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Ground-based stratospheric NO_2 monitoring at Keflavik (Iceland) during EASOE

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Abstract. Measurements of nitrogen dioxide total amounts have been performed by ground-based visible spectrometry at Keflavik, Iceland (64.0°N, 22.6°W) during EASOE. NO_2 column amounts below 1×10^{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 particles. However the low NO_2 contents observed could be attributed partly to the advection of air masses from the polar night region.

Introduction

The ground-based measurements of nitrogen dioxide column abundance performed by Noxon in the late seventies (*Noxon*, 1979) revealed the existence of a winter drop in NO_2 at high latitude which was not expected by the contemporarily accepted photochemistry. These observations have been largely explained by the coupling between dynamical and chemical processes (*Solomon and Garcia*, 1983). After the discovery of the Antarctic ozone hole, it has been suggested that heterogeneous reactions play an important role in the partitioning of nitrogen compounds. This has been since confirmed by numerous observations in the Antarctic winter and spring. In the Northern Hemisphere, the observations performed in 1988 and in 1989 showed very low amount of NO_2 (e.g. *Pommereau and Goutail*, 1988; *Wahner et al.*, 1990) but the denitrification in the Arctic vortex was more limited at least in geographical extent than the almost complete denitrification observed over Antarctica (*Turco et al.*, 1990). One objective of EASOE was to study the behaviour of nitrogen compounds. For that purpose several ground-based instruments measuring NO_2 were deployed around the Arctic circle and at higher latitudes, in connection with intensive measurements made from balloon and airplanes.

This work reports ground-based observations of NO_2 total amounts made at Keflavik, Iceland (64.0°N, 22.6°W) during EASOE from November 15, 1991 to March 30, 1992 by two instruments operated independently by the "Instituto Nacional De Tecnica Aerospacial" (INTA) and the "Belgian Institute for Space Aeronomy" (BISA). Ozone soundings and ground-based O_3 total amounts measurements performed at the same time will be the subject of a future communication.

Instrument description and data analysis

The instruments operated by INTA and BISA are based on differential absorption spectroscopy using the highly structured absorption cross-section of NO_2 in the visible spectral region near 440 nm. Observation of the light scattered from the zenith-sky is performed twice a day during the twilight period when enhanced optical path through the atmosphere significantly increases the slant column of stratospheric absorbers (*Noxon et al.*, 1979).

The INTA instrument has been fully described in *Gil and Cacho* (1992). It uses a scanning monochromator (20° field of view) covering the region from 430 to 450 nm with a bandpass of 1 nm. The BISA spectrometer is based on a grating spectrograph coupled to a photodiode array detector. The spectrograph is a commercial F/3.7 crossed Czerny-Turner from ORIEL of 125 mm focal length, equipped with a 600 line/mm ruled grating. Its field of view is 15°. The entrance slit width is 100 µm resulting in a measured bandpass of 1.35 nm FWHM and a sampling of about 4 pixels/FWHM. The spectral range extends from 280 to 600 nm. The detector assembly, made by Princeton Instruments, is equipped with a 1024 pixel EG&G Reticon silicon photodiode array protected by a quartz window. The array is cooled to -45°C by a 2-stage Peltier cooler with methanol flowing at the regulated temperature of -8°C through the heat removal circuit. The spectrograph is mounted inside a watertight container whose temperature is regulated within 2°C. The analysis procedure is similar to the SAOZ method described in *Pommereau and Goutail* (1988).

The NO_2 absorption cross-sections are taken from *Leroy et al.* (1987) for INTA and *Johnston* (unpublished data) for BISA, and convolved with respect to the instrumental functions. The NO_2 amount in the reference spectrum (INTA: 4.6×10^{15}, BISA: 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.

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Results and discussion

NO_2 vertical column amounts deduced at sunrise and sunset between 88 and 92° SZA for the whole observational period (from mid-November 1991 to end March 1992 excluding the first week of January) are shown in figure 1. INTA data are represented by white and black dots, BISA data by solid and dashed lines. The observed disagreement between the data sets 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 were experienced on December 19, 1991 and March 10, 1992.

Figure 2(b) shows the NO_2 column amounts at sunset (BISA data set) recorded from December 1991 to March 1992 together with 20 hPa temperatures provided by the Icelandic Meteorological Office. In addition, figure 2(a) shows potential vorticities (PV) on the 550 K potential surface produced by the European Center for Medium-term Weather Forecasting (ECMWF) which are indicative of the vortex position around 21 km 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 amounts measured during these periods were very low most of the time close to 5×10^{14} molec/cm^2 and the observed diurnal variations small (see figure 1). 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).

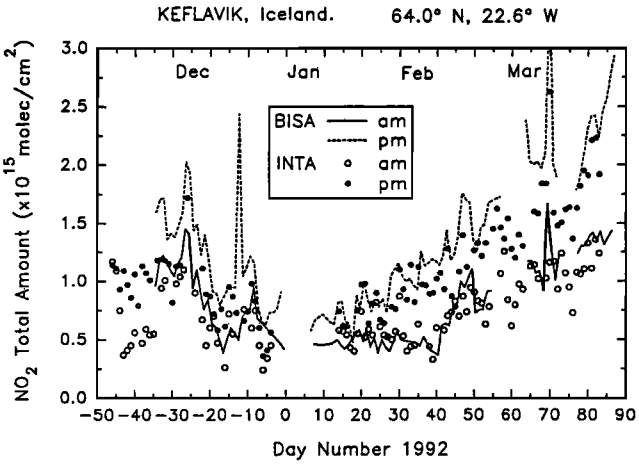

Fig. 1 Sunrise and sunset observations of NO_2 column amounts at Keflavik (Iceland) during EASOE, with INTA and BISA UV-visible ground-based spectrometers.

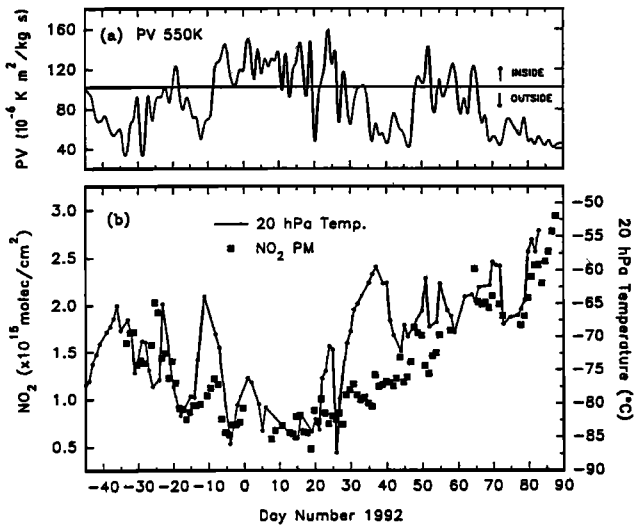

Fig. 2 (a) Potential vorticity evolution at the 550 K isentropic level. The dotted line indicates the boundary of the polar vortex. (b) Sunset NO_2 column amounts (BISA data) together with temperature at 20 hPa.

Figure 2(b) shows that the evolution of the NO_2 total amounts follows the stratospheric temperature trends. 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*, 1988). This coupling is likely to be 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 is very clear from figure 2(b) that the short term correlation between NO_2 and 20 hPa temperature was very poor at Keflavik between mid-November 1991 and March 1992. This is particularly obvious 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 1×10^{15} molec/cm^2. These observations suggest 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 volcanic aerosols such as suggested by *Austin et al.* (1986). However it is known that the NO_2 photochemistry is strongly coupled to the dynamics so that the possible role played by the stratospheric transport must be investigated further.

Figure 3 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 3(b) by three calculated backward trajectories ending at Keflavik on February 2, 7

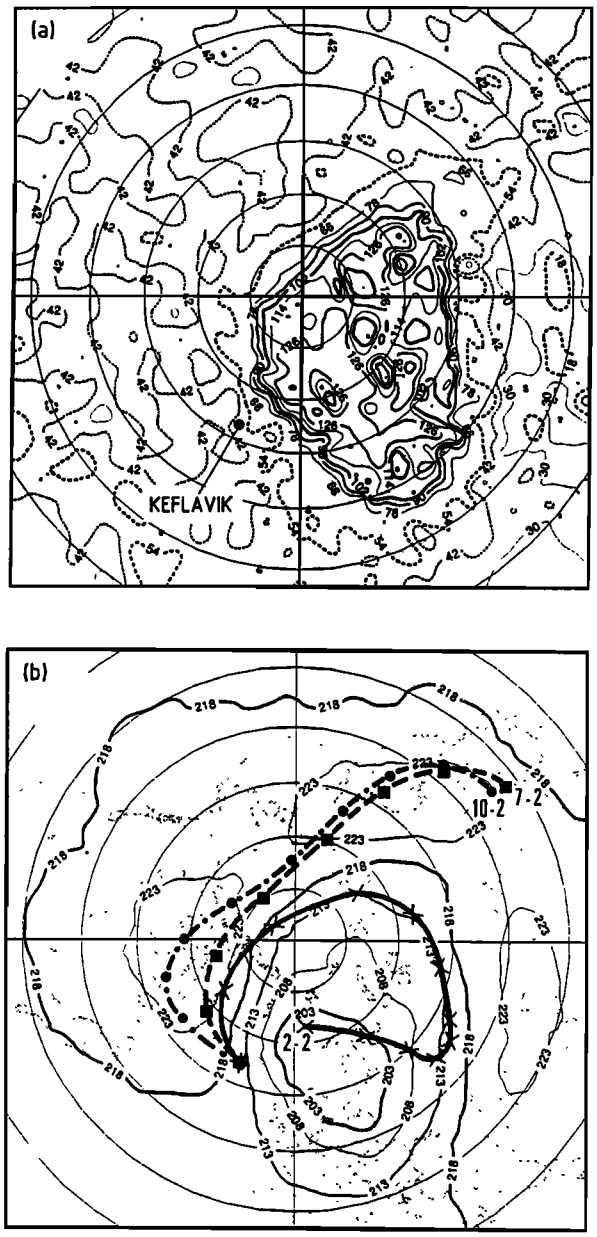

Fig. 3 (a) ECMWF potential vorticity analysis on the 550 K isentropic surface for February 7, 1992. The position of Keflavik is marked by a black point. (b) Temperature analysis on the same level and for the same day, together with trajectories for stratospheric air at 550 K arriving over Iceland on the date shown.

and 10. It is characterised 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 3(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):

$$NO_2 + O_3 \xrightarrow{k_1} NO_3 + O_2 \qquad (1)$$

$$k_1 = 1.2\times10^{13} \exp(-2450/T)$$

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

Reaction (1) is the rate limiting step, so that the ratio between sunset NO_2 and sunrise NO_2 is given by the expression:

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

where $[O_3]$ is the ozone concentration and Δt the night duration at the altitude of the bulk of NO_2. Figure 4(b) shows observed (open circles: 3-day running averages) and calculated (solid line) pm/am ratios for the period between day 10 and 85 which covers the stratospheric warming of February 1992. The 20 hPa temperature and night duration values used for the calculations are shown in figure 4(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 4(b) shows that the calculated NO_2 pm/am ratios reproduce quite well the observed data in particular during the February warming. However the effect of temperature on the NO_2 nighttime decay operates only on short time scales (~ 1 day) and so this explanation does not exclude a dynamically induced redistribution of the NO_2 column amounts on a longer time scale (a few days).

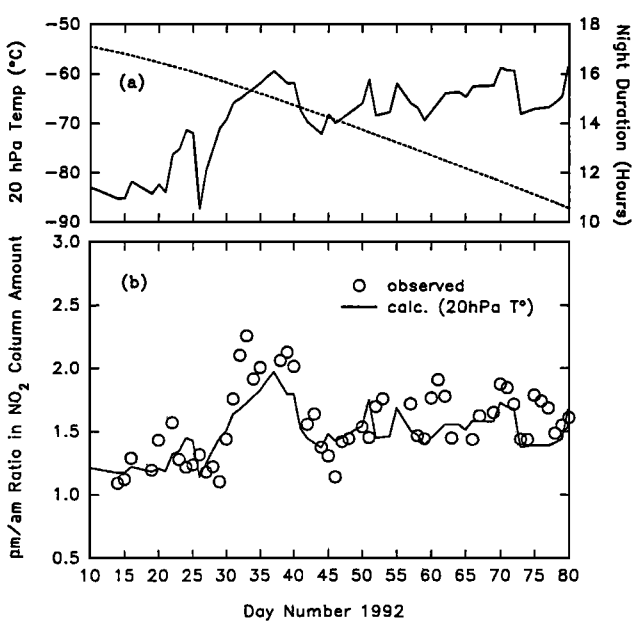

Fig. 4 (a) Temperature at 20 hPa (solid line) together with calculated night duration at the same level. (b) Observed nighttime decays in NO_2 column amount (3 day-running average, INTA data) compared to calculated values obtained with given temperatures and night durations.

Conclusion

Ground-based observations of NO_2 total amounts performed at Keflavik, Iceland, by two UV-visible spectrometers looking at the zenith-sky show very low values during winter 1991/92. 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 low NO_2 contents outside the vortex.

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