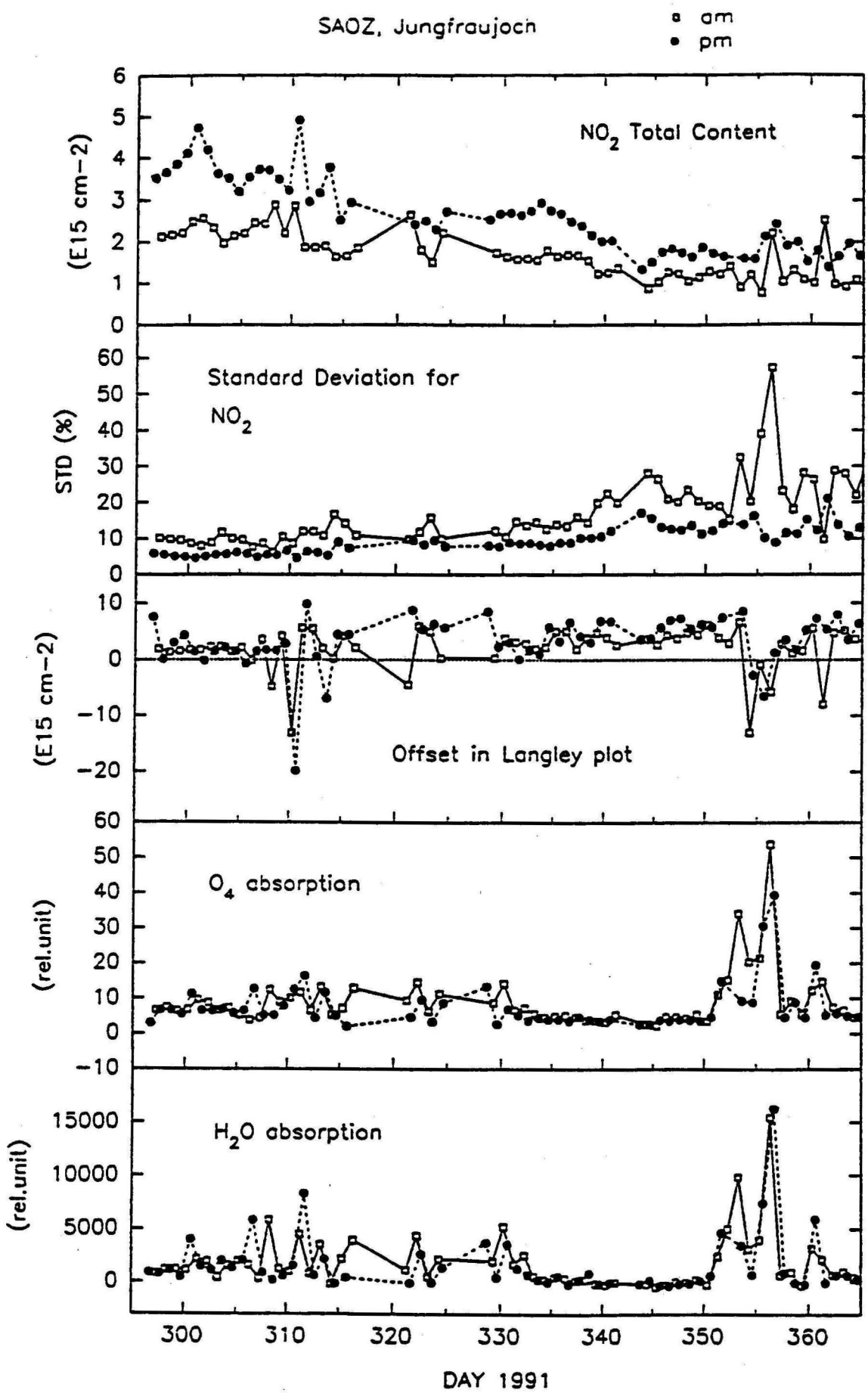

Figure 3 : Time series of the SAOZ measurements of vertical amount of NO_2, the corresponding standard deviation, the offsets of the Langley plots, and the O_4 and H_2O absorption, in November and December 1991.

The validated time series is presented in figure 4 with respect to the day of year, with the same scale for 1990, 1991 and 1992 for comparison purposes. Monthly mean NO_2 column have also been calculated and are presented in figure 5 with the standard deviation at 1σ for each average. Spring and summer values show the greatest short term variabilities, possibly due to dynamical causes. A systematic decrease in NO_2 amounts can be observed in 1992, after the Pinatubo eruption, compared to 1991, before the eruption. January and February sunrise NO_2 total contents show no sizable reduction because of the very low abundances of NO_2. A decrease of about 15% is observed in the spring and reaches a maximum of 30% in the summer. Subsequent measurements in October and November show values close to those obtained in 1990 and 1991 during the same months.

NO_2 depletion after a volcanic eruption has been observed in the Northern Hemisphere from balloon observations (Roscoe et al., 1986) and from the ground in the Southern Hemisphere, at Lauder (New Zealand, 45°S, 170°E). The effects of the El Chichon eruption in April 1982 (17.3°N, 93.2°W) on NO_2 columns were reported by Johnston and McKenzie (1989). They started in mid 1982, reaching a maximum of 20% reduction in March 1983. After 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 the Spring. Reductions of about 30% observed in the summer at the ISSJ have not been reported so far in other latitudes.

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 reactions on sulfuric acid aerosol decreasing both ozone and NO_2.

II.3.2. Ozone

The time series of ozone abundances obtained at the ISSJ shows the well known seasonal variability with the usual day-to-day variations mainly controlled by the dynamical processes in the troposphere.

The sources of uncertainties for the determination of the O_3 content have been studied in the literature (Pommereau et al.,1990; Goutail et al., 1992). They come both from the spectral analysis (random noise, uncertainties on absorption cross-section,...) and from the AMF used to retrieve the vertical amounts. At large SZA, the uncertainty is shown to be mostly dominated by the sensitivity of the AMF to the variability of the O_3 vertical distribution. At 90° SZA, the precision of the O_3 measurements is evaluated to be 6% and the total accuracy to be 10% (Goutail et al., 1992). However this

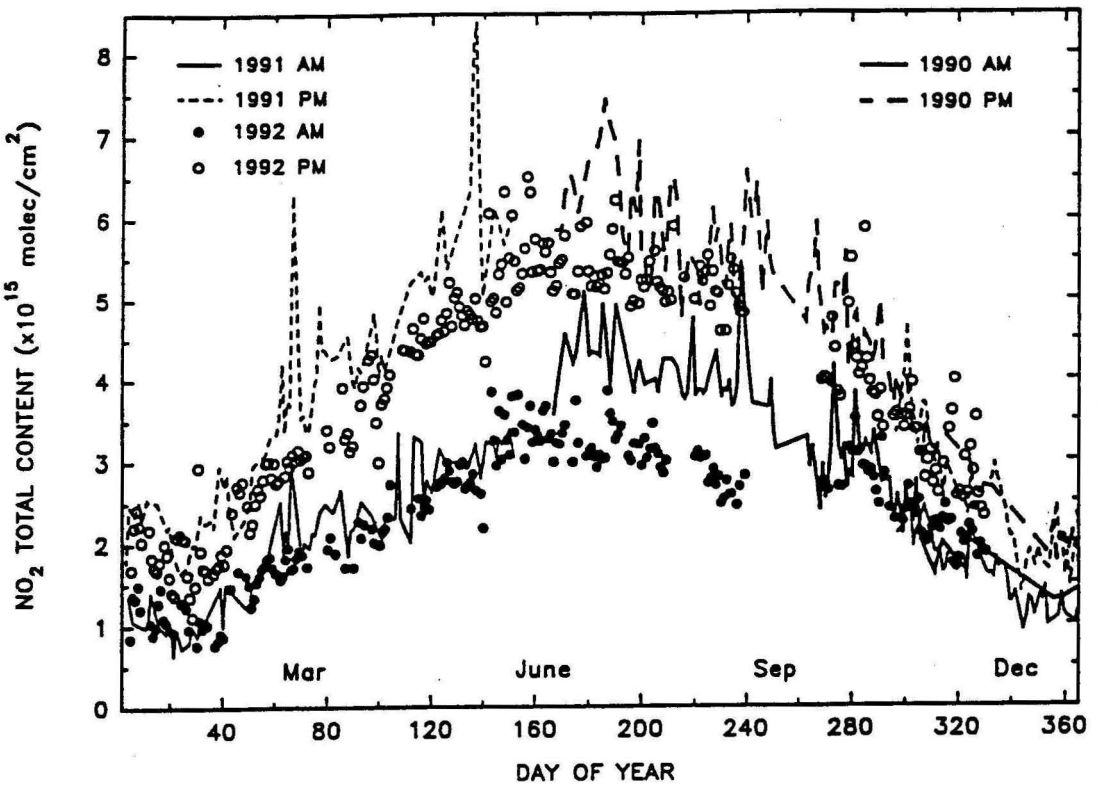

Figure 4 :Daily observations of NO_2 vertical columns in 1990, 1991 and 1992 made at the ISSJ after removing the values obtained for days with perturbed tropospheric conditions (see text).

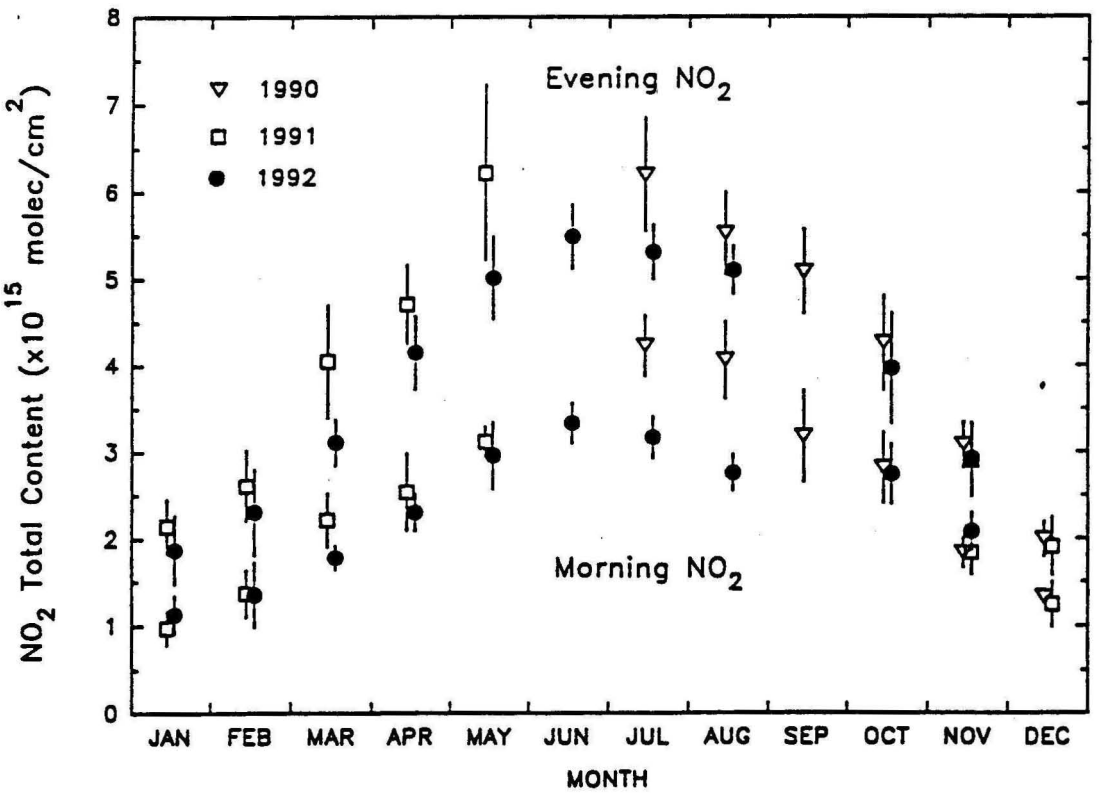

Figure 5 : Comparison of monthly mean NO_2 vertical abundances from measurements obtained at the Jungfraujoch (figure 4). The vertical bar represents the 1 sigma variability of the data during the considered month.

error budget does not take into account the effect of local atmospheric perturbations which can significantly alter the measurement precision. At stratospheric levels, perturbations can be induced by Polar Stratospheric Clouds (PSC's) or by any significant source of stratospheric aerosols (e.g. volcano eruptions). PSC's and stratospheric aerosol loading like the one resulting from the eruption of Mt. Pinatubo in June 1991 cause underestimation of the column amount. This effect has been clearly identified in the O_3 data set. As for the NO_2 results, tropospheric perturbations can severely affect the O_3 abundance results. Similar methodology can be used to detect and quantify episodes marked by either high tropospheric pollution or enhanced multiple scattering conditions.

The deviations in Langley plots are always correlated with large increases of the O_4 and H_2O line-of-sight amounts. The amplitude of the deviation is roughly proportional to the amplitude of the change in O_4 and H_2O. If the O_4 slant content remains at the same (high) level during twilight, the Langley plot is shifted by a constant value. Its slope is not altered and can be used to retrieve the vertical content. The known spectral interference between O_3 and O_4 absorption spectra does not lead to significant increase of the error bar on O_3 results even in case of very large perturbation

It has been pointed out by Goutail et al (1992) that the best compromise in terms of precision and accuracy for SAOZ measurements of O_3 and NO_2 is to consider data recorded only between 87 and 91° SZA. At lower SZA, the error increases mainly due to loss of sensitivity, enhanced effect of tropospheric perturbations and uncertainty in the residual amount in the reference spectrum. At larger SZA, the increased dependence of the AMF on the absorber profile introduces large uncertainties. From the preceding discussion it is clear that a selection on the SZA alone cannot guarantee accurate results in case of large tropospheric perturbations. Therefore additional filtering must be introduced in order to remove data with large error from the time-series of measurements.

Figure 6 displays the complete time-series of SAOZ measurements of O_3, O_4 and H_2O performed at the ISSJ from November 1991 up to December 1992. Sunrise data are represented with a solid line and sunset data with a dashed line. For comparison purpose, coincident measurements of daily total O_3 by TOMS satellite and by the Dobson spectrophotometer at the "Observatoire de Haute provence (OHP)" (Barbe and Merienne, private communication) are shown on the top panel, respectively with black dots and triangles. In addition to this, figure 6(b) displays values of offsets in Langley plots. Offsets are determined for each twilight period (up to 91° SZA) from a weighted least-squares linear fit of the measured amounts against AMF extrapolated to zero air mass. Vertical O_3 in figure 6(a) and slant O_4 and H_2O in figure 6(c) and (d) are obtained from a weighted average of individual data recorded between 87 and 91° SZA. Noisy data whose standard deviation at 1σ is greater than 40% (O_3, O_4) or 90% (H_2O) are systematically rejected.

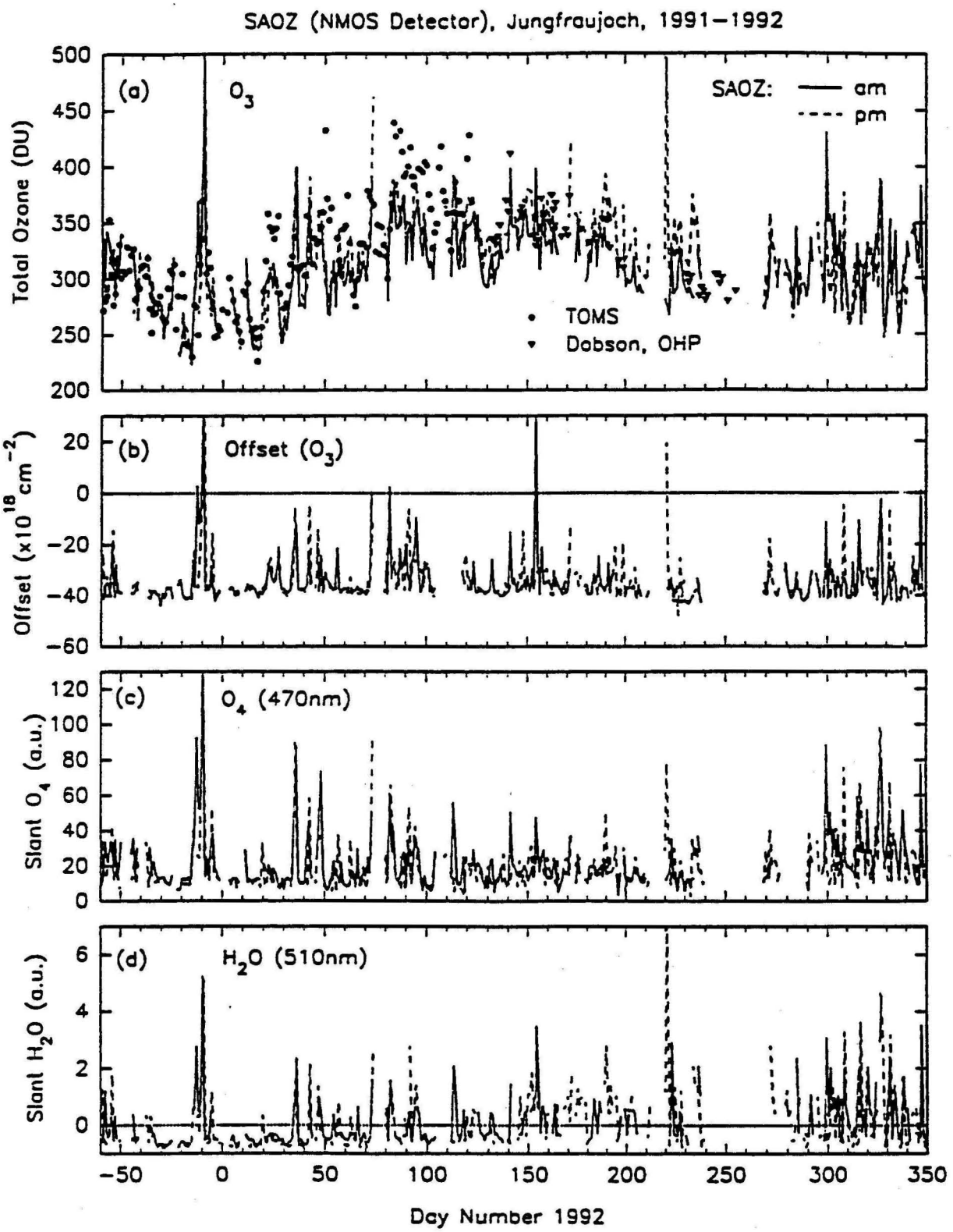

Figure 6 : Time series of the SAOZ measurements of O_3, O_4 and H_2O performed at the ISSJ from November 1991 to December 1992, with the offsets of Langley plots for O_3 (b).

The comparison of SAOZ and TOMS measurements in figure 6(a) shows a very good general agreement up to the end of 1991. In the beginning of 1992 SAOZ reports lower values (but not systematically) due to the effect of the Mt. Pinatubo stratospheric aerosols. The good agreement obtained with Dobson data of OHP indicates that the impact of the aerosols is reduced later in the year. Besides this, SAOZ measurements are characterized by the regular occurrence of positive peaks, some of them very large (100 DU or even more). Those peaks are clearly correlated with large deviations from the mean value of the O_3 offsets as well as with large peaks in slant O_4 and H_2O, which demonstrates their tropospheric origin. The correlation between O_3 offsets and O_4 slant columns is significant. It must be noted that this correlation is not expected to be perfect due to:

- the variability of the O_3 tropospheric content
- possible changes of the tropospheric conditions during the twilight period.

Finally it is interesting to note the very well defined baseline of the O_3 offsets in figure 6(b) which allows an accurate estimation of its amount in the reference spectrum.

Based on these observations, a strategy can be elaborated in order to improve the O_3 data set quality. This could be achieved as follows:

(1) remove noisy data whose statistical error is larger than a given threshold;

(2) calculate weighted average of O_4 and H_2O line-of-sight amounts between 87 and 91° SZA and remove O_3 data corresponding to O_4 and/or H_2O values higher than a given threshold (e.g. 2.5 times the mean clear sky value);

(3) use of Langley plots with the remaining points in order to determine the amount in the reference spectrum. As pointed out by Roscoe et al. (1993) this step allows in addition to check for possible instrumental drift leading to an apparent change of the amount in the reference spectrum;

(4) determine O_3 vertical amounts by a weighted average of the remaining individual data between 87 and 91° SZA.

II.3.3. UV-Visible and FTIR ozone intercomparison

FTIR observations performed at the ISSJ can be used to retrieve ozone total amount provided adequate wavenumber intervals are covered when measuring the other species.

Two specific lines situated at 1163.422 cm^{-1} and 2024.265 cm^{-1} were selected to make the intercomparison with the UV-Visible results. Two retrieval methods were applied namely the Equivalent Width (EQW) method and the least-squares fit. The first one is very dependent on the definition of the so-called continuum which either could contain weak absorptions or being on the wing of another strong line. The results

obtained by means of the two methods clearly shows a systematic difference in the ozone total amount, the equivalent width method being around 18% lower than the least-squares fit results. Figure 7 presents the offset needed to correct the EQW results by 18% in the continuum baseline (calculated spectrum at infinite resolution).

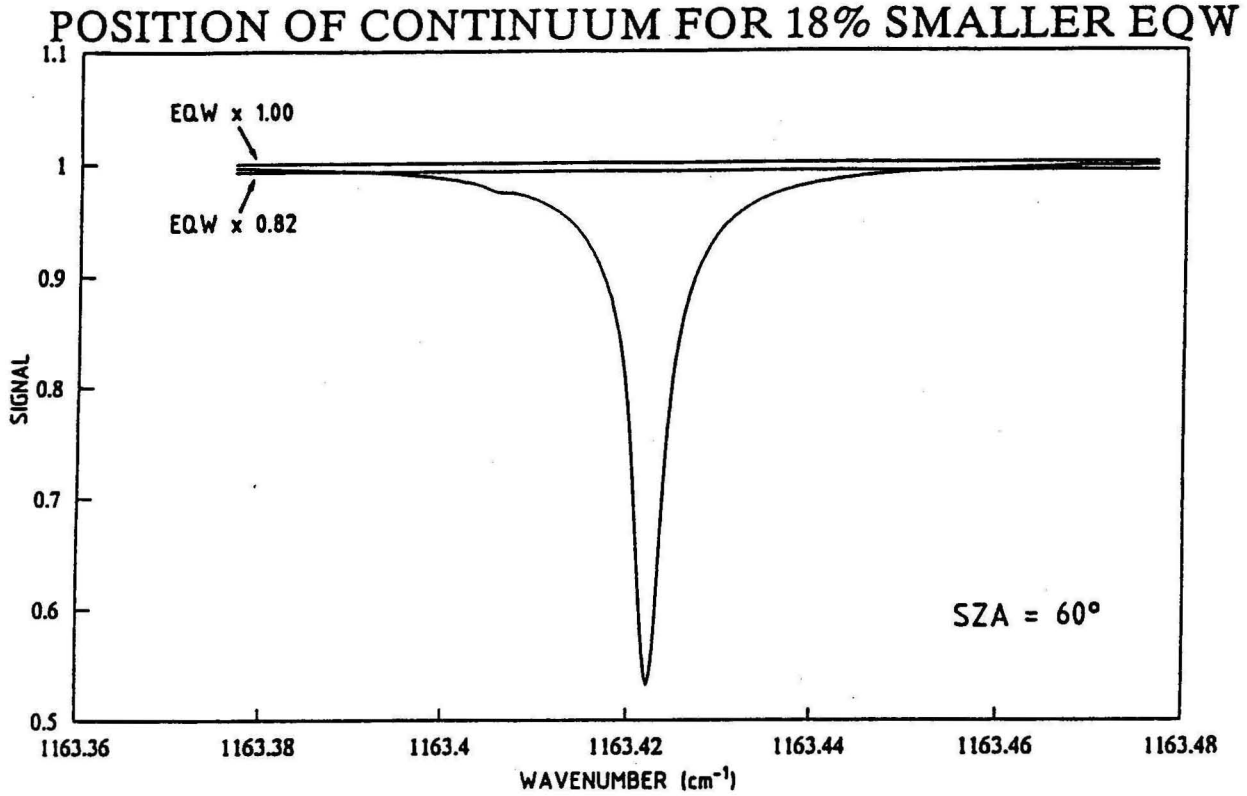

Figure 7 : Offset in the baseline continuum needed to correct the ozone amount by 18%, using the EQW retrieval method.

The FTIR results with the fit retrieval method are plotted with the SAOZ time series in figure 8. The agreement is reasonably good except during the first third of 1992, especially with the line at 1163.4 cm^{-1}. The results with the line at 2024 cm^{-1} are systematically lower than the previous one. This could be explained by the fact that this line lies in the wing of a strong solar line, making the fit less accurate. The relative differences between the two data sets show that FTIR results at 1163.4 cm^{-1} are in majority between 0 and 10% higher than the SAOZ values. Differences in the beginning of 1992 are larger and more variable, from about 0 to - 25%. This period corresponds to unusually low ozone amounts above the Alps as confirmed by comparison with the ozone climatology defined by the Dobson instrument installed at Arosa since 1931 (see figure 9). It is obvious that the zenith-sky measurements of ozone were perturbed by the aerosol loading of the stratosphere. The changes in the scattering geometry at twilight have been investigated by radiative transfer modelling (Chen et al., 1993) and corrections of the order of 10% or even more need to be applied. This work is still in progress. In addition, the comparison with the other measurements performed

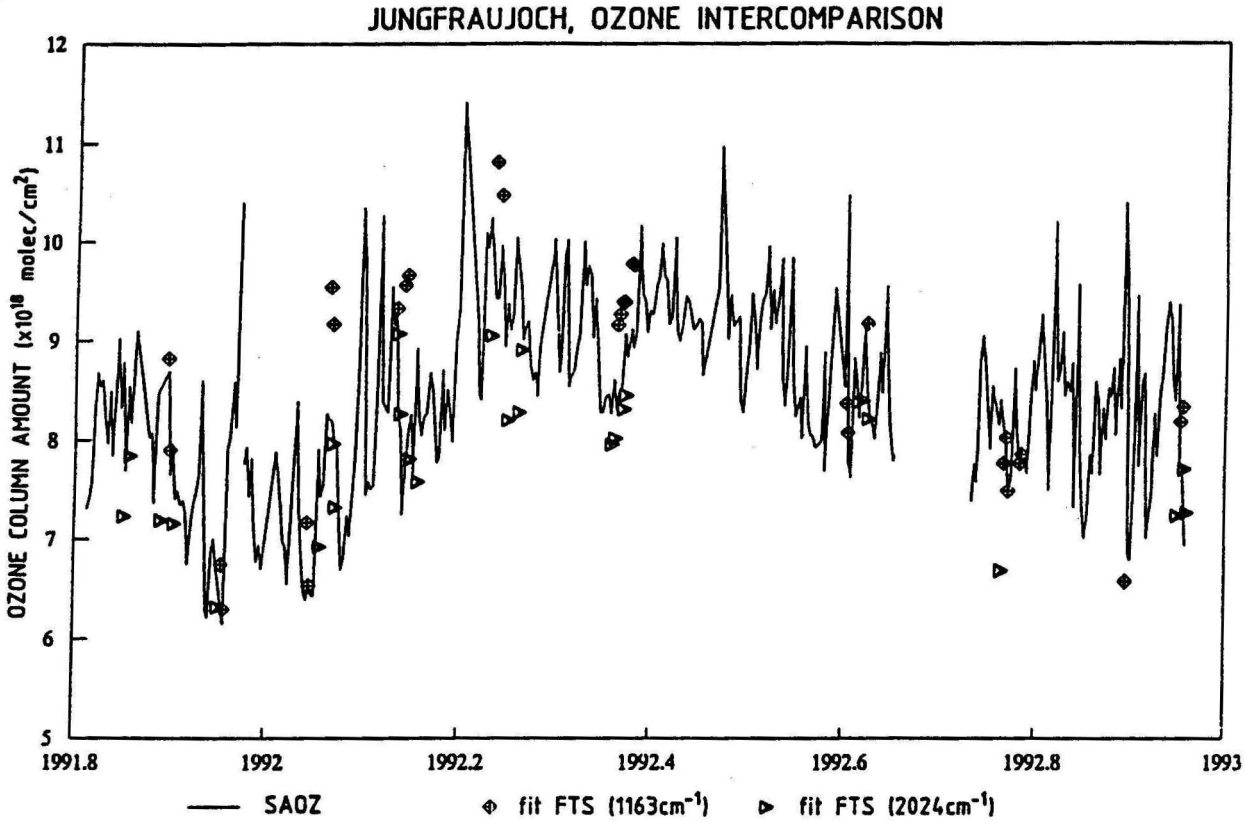

Figure 8 : Comparison of ozone column amount retrieval from visible absorption spectroscopy (SAOZ) and from FTIR, at 1163 and 2024 cm^{-1}

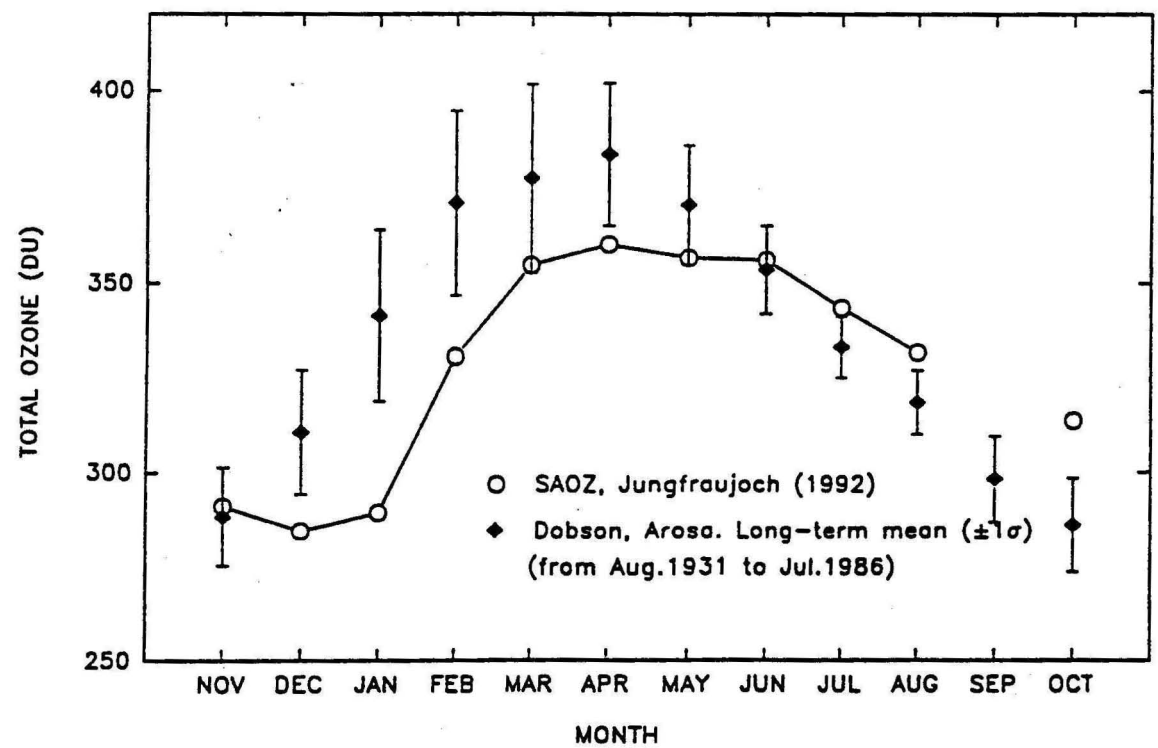

Figure 9 : Comparison of monthly averaged O_3 vertical amounts observed at the ISSJ (SAOZ) from November 1991 to October 1992 with the average of Dobson observation performed at Arosa from 1931 to 1986.

at different sites in Alps with Dobson, Brewer and Lidar observations has been started and will be pursued in 1993.

III. STRATOSPHERIC OBSERVATIONS AT KEFLAVIK (ICELAND) DURING THE EUROPEAN ARCTIC STRATOSPHERIC OZONE EXPERIMENT (EASOE)

III.1. Introduction

The Belgian Institute for Space Aeronomy (IASB/BIRA) has contributed with the Astrophysics Institute (ULg) to the monitoring of the stratosphere at mid- and high latitudes by performing ground-based observations from the Jungfraujoch (Swiss Alps) and from Keflavik (Iceland).

In addition to the two FTIR spectrometers (see Delbouille et al., this volume) and one UV-Visible spectrometer in operation at the Jungfraujoch, (see section II) an UV-Visible photodiode array spectrometer was developed at IASB/BIRA and installed at Keflavik (Iceland, 63.97°N, 22.6°W) in November 1991. This instrument provided O_3 and NO_2 total amounts during the winter, until the end of March 1992, from the observation of the zenith scattered sunlight at sunrise and sunset.

III.2. Experimental and data evaluation

The spectroscopic instrumentation used in Keflavik is described in Van Roozendael et al. (1993).

The ozone total amount is deduced from its differential absorption spectrum between 450 and 570 nm, while the nitrogen dioxide abundance, from spectral measurements between 410 and 470 nm.

Two additional UV-Visible instruments from the "Instituto National De Tecnica Aerospacial (INTA, Spain) were also installed at the same location. Ozone was observed in the Chappuis bands between 440 and 540 nm with a 6° crossed Czerny Turner spectrograph coupled to a 512-elements intensified EG&G reticon and having a bandpass of 0.5 nm. Nitrogen dioxide was observed with a scanning monochromator covering the spectral range from 430 to 450 nm with a resolution of 1 nm. It has been fully described in Gil and Cacho (1992).

All measurements are based on differential absorption spectroscopy using the highly structured absorption cross section of O_3 and NO_2 in the visible spectral region. Observation of the light scattered from the zenith-sky is performed twice a day at dawn and dusk when enhanced optical path through the atmosphere significantly increases the slant column of stratospheric absorber (Noxon et al., 1979).

III.3. Results

The measurements of ozone and nitrogen dioxide performed at Keflavik are presented in figures 10 and 11.

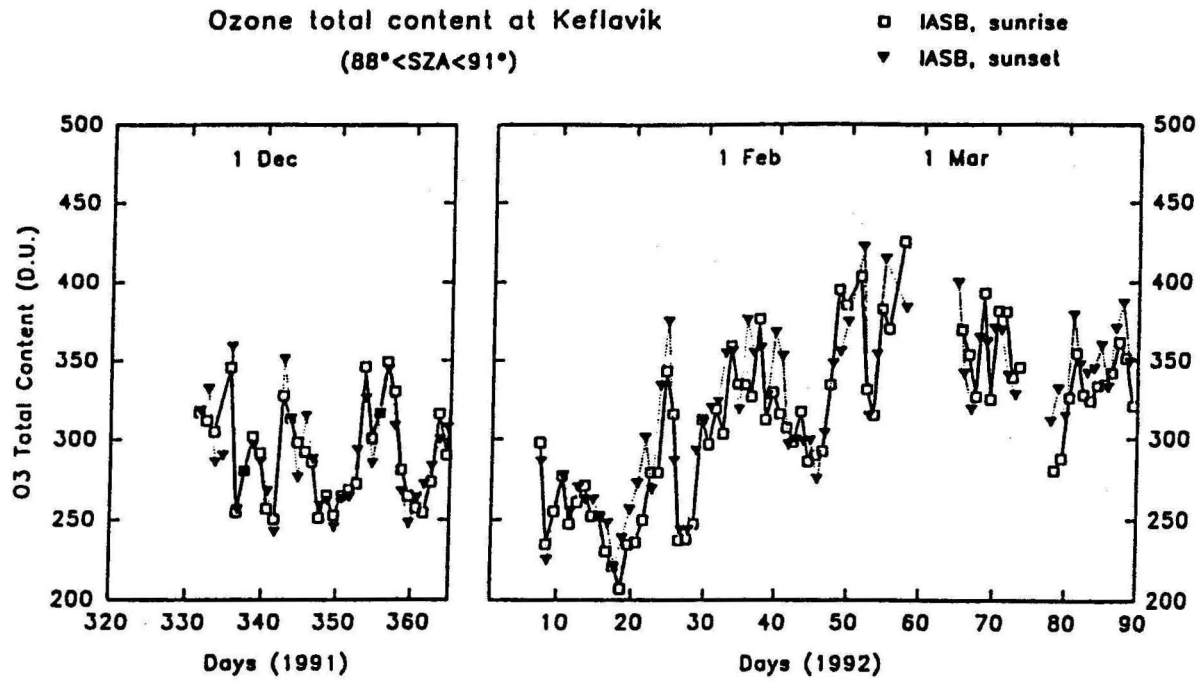

Figure 10 : Ozone total amounts obseved in Keflavik from November 1991 to March 1992.

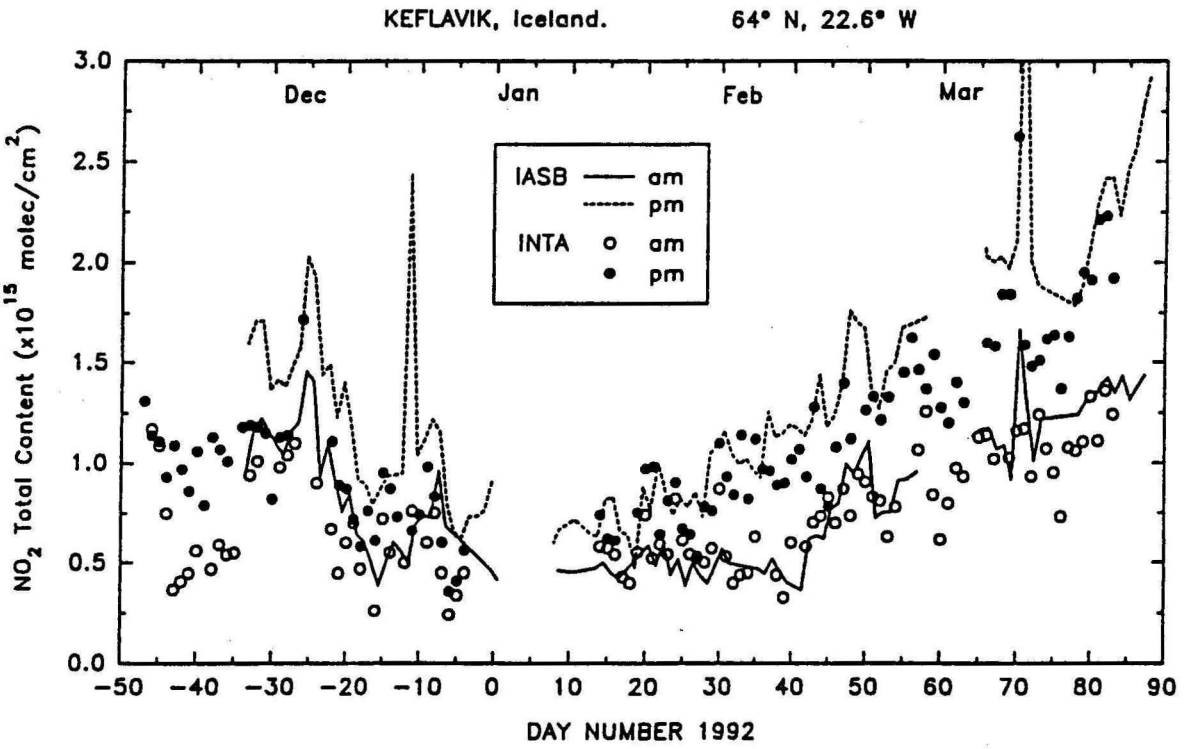

Figure 11 : Sunrise and sunset observations of NO_2 column amounts at Keflavik (Iceland) during EASOE.

Results presented here are averages of data obtained between 87° and 91° SZA. They are based on the unpublished cross section values of Johnston and are convolved according to the instrument function of the respective spectrographs.

III.3.1. Ozone

The stratospheric aerosol effect on the AMF used to retrieve the vertical total amount of ozone has been corrected on the basis of a radiative transfer model (Pommereau and Sarkissian, private communication) including an aerosol layer of 5×10^{-3} km^{-1} optical thickness at 18 km altitude. In addition, the range of reported data has been restricted to SZA below 91T due to the model limitations in the AMF calculation when the multiple scattering effects become very important.

III.3.2. Nitrogen dioxide

The NO_2 absorption cross sections are taken from Leroy et al. (1987) for INTA and from Johnston (unpublished data) for this work. They are convolved with respect to the instrumental functions. The NO_2 amount in the reference spectrum (INTA : 4.6×10^{15}, this work 6×10^{15}) is estimated by minimisation of the NO_2 diurnal variation on several clear days (Lee et al., 1993) with an accuracy of about 20%. Despite the presence of an enhanced sulphuric acid aerosol layer around 20 km due to the eruption of Mt. Pinatubo, vertical column amounts are deduced from slant columns by using airmass factors (AMFS) calculated for clear sky conditions with a single scattering ray-tracing model (Solomon et al., 1987). Following the calculations by Perliski and Solomon (1992), the impact of the Mt. Pinatubo aerosol on the scattering geometry is considered to be negligible for NO_2.

NO_2 vertical column amounts deduced at sunrise and sunset between 88 and 92° SZA for the whole observational period (from December 1991 to end March 1992 excluding the first week of January) are shown in figure 11. INTA data are represented by white and black dots, and our data by solid and dashed lines. The observed disagreement between both data set is mainly due to the difference of about 20% between Leroy et al. and Johnston's cross-sections measured respectively at 235 K and at room temperature. This difference introduces a constant bias in relative value which is more evident for large NO_2 columns. The low NO_2 values reported by INTA around day -40 are related to low temperatures observed at the 20 and 30 hPa pressure levels during this period. Only two episodes of pollution have been experienced on December 19, 1991 and March 10, 1992.

Figure 12 shows the NO_2 column amounts at sunset (our data set) recorded from December 1991 to March 1992 together with 20 hPa temperatures provided by the Icelandic Meteorological Office. In addition, the upper curve(a) shows potential vorticities (PV) on the 550 K potential surface produced by the European Center for Medium-term Weather Forecasting (ECMWF)

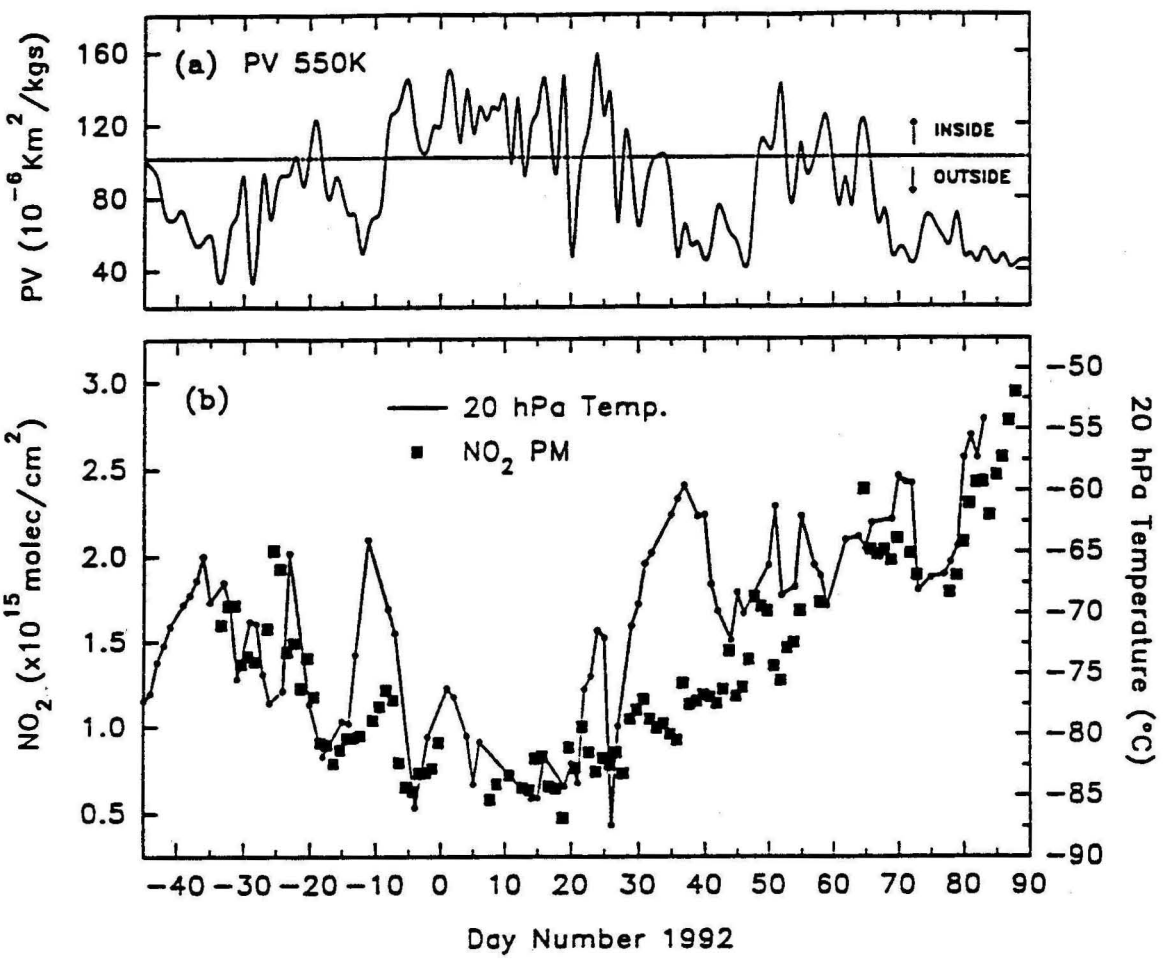

Figure 12 : (a) Potential vorticity evolution at the 550 K isentropic level. The dotted line indicates the bounday of the polar vortex. (b) Sunset NO_2 column amounts together with temperature at 20 hPa.

altitude. The PV contour at 102×10^{-6} K.m^2/(kg.s) has been chosen arbitrarily as the boundary of the vortex.

During the winter 1991-1992, Keflavik experienced two episodes of very low stratospheric temperature, one very short in December the other one in January. In both cases the site was inside the polar vortex. In early January the temperature at all levels in the lower stratosphere were the lowest of all the winter and sometimes below the theoretical PSC type I formation point (-85°C at 20 hPa). The NO_2 total contents measured during these periods were very low, most of the time close to or even below 5×10^{14} molec/cm^2 according to the INTA results, and the observed diurnal variations small (see figure 17). These observations are in agreement with the already reported conversion of the NO_x compounds ($NO+NO_2$) into their reservoir species N_2O_5 and HNO_3 occurring inside the Arctic polar vortex partly through heterogeneous chemistry on PSC particles (e.g. Wahner et al., 1990; Fahey et al.,1990).

Figure 12(b) shows that the evolution of the NO_2 total amounts follows the long term trend of the stratospheric temperature. This reflects mainly a parallel response to the changing illumination during high latitude winter when the simultaneous decrease of the temperature and of the solar elevation causes a change in the partitioning of the reactive nitrogen species leading to the formation of the well-known Noxon cliff. On the other hand, NO_2, observations made during Southern and Northern high latitude winters and springs have shown that short term changes in NO_2 column are usually positively correlated with the local stratospheric temperature (Keys and Johnston, 1986; Mount et al., 1987; Pommereau and Goutail 1988b). This coupling is likely to be largely due to the temperature dependence of the rates of the N_2O_5 photolysis and of the reaction $NO+O_3 \rightarrow NO_2+O_2$. It appears very clearly in Figure 12(b) that the short term correlation between NO_2 and 20 hPa temperature was very poor at Keflavik between December 1991 and March 1992 and more particularly during the stratospheric warming of February 1992. Around February 7, even though Iceland is definitely outside the vortex and the local 20 hPa temperature has risen to -60°C, the NO_2 column is only $1x10^{15}$ molec/cm^2. These observations suggest unusual low N_2O_5 amounts outside the vortex supporting the idea of an efficient conversion of N_2O_5 to HNO_3 due to a heterogeneous reaction on the Pinatubo aerosols such as first suggested by Austin et al. (1986). However it is known that NO_2 photochemistry is strongly coupled to the dynamics so that the possible role played by the stratospheric transport must be investigated further. Figure 13 shows ECMWF maps of potential vorticity(a) and temperature(b) at the 550 K isentropic level for February 7, 1992. The situation is typical of a stratospheric warming the vortex being displaced from the pole towards Europe and the zonal mean temperature gradient reversed, i.e. temperatures increasing poleward. The typical circulation during early February is illustrated in Figure 13(b) by three calculated backward trajectories ending at Keflavik on February 2, 7 and 10. It is characterized by the existence of an important meridional flow at least during the first days of February. The simulation of a major stratospheric warming using a coupled chemical general circulation model (Lary, 1990) has shown that under the influence of a strong cross-polar flow air masses can be transported from polar night to lower latitudes on a time short enough (less than 1 day) that little chemical readjustment can occur. The backward trajectories in figure 13(b) indicate that this mechanism could have been efficient and could have contributed to maintain low NO_2 contents above Iceland in the very beginning of February. It is however unlikely that this situation persisted for a long time because of the slowing down of the flow and the return to more usual zonal circulation later in February.

Additional information on the coupling of NO_2 with the local stratospheric temperature can be provided by an investigation of the nighttime decay of NO_2 which can be estimated using a simplified model assuming only N_2O_5 chemistry based on the following two reactions (Solomon and Garcia, 1983):

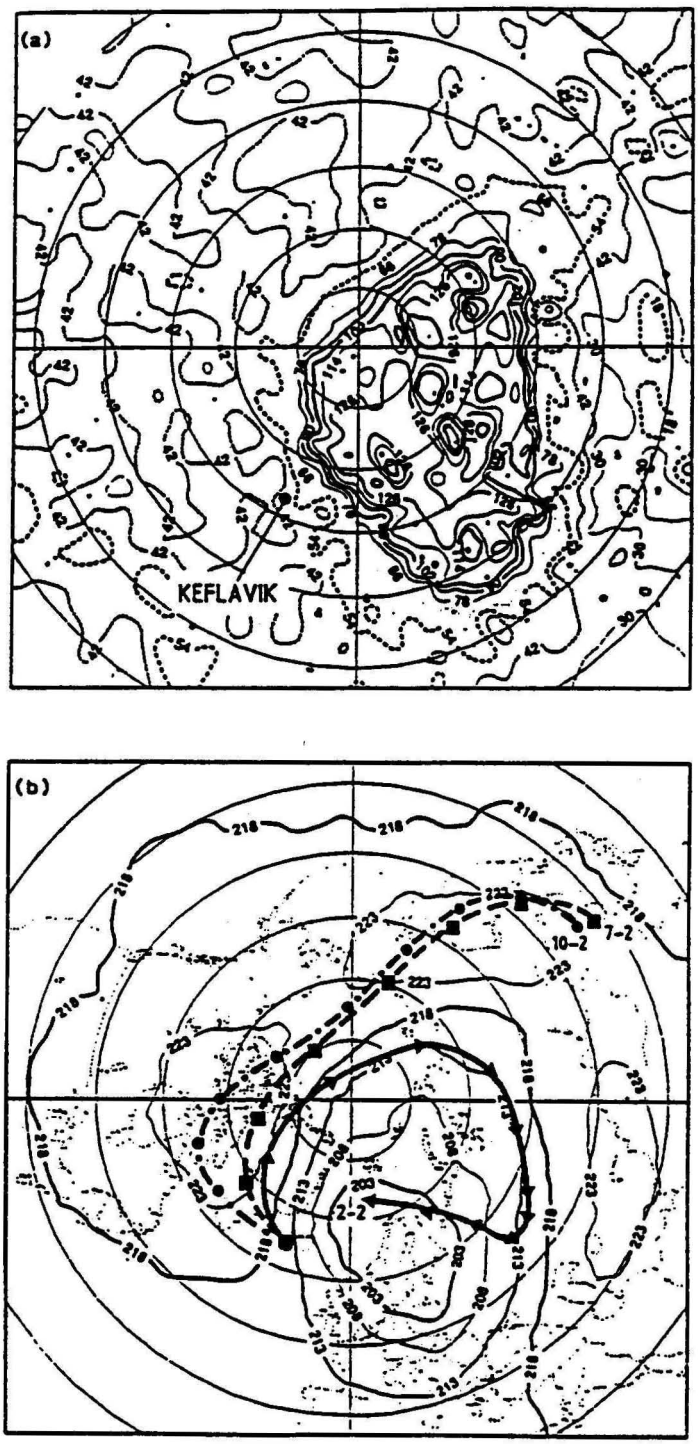

Figure 13 : (a) ECMWF potential vorticity analysis on the 550 K isentropic surface for February 7, 1992. The position of Keflavik is marked by a black point. (b) Temperature analysis on the same level and for the same day, together with trajectories for stratospheric air at 550 K arriving over Iceland on the datE shown.

$$NO_2+O_3 \rightarrow NO_3+O_2 \qquad k_1 = 1.2\times10^{13}\ \exp(-2450/T) \qquad (1)$$

$$NO_3+NO_2+M \rightarrow N_2O_5+M \qquad (2)$$

Reaction (1) is the rate limiting step, so that the ratio between $[NO_2]_{sunset}$ and $[NO_2]_{sunrise}$ (pm/am) is given by the expression:

$$pm/am = \exp(2.k_1.[O_3].\Delta t) \qquad (3)$$

where $[O_3]$ is the ozone concentration, Δt the night duration at the altitude of the bulk of NO_2 and k_1 the temperature dependent rate constant of equation (1). Figure 14(b) shows observed (open circles, INTA data set) and calculated (solid line) pm/am ratios for the period between day 10 and 85 which covers the stratospheric warming of February 1992. The observed values have been determined from 3-day running average on the column densities in order to smooth out short term fluctuations. The 20 hPa temperature and night duration values used for the calculations are shown in figure 14(a), a constant O_3 concentration of 4×10^{12} molec/cm^3 has been assumed on the basis of ozonesonde data recorded by INTA at the same period. Figure 14(b) shows that the calculated NO_2 pm/am ratios reproduce quite well the observed data in particular during the February warming. However the temperature effect on the NO_2 nighttime decay on the time scale of one night cannot exclude a dynamically induced redistribution of the NO_2 column amounts on a longer time scale (a few days).

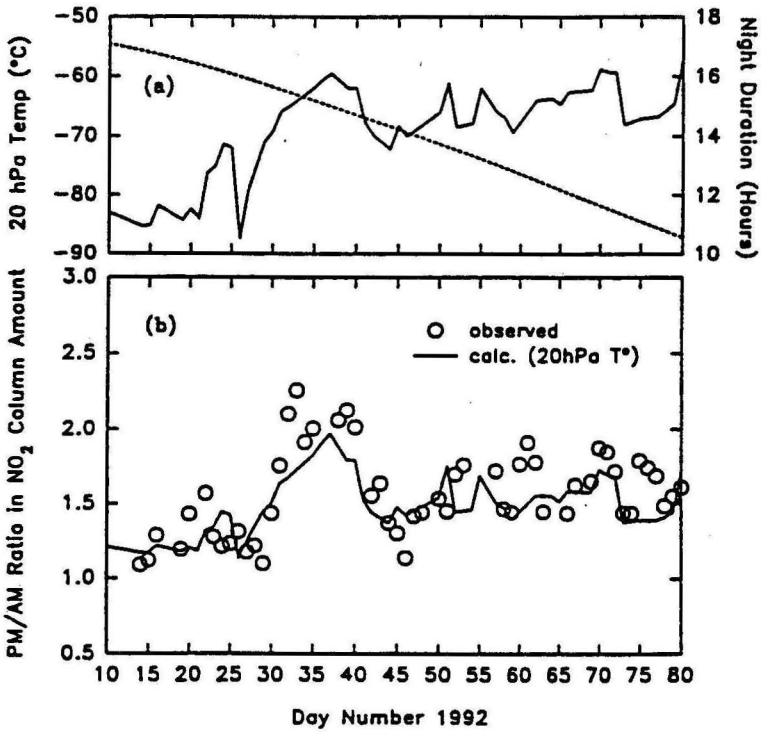

Figure 14 : (a) Temperature at 20 hPa (solid line) together with calculated night duration at the same level. (b) Observed nighttime decays in NO_2 column amount (3 day-running average, INTA data) compared to calculated values obtained with given temperatures and night durations.

IV. CONCLUSIONS

Systematic measurements of O_3 and NO_2 abundances covering the last two winters have been performed by means of a SAOZ instrument at the ISSJ (45°N). The data have been carefully analyzed to eliminate twilight values perturbed by unusual tropospheric conditions. The monthly mean values indicate a NO2 reduction of 15% at morning and evening in March-May 1992 and of 30% during the summer 1992, after the Mt. Pinatubo eruption, by comparison with the results obtained in 1991. Considering that the measurements by visible absorption of NO2 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 those reported by Johnston et al. (1992) at Lauder (45°S) in the Southern Hemisphere.

Ground-based observations of O_3 and NO_2 total amounts performed at Keflavik, Iceland, by two UV-visible spectrometers looking at the zenith-sky show very low values during the winter 1991/1992. The lowest columns are observed during the coldest period of the campaign when the station is inside the polar vortex, which indicates that the NO_x compounds have been largely converted into their reservoir species. The usual short term correlation between sunset NO_2 columns and 20 hPa temperatures is not observed during the stratospheric warming of February 1992, suggesting unusually low N_2O_5 amounts. This would support the idea of the conversion of N_2O_5 into HNO_3 by heterogeneous reaction on Pinatubo aerosol. However, transport of air masses from the polar night region to Keflavik under the action of a strong cross-polar flow could have contributed partly to the observation of the low NO_2 contents outside the vortex.

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References

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

Brewer, A. W., C.T. McElroy and J.B. Kerr, Nitrogen dioxide concentrations in the atmosphere, Nature, 246, (5429), 129-133, 1973.

Fahey D. W., Kawa S. R. and Chan K. R. 1990. Nitric oxide measurements in the Arctic winter stratosphere. Geophys. Res. Lett. 17: 489 - 492, .

Gil M. and Cacho J. 1992. NO_2 total column evolution during the 1989 spring at Antarctica Peninsula. J. Atmos. Chem.. 15: 187 - 200.

Goutail F., Pommereau J.P., Sarkissian A. 1992. Four years of ground-based total ozone measurements by visible spectrometry in Antarctica. Proc. Quad. Ozone Symposium, Charlottesville.

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

Johnston P.V. and McKenzie R.L. 1989. NO_2 observations at 45°S during the decreasing phase of solar cycle 21, from 1980 to 1987. J. Geophys. Res. 94: 3473 - 3486.

Johnston P.V., McKenzie R.L., Keys J.G. and Matthews W.A. 1992. Observations of depleted stratospheric NO_2 following the Pinatubo volcanic eruption. Geophys. Res. Lett. 19: 211 - 213.

Keys J.G. and Johnston P.V. 1986. Stratospheric NO2 and O3 in Antarctica : dynamic and chemically controlled variations. Geophys. Res. Lett. 13: 1260-1263.

Lary D. J. 1990. Photochemical studies with a three-dimensional model of the atmosphere. PhD Thesis, University of Cambridge, England.

Lee A.M., Roscoe H.K., Oldham D.J., Squires J.A.C., Sarkissian A., and Pommereau J.-P. Improvements to the accuracy of measurements of NO2 by zenith-sky visible spectrometers. Submitted to J. Geophys. Res.

Leroy B., Rigaud P. and Hicks E. 1987. Visible absorptions cross-sections of NO2 at 298 and 235 K. Annals. Geophys. 5A: 247 - 250.

Mount G. H., Sanders R. W., Schmeltekopf A. L. and Solomon S. 1987. Visible spectroscopy at McMurdo station, Antarctica, 1. Overview and daily variations of NO_2 and O_3, Austral Spring, 1986 J. Geophys. Res. 92: 8320 - 8328.

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

Noxon J. F., Whipple E. C. Jr. and Hyde R. S. 1979. Stratospheric NO_2, 1. Observational method and behavior at Mid-Latitude. J. Geophys. Res. 84: 5047 - 5065.

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

Pommereau J.-P. and Goutail F. 1988a. Stratospheric O_3 and NO_2 observations at the southern polar circle in summer and fall 1988. Geophys. Res. Lett. 15: 895-898.

Pommereau J. P. and Goutail F. 1988b. O_3 and NO_2 ground-based measurements by visible spectrometry during Arctic winter and spring 1988. Geophys. Res. Lett. 15: 891 - 894.

Pommereau J.P., Goutail F., Pinharanda M., Piquard J., Sarkissian A. October 1990. Ground-based total ozone measurements in the Visible Chappuis Bands. Proc. First European Workshop on Polar Stratospheric Ozone Research, Schliersee.

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

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

Roscoe H.K., Squires J.A.C., Oldham D.J., Sarkissian A., Pommereau J.-P. and Goutail F. 1993. Improvements to the accuracy of zenith-sky measurements of total ozone by visible spectrometers. Submitted to J. Geophys. Res.

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

Solomon S. and Garcia R. 1983. On the distribution of nitrogen dioxide in the High-Latitude stratosphere. J. Geophys. Res. 88: 5229 - 5239.

Van Roozendael M., Fayt C., Bolsée D., Simon P.C., Gil M., Yehe M. and Cacho J. 1993. Ground-based stratospheric NO2 monitoring at Keflavik (Iceland) during EASOE. Accepted in Geophys. Res. Lett.

Wahner A., Callies J., Dorn H.-P., Platt U. and Schiller C. 1990. Near UV atmospheric absorption measurements of column abundances during Airborne Arctic Stratospheric Expedition, January - February 1989: 1. Technique and NO_2 observations. Geophys. Res. Lett. 17: 497 - 500.