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Observation of NO_x Enhancement and Ozone Depletion in the Northern and Southern hemispheres after the October-November 2003 Solar Proton Events

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Abstract. The large solar storms in October-November 2003 produced enormous solar proton events (SPEs) where high energetic particles reached the Earth and penetrated into the middle atmosphere in the polar regions. At this time, the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) was observing the atmosphere in the 6–68 km altitude range. MIPAS observations of NO_x ($NO+NO_2$) and O_3 of the period from 25 October to 14 November 2003 are the first global measurements of NO_x species, covering both the summer (daylight) and winter (dark) polar regions during an SPE. Very large values of NO_x in the upper stratosphere of 180 ppbv (parts per billion by volume) have been measured, and a large asymmetry in Northern and Southern polar cap NO_x enhancements was found. Arctic mean polar cap (>60°) NO_x enhancements of 20 to 70 ppbv between 40 to 60 km lasted for at least two weeks, while the Antarctic mean NO_x enhancement was between 10 and 35 ppbv and was halved after two weeks. Ozone shows depletion signatures associated with both HO_x ($H+OH+HO_2$) and NO_x enhancements but at different time scales. Arctic lower mesospheric (upper stratospheric) ozone is reduced by 50–70% (30–40%) for about two weeks after the SPEs. A smaller ozone depletion signal was observed in the Antarctic atmosphere. After the locally produced Arctic middle and upper stratospheric as well as mesospheric NO_x enhancement, large amounts of NO_x were observed until the end of December. These are explained by downward transport processes. These enhancements drastically declined with the mid-December stratospheric warming. Significant O_3 depletion was observed inside the po-

lar vortex in a wide altitude range during this period. From mid-January until the end of March 2004 MIPAS observed extraordinary high values of NO_2 in the upper stratosphere of the Northern polar region (mean in-vortex values up to 350 ppbv at $\sim$54 km), which seem to be caused by the unusually strong vortex and downward transport at that time together with an uncommonly large auroral activity starting with the solar storms in October-November and continuing over the winter. In-vortex ozone was observed to significantly decline in the mid-February to late March period above the 1750 K potential temperature level.

1. Introduction

It has been shown that solar proton events (SPEs) have significant effects on the composition of the stratosphere and mesosphere in the polar regions (see, e.g., *Jackman and McPeters* [2004] for a recent review). The major effects have been found to be significant enhancements in HO_x ($H+OH+HO_2$) and NO_x ($NO+NO_2$), followed by large depletions of O_3 in these atmospheric regions. While the direct experimental confirmation of HO_x increases still remains to be done, its theoretical prediction is well based and indirectly confirmed by the observed O_3 depletions and, recently, by HOCl enhancements [*von Clarmann et al.*, 2005]. On the other hand, NO_x enhancements as well as O_3 depletions are well confirmed in a large number of observations [*Weeks et al.*, 1972; *Crutzen et al.*, 1975; *Heath et al.*, 1977; *McPeters et al.*, 1981; *Thomas et al.*, 1983; *Solomon et al.*, 1981, 1983; *McPeters and Jackman*, 1985; *McPeters*, 1986; *Reid, et al.*, 1991; *Jackman et al.*, 1995, 2001; *Randall et al.*, 2001]. The quantitative assessment of these changes, however, still remains to be completely understood [see, e.g., *Jackman and McPeters*, 2004], partly due to the lack of global and continuous measurements.

During late October and early November 2003, three active solar regions produced solar flares and solar energetic particles of extremely large intensity, the fourth largest event observed in the past forty years [*Jackman et al.*, 2004, 2005a]. Some of the Geostationary Operational Environmental Satellite (GOES)-11 instruments measured very large fluxes of highly energetic protons [*Space Environment Center*, 2004] (see Fig. 1). The protons are guided by the Earth's magnetic field to both polar regions (geomagnetic latitudes > 60°), where they penetrate down to ~87 km, if their energy is >1 MeV, or even down to ~30 **Fig. 1** km, if their energy is >100 MeV [*Jackman et al.*, 2004; 2005a]. Atmospheric changes induced by these events have been reported recently. In this sense, *Seppälä et al.* [2004] have shown significant effects in the Northern hemisphere polar winter with GOMOS data; and *Jackman et al.* [2005b] have reported significant effects in O_3 and NO_x from NOAA 16 SBUV/2 and HALOE data, respectively, in the Southern hemisphere polar region. O_3 depletions in the stratosphere and lower mesosphere have also been observed for the Oct/Nov 2003 SPE events by SCIAMACHY [*Rohen et al.*, 2005]. *Orsolini et al.* [2005] have also studied the MIPAS data of HNO_3 and NO_2 in November and December 2003.

The operation of the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) instrument on board the Environmental Satellite (ENVISAT) during that period gave us the opportunity to measure the global changes (in particular in the polar regions) in many NO_y species (including NO, NO_2, HNO_3, N_2O_5, $ClONO_2$) as well as in O_3 in the stratosphere and mesosphere during and after these very large SPEs. In this paper we analyze the NO_x (NO and NO_2) and O_3 abundances over the Northern and Southern poles measured by MIPAS/Envisat during and after the major SPEs of this period, from 25 October to 14 November 2003. In addition we also present the evolution of NO_2 and O_3 abundances in the upper stratosphere and lower mesosphere in the arctic winter region after these SPEs. To our knowledge, this is the first time that global and simultaneous observations (winter and summer hemispheres) of NO_x and O_3 changes caused by solar proton events have been made. The changes observed in other species are reported in companion papers [*López-Puertas et al.*, 2005a; *von Clarmann et al.*, 2005].

2. MIPAS data

The Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) [*Fischer and Oelhaf*, 1996; *European Space Agency*, 2000] was launched on board the Environmental Satellite (ENVISAT) into its sun-synchronous polar orbit on 1 March 2002. MIPAS measures limb radiance spectra in the mid-infrared from 4.1 to 14.7 μm with high spectral resolution (0.05 cm^{-1}, apodized as described by *Norton and Beer* [1986]), thus offering the opportunity to infer abundances of many atmospheric species including NO, NO_2 and O_3, among others. The field of view of MIPAS is 30 km in horizontal and approximately 3 km in vertical direction. The L1B processing of the data (Version 4.59 used here), including the processing from raw data to calibrated spectra, has been performed by the European Space Agency (ESA) [*Nett et al.*, 2002].

The retrieval of NO, NO_2 and O_3 abundances was performed with the IMK-IAA data processor [*von Clarmann et al.*, 2003a], which is based on a constrained non-linear least squares algorithm with Levenberg-Marquardt damping and line by line radiative transfer calculations with the Karlsruhe Optimized and Precise Radiative Transfer Algorithm (KOPRA) [*Stiller et al.*, 2000]. The first step in the L2 processing was the determination of the spectral shift, followed by the retrieval of temperature and elevation pointing [*von Clarmann et al.*, 2003b], where pressure is implicitly determined by means of hydrostatic equilibrium. The retrieval of volume mixing ratio (vmr) profiles of species was carried out in the following order: O_3, H_2O, HNO_3, then CH_4 and N_2O simultaneously, $ClONO_2$, F-11, ClO, N_2O_5, NO_2, and finally NO. Other species were retrieved in arbitrary order. The results of a preceding retrieval are used in the subsequent retrievals. Ozone was retrieved mainly from its ν_2 emission near 14.8 μm, while NO_2 and NO were retrieved from their emissions near 6.2 and 5.3 μm, respectively [*Funke et al.*, 2005a]. The retrievals were performed from selected spectral regions (micro-windows) which vary with observation geometries in order to optimize computation time and minimize systematic errors [*von Clarmann and Echle*, 1998]. Thus, height dependent combinations of micro-windows were selected with a trade-off between computation time and total retrieval error. NO_x is retrieved in the 15–55 km altitude range with an accuracy better than 15% [*Funke et al.*, 2005a]. O_3 is retrieved in the 10–68 km altitude range with an accuracy of 10% at 30 km and 20% at 50 km *Glatthor et al.* [2005]. More details on the O_3 retrieval can be found in *Glatthor et al.* [2005] and for NO_2 and NO in *Funke et al.* [2005a]. In addition to these gases, we also use a distribution of CO to explain some of the features observed in the temporal evolution of NO_x. CO was retrieved in a similar manner as the other gases using the same retrieval scheme. The details of CO retrievals including aspects related to its non-local thermodynamic equilibrium emission are reported in *Funke et al.* [2004, 2005b].

The nominal observation mode scans the limb in 17 sweeps, covering tangent altitudes from 6 to 68 km in 3 km steps up to 42 km, followed by sweeps at 47, 52, 60, and 68 km. Flown on a sun-synchronous orbit of 98.55° inclination at approximately 800 km altitude, MIPAS passes the equator in a southerly direction at 10.00 am local time 14.3 times a day. During each orbit up to 72 limb scans are recorded. This study is focussed mainly on MIPAS data of 25 October to 14 November, including nearly 10000 elevation scans, which were retrieved by the IMK-IAA processor (data version V2_2). In addition, ESA off-line (reprocessed) MIPAS data (version 4.61) for O_3, NO_2 and CH_4 vmrs profiles for the arctic polar winters of 2002–2003 and 2003–2004 were used since, contrary to the episode-based scientific IMK-IAA data, these data are available for a longer period. The MIPAS off-line data is retrieved by ESA using the operational retrieval algorithm as described by *Ridolfi et al.* [2000] and *Carli et al.* [2004]. The ESA off-line data used here is believed to be more accurate than the ESA near-real time data used in former studies (e.g. *Orsolini et al.* [2005]). In particular, the off-line NO_2 profiles are retrieved to altitudes up to ~68 km (although reliable only up to ~60 km [*Wetzel et al.*, 2004]) while near-real time NO_2 profiles are retrieved to altitudes up to only ~50 km.

The analysis of the SPE period from the end of October to the beginning of November was based entirely on IMK/IAA data for the following reasons: First, not all relevant species are included in the ESA data product, namely NO and CO (used here), and N_2O_5, $ClONO_2$, HOCl and ClO (used in the companion papers) are missing. Second, NO_2 is retrieved more accurately by the IMK-IAA processor since non-local thermodynamic equilibrium effects are considered. Third, ESA data are shifted relative to IMK-IAA data in altitude by about 1 km, with even larger values at high Southern latitudes because ESA-profiles are not tangent-altitude corrected [*von Clarmann et al.*, 2003b]. This complicates comparison of profiles from the different data sources. And finally, the IMK-IAA data come with extensive diagnostics and provide consistency for all retrieved species.

3. NO_x Enhancement and O_3 Destruction in Polar Regions

Solar proton events affect the atmospheric constituents at the polar caps (>60° geomagnetic latitude). Figure 2 shows the MIPAS measurements of NO_x ($NO+NO_2$) and O_3 abundances in the Northern polar cap (70°N–90°N) at a potential temperature of 2250 K (~52 km) for the day before the first major SPE (27 October) and for the days during (29 October) and just after (30 October). The polar vortex boundary has also been plotted. **Figure 2**

It has been calculated using the Nash criterion [*Nash et al.*, 1996] but modified in such a way that a dynamical tracer (CH_4 below 1500 K and CO above) has been used, instead of the mean zonal winds, in addition to the potential vorticity gradient criteria.

A dramatic increase in NO_x abundance is observed at polar latitudes (see Fig. 2). Individual profiles reach values up to 180 ppbv (parts per billion by volume) on 30 October in the upper stratosphere, which is about a factor 10 larger than for unperturbed conditions. These observations are among the largest NO_x abundances ever recorded at these altitudes.

Maximum NO_x abundances are observed on 30 October, just after the huge proton fluxes during the SPEs, as predicted by model simulations (see, *Jackman et al.* [2005b]). The MIPAS NO_x enhancements are not uniformly distributed around the geomagnetic pole (see, e.g. top right panel for 30 October) but they show larger values inside the polar night region. In contrast, MIPAS observations at longitudes of 80 W–180 W where NO_x shows smaller enhancements were all made during daylight. NO_x enhancements also seem to be roughly confined to the polar vortex (or better called, at this altitude, subsidence zone) in these early days after SPEs. It is not clear, however, if this is fortuitous or due to enhanced mixing outside the vortex.

O_3 depletion of about 30–40% is observed at these altitudes (~52 km), mainly in a circle around the geomagnetic pole. This is consistent with the expectation that the major HO_x enhancement takes place inside the 60° geomagnetic polar cap and that O_3 loss is mainly caused by the HO_x catalytic cycle at this altitude (see, e.g., *Jackman et al.* [2001, 2005b]). The circle O_3 loss structure around the polar night region seems to be caused by the lower background values of HO_x corresponding to the larger solar zenith angles, which, as showed by *Solomon et al.* [1983], make the HO_x–driven ozone loss more efficient. Ozone depletion is largest on October 29, and then decreasing fast on Oct 30. This also supports the predominant role of the HO_x cycle, because HO_x species are very short-lived (lifetime of the order of 1 day). The different way in which solar illumination affects the NO_x production and the O_3 depletion (HO_x increase) seems to be the reason for the different spatial distributions they exhibit. The facts mentioned above of illumination conditions and MIPAS sampling can significantly alter the NO_x enhancements (visible, e.g., in the polar night region on 30 Oct, Fig. 2a), and could then be the reason for the different spatial distributions observed.

Similar features are observed at the South pole (Fig. 3). Both NO_x and O_3 exhibit large perturbations during and just after the SPEs. The enhancements in NO_x are of smaller magnitude than for the Northern hemisphere (note the different scales) and also show a significant dependency on the solar illumination and MIPAS sampling. Thus, NO_x is less enhanced in the polar daylight region ($\gtrsim$80°S). Further, NO_x shows larger values at longitudes 80E–160E, where all MIPAS measurements were taken under nighttime conditions. The overall smaller enhancements for this hemisphere seem then due to the larger solar elevation angles, which makes photo-dissociation of NO more effective. **Fig. 3**

Antarctic O_3 depletion is similar to that in the Northern hemisphere. It seems larger at some particular locations, e.g., at 100E-180E on October 29, where it is nearly 100%. This is in very good agreement, both in the location and intensity of the depletion, with NOAA 16 SBUV/2 measurements (see Fig. 3 in *Jackman et al.* [2005b]). For the Southern hemisphere, O_3 depletion and NO_x enhancement appear to be quite well spatially correlated. We should note that the longitudinal gradient of O_3 shown on 27 October is mainly due to the illumination conditions of MIPAS measurements. Measurements taken at 80E–180E are taken at nighttime, those for 0–90W for daytime, and the rest includes both day and nighttime observations. This, however, does not significantly alter the O_3 changes visible in this figure nor the polar cap averages shown in Fig. 4 because the fraction (and location for the first two days) of day to nighttime measurements is approximately the same during the 27 October-14 November period.

The temporal evolutions of NO_x enhancement and O_3 depletion in the following weeks after the SPEs are, however, quite different in both hemispheres, as shown below.

4. Temporal Evolution of NO_x and O_3

The zonal mean average of NO_x for the polar caps (latitudes pole-wards of 70° geographic) shows an enormous increase (of up to 70 ppbv) particularly in the Northern hemisphere (NH) winter polar region for at least two weeks after the major SPE (Fig. 4b). **Fig. 4** The signals of the four major SPEs that occurred on 28 and 29 October and on 2 and 4 November (Fig. 1) are visible in the corresponding NO_x abundances (Fig. 4b). The rapid increase of NO_x just after the major SPEs hints towards local production, although it seems that downward transport, superimposed some days later, also plays a significant role at altitudes of 35 to 50 km (see below). The enhancement in NO_x diminishes slowly, continuing to be large until at least two weeks after the first SPE. We should note that the small decline at altitudes above 55 km is not significant because MIPAS spectra contain only little information on NO abundances there, and *a priori* information might be mapped onto the retrievals [see, *Funke e al.*, 2005a].

During the next two days after the solar storm, i.e. on 29–31 October, NO_x decreases by about 1–3 ppbv in the 30–40 km region. This is attributed to high OH, which reacts with

NO_2 and forms HNO_3 and hence depletes NO_2. Evidence for the increase in HOCl and HNO_3 in this region and time are given by *von Clarmann et al.* [2005] and *López-Puertas et al.* [2005a], respectively.

The increase of NO_x in the Southern hemisphere (SH) polar cap (summer pole) is not as dramatic as in the Northern polar cap but is still very large reaching maximum zonal mean values of ~35 ppbv. A reason for the lower enhancement in the polar cap averages compared to the Arctic is, apart from the physical and chemical reasons discussed below, that major parts of the enhancements happened equatorwards of 70°S and thus are not captured by the polar cap averages (see Fig. 3). The large instantaneous increase in the SH is, however, rather quickly damped, decreasing to half the maximum values in about one week, and to about a factor of 4 (although still double of typical background levels) in about two weeks (Fig. 4a).

The illumination conditions and the meridional (summer pole-to-winter pole) atmospheric circulation play key roles for explaining this polar asymmetry. The dark conditions in most of the Northern polar cap during late October/early November prevent the destruction of the SPE-produced NO by sunlight above the stratopause; while in the summer (Southern) hemisphere, above around 40–50 km, NO_x is quickly destroyed via photolysis of NO and the subsequent recombination of N with NO, $N + NO \rightarrow N_2 + O$. In addition, NO_x is slowly transported downwards by the meridional circulation in the Northern hemisphere, thus increasing NO_x in the polar upper stratosphere and also preventing the NO transported from above to below around ~50 km to be photo-chemically destroyed, even in the presence of sunlight.

The role of the downward transport below 40–50 km in the NH polar cap is reflected in the temporal evolution of NO_x measured by MIPAS. Note, for example, the descending of the lower edge of NO_x, e.g., the 20–ppbv contour, from 30 October to 10 November (Fig. 4b), which is closely correlated with the descending of CO, 0.2 ppmv contour (Fig. 4f), a species which is normally used as a tracer of the meridional circulation in the polar region [e.g., *López-Valverde et al.*, 1996; *Allen et al.* 2000]. NO_x mixing ratios decrease on 2 to 5 November at 35–50 km. It can be ruled out that this is caused by chemical loss since a similar behavior is observed in the CO field (Fig. 4f). Instead, this seems to be due to a displacement and extension of the polar vortex outside the 70–90°N polar cap (see, Fig. 1 in *López-Puertas et al.* [2005a]). The two effects above can also be illustrated when comparing the NO_x and CO evolution at given altitudes (Fig. 5). The figure clearly shows the good correlation between the two species for the studied period. **Fig. 5**

From the comparison of figures 4b and 4f we also note that the large decrease in CO on days 12–14 November at 50–60 km is also well correlated with the decrease in NO_x. Furthermore, the CO isolines at 30–40 km altitude also support subsidence during the 2-week period, in consonance again with the descending observed in NO_x.

Overall, the effects of both dark conditions and subsidence of air are responsible for the high and persistent NO_x abundance in the polar winter region. In contrast, in the Southern polar summer region, the absence of downward (or even weak up-welling) transport (see Fig. 4e) and the longer illumination continuously destroy NO_x through NO photolysis at altitudes above ~50 km. This is consistent with the smaller NO_x values measured in the summer pole.

O_3 depletion in both polar regions is evident, although the decrease in the Northern polar region is much larger (Figs. 4c,d). Concentrating in the NH polar region (Fig. 4d), a large depletion of O_3 is apparent above ~55 km (dark blue regions) during the major SPEs and shortly after (1–2 days). O_3 decreases in this region by up to 60–80% at 60–68 km. This decrease is significantly larger than that in the Southern hemisphere, has a short lifetime ($\leq$1 day), and is attributed to enhanced HO_x produced by the SPEs (see, e.g., *Solomon et al.*, [1983], *Jackman and McPeters* [2004], *Jackman et al.* [2005b]). The larger ozone loss in the NH is probably caused, as mentioned above, by the lower background values of HO_x corresponding to the higher solar zenith angles in this hemisphere, which, as showed by *Solomon et al.* [1983], make the HO_x–driven ozone loss more efficient.

Ozone is also depleted, with larger absolute values, although smaller percentages, at lower altitudes and during the subsequent days after the SPEs. The depletion takes place down to ~35 km and lasts for at least two weeks after the SPEs. This decrease is explained by models to be due to the increase of NO_x [*Jackman et al.*, 1995, 2001; *Jackman and McPeters*, 2004] and is also supported by the good temporal correlation between O_3 depletion and NO_x enhancement in the NH polar cap observed by MIPAS (Figs. 4b, d), both in the shape of the change, and in the lowering with time of the lower edge contour. Overall, O_3 is reduced between 20–80%, depending on the time and altitude. The O_3 reduction, as well as the NO_x enhancement, is also larger towards the poles. In the SH polar cap (Fig. 4c) the decrease in O_3 is smaller and is mainly associated with the short-lived HO_x production. The O_3 depletion by NO_x is rather weak in this hemisphere since, as explained above, the increase of NO_x is much smaller (Fig. 4a).

5. Mid-term effects of SPE on NO_x and O_3

Models predict that significant NO_x enhancement and O_3 depletion can persist during the whole winter season after the SPEs until next spring [*Jackman et al.*, 1995, 2001; *Jackman and McPeters*, 2004]. *Seppälä et al.* [2004] have reported from GOMOS/Envisat data, that the effects of the SPEs on NO_2 and O_3 vertical columns (36–50 km) at 70–75°N are significant until about early December 2003. Related to this, *Natarajan et al.* [2004] have shown observations from the HALOE experiment with anomalously enhanced NO_x in the arctic upper stratospheric polar region in April 2004, which they attributed to the powerful solar flares and the associated energetic particle precipitation that took place during October–November 2003. *Randall et al.* [2005] have also shown upper stratospheric enhancements in NO_x at high northern latitudes from March through July 2004 from several instruments, which they attributed to the energetic particle precipitation starting with the October-November 2003 solar flare and possibly persisting through January 2004. Also, *Orsolini et al.* [2005], using ESA MIPAS near-real time data, showed significant enhancements in HNO_3 and NO_2 in November and December 2003.

Figures 6a, b, and c show the time series for in-vortex Northern hemisphere abundances of NO_2, O_3, and CH_4, respectively. The equivalent latitudes needed for calculating the in-vortex abundances were computed using the ECMWF analysis data. **Figures 6**

Instead of using the *Nash et al.* [1996] criteria, the vortex boundary has been defined at a fixed 65° equivalent latitude in order to keep the considered area constant in time and altitude. At high potential temperatures, the vortex, or better said, subsidence zone, is very much extended and variable, being exposed to sunlight to a significant fraction. Since NO_2 is quickly photo-chemically destroyed in sunlight, a variable vortex region would lead to a significant variability in the in-vortex NO_2 not attributed to downwards transport or mid-term chemical processes. Also, with a 65° equivalent latitude we assure that the vortex at lower altitudes is fully included (see Fig. 1 in *Orsolini et al.* [2005]).

MIPAS observations show clear enhancements in the NO_2 abundances inside the NH polar vortex at altitudes above 1000 K (~35 km) during most of the post-SPE Arctic winter (2003–2004) with respect to the previous winter (2002–2003) (Fig. 6a). The enhancements start with the appearance of the first SPEs on 29 October and are very large during November and the first half of December 2003. NO_2 mixing ratios then start to decrease, reaching typical values by the end of December. It is clearly seen that the maxima of NO_2 abundances occur first at higher altitudes, immediately after the SPEs on 29 October, and then descend to lower altitudes as time progresses. The descent in the altitude range of 40–50 km is ~0.5 km/day which is qualitatively consistent with typical wintertime downwards transport in the lower mesosphere [*Garcia and Solomon*, 1985]. There is a smaller second maximum in the time series for NO_2 at 2750 K just after November 20, when another smaller solar storm occurred. This enhancement does not seem to be caused by the solar protons from this event, since only the fluxes of protons with energies below 10 and 3 MeV were enhanced and these were still 100 times smaller than those in the SPEs of Oct/Nov. However, the fluxes of high-energy electrons were largely enhanced (http://www.sec.noaa.gov/tiger/intro.html) and these could produce local enhancements of NO (and hence of NO_2) at altitudes above 2500 K. Another small maximum in NO_2 appeared near 10 December. A large enhancement of the geomagnetic index, A_p, (a measure of the electron fluxes) (ftp://ftp.ngdc.noaa.gov/STP/GEOMAGNETIC_DATA/INDICES/KP_AP) also

Fig. 6

occurred at this time, which also possibly induced local enhancements of NO_2. This maximum, however, is within the dynamically-induced variability in the continuous increase in NO_2 taking place since mid-November by downward transport and, hence, it can also be explained by this effect.

The decline in the NO_x abundance in the second half of December seems to be related to the stratospheric warming and to the very weak polar vortex that occurred at this time [*Angell et al.*, 2004; *Manney et al.*, 2005], favoring the intrusion of mid-latitude air into the polar region. This is supported by the temporal development of in-vortex CH_4 (Fig. 6c). CH_4 abundances start increasing around mid-December, a few days earlier at lower altitudes, thus showing that mid-latitude air masses have been transported into the polar region.

MIPAS data in this version are not available from late December 2003 until 17 February 2004. In the second half of February, extraordinary high values are observed. Mean in-vortex values for NO_2 of 260 ppbv and 320 ppbv at 2750 K and 2500 K (out of the scale of Fig. 6a) were measured on February 17, 2004. These mean values are even larger, 300 and 350 ppbv, respectively, and 230 ppbv and 160 ppbv in-vortex mean values at 1750 and 1250 K, if only the nighttime measurements are considered. This period coincides with the movement of the stratospheric warming to the troposphere and its replacement by record cold air in the mid-upper stratosphere in late January and February [see Fig. 9 in *Angell et al.*, 2004]. This cold mid- and upper-stratosphere air would favour the descent of NO_x-rich mesospheric air and could then explain the increase of NO_2 in the lower mesosphere/upper stratosphere observed by MIPAS in mid-February. Evidence for subsidence of mesospheric air in this region is also clearly seen in the time series of CH_4 (Fig. 6c). CH_4 concentrations are very low in the mid and upper stratosphere, much lower than in the previous winter. The descent of NO_2 is also evident during this period with maxima occurring earlier and at higher altitudes. The rapid decline at higher altitudes (above ~50 km) could be due to the photochemical destruction of NO at a time when the vortex is already exposed to sunlight by several hours. However, higher values still persist at lower altitudes (e.g., at the 1750 K surface).

The origin of the high values of NO_2 in February and March is not completely clear. *Natarajan et al.* [2004] have reported very high values of NO_x in the NH upper stratosphere during April 2004 from HALOE measurements, and mentioned as a possible origin the NO formed in the high latitude upper mesosphere/thermosphere region due to the solar flares and the associated energetic particle precipitation that occurred in late October/early November, followed by downward transport in the polar winter. *Randall et al.* [2005] also discuss the NO_x stratospheric enhancements in the upper stratosphere from March to July 2004 by using several satellite measurements. They suggested that the NO_x enhancement during that period is caused by the energetic particle precipitation that led to substantial NO_x production in the upper atmosphere beginning with the remarkable solar storms in late October 2003 and possibly persisting through January, followed by downwards transport facilitated by the strong upper stratospheric vortex during February and March. MIPAS NO_2 data version 4.62, that cover the whole winter until 26 March 2004, shows an enormous and abrupt increase around 20 January at 60–70 km in the polar region, reaching mean values of about 180 ppbv in the 65°N–90°N latitude interval, and up to 300 ppbv at 85°N–90°N [*López-Puertas et al.*, 2005b]. This enhancement persisted for about one month and descended to lower altitudes during the second half of January, February and March. Since no major SPEs occurred at that time that could produce such a large local enhancement, the large amounts of NO_2 around 20 January at 60–70 km seem to have descended quickly from the upper mesosphere following the rapid development of the strong vortex [*Manney et al.*, 2005]. The origin of the descended NO_2 is also related to the large solar and geomagnetic activity in the preceding months. The solar storms of Oct/Nov produced enhanced protons and electrons fluxes. The production of NO_x by solar protons was mainly concentrated between 40 and 80 km and took place just after the storm [*Jackman et al.*, 2005]. This NO_x production is expected to contribute little to the lower mesospheric enhancement in 20 January since NO_x was already transported downward through November and December (see Sec. 4 above). NO_x could also be heavily produced by high-energetic electrons between 90 and 110 km during this solar storm. Part of this production could be transported downward, below 70 km, before the stratospheric warming appeared in mid-December; and also part could be destroyed in the sunlight since the polar night was not very extended when the solar storm took place (see Fig. 2). But some of the NO_x produced by auroral electrons during the storm could last in the upper mesosphere until mid-January, partly favored by the stratospheric warming that took place from mid-December until mid-January, when the mesospheric descent was very slow. Other SPEs took place on 20–23 November and 3–5 December, but the protons fluxes were very small and did not produce a significant amount of NO_x. However, large auroral activity, with large electron fluxes, took place during 11–16 and 20 of November, and during 5, 8–12 and 21 of December (http://www.sec.noaa.gov/tiger/intro.html, ftp://ftp.ngdc.noaa.gov/STP/GEOMAGNETIC_DATA/INDICES/KP_AP). Assuming that the production of NO_x was directly proportional to the geomagnetic index, A_p, the production of NO_x from 11 November until mid-December was twice that produced during the Oct/Nov solar storm. All this then suggests that the major part of the NO_x observed in the second half of January in the lower mesosphere was originated during the winter after the Oct/Nov solar storm. This is more in favor of *Randall et al.* [2005] suggestions than those reported by *Natarajan et al.* [2004].

The O_3 abundances are closely anti-correlated with those of NO_2 (Fig. 6b) for the period of late October/early November (just after the SPEs) until late December. O_3 decreases from early November until early December at essentially all altitudes shown (potential temperatures of 1000–2500 K). The decline recovers earlier at higher altitudes (Θ=2500 K), but it persists until early December at the other altitudes. We think that this significant depletion in O_3 is caused by chemical destruction produced by the larger NO_x abundances. The dynamical contribution to this loss, i.e., down-welling of O_3-poor air, seems to be small since CH_4 abundances show nearly constant values (Θ=1000, 1750 K), or significantly increase (Θ=1250 K) during this period.

In the second half of December, O_3 abundances increase at most altitudes, consistent with the lower NO_2 levels observed and the higher CH_4 concentrations. This suggests that the intrusion of mid-latitude air significantly recovered much of the O_3 loss.

In comparison with the previous winter, the in-vortex NH O_3 abundances in early November at Θ=1000 and 1250 K, were larger in 2003 than in 2002. However, after the SPEs, O_3 in 2003 becomes significantly smaller from about mid-November until mid-December at levels of Θ=1250 K, for the whole period from early November until mid-December at Θ=1750 K, and for a shorter period just after the SPEs at the higher altitudes of Θ=2500 K. Only at lower altitudes (Θ=1000 K), although O_3 was depleted, the O_3 abundances were larger or similar to those in 2002. Overall, this figure shows the significant impact of SPEs in O_3 loss.

In February and March 2004, when the NO_2 abundances increase again, O_3 abundances are again significantly smaller than in 2003 mainly at the level of Θ=1750 K. It is not clear whether this decrease in O_3 is due to the larger NO_2 concentrations, i.e., a larger chemical loss, or due to subsidence of O_3-poor air from the mesosphere since CH_4 values suggest that the downward transport in 2004 was much stronger than in 2003. Probably both effects contribute to the lower O_3 columns observed in February-March 2004. The O_3 abundances at 2500 K are also significantly lower in mid-February 2004 which is consistent with the high NO_2 at this level and time. Ozone depletions at potential temperature levels below ~1500 K were not observed by MIPAS because it stopped taking measurements before the NO_x enhancements reach these levels.

Overall, in this unusual 2003-2004 polar arctic winter we can distinguish two differentiated periods. The first period commenced with the very strong SPE events that produced large amounts of NO_x in the middle and upper stratosphere and in the lower mesosphere, first locally and later by downwards transport. This period terminated with the stratospheric warming that occurred in mid-December and redistributed the NO_x to mid-latitudes. In this period, significant depletion of O_3 inside the polar vortex was observed in a wide altitude range and extended period. The second period, from mid-January until the end of March (Fig. 6a and *López-Puertas et al.* [2005b], is characterized by extraordinary high values of NO_2 in the upper stratosphere, which seems to be caused by the unusually strong vortex and downward transport together with a continuous unusually large auroral activity in November-December of 2003. The NO_x produced by electrons in the upper mesosphere/lower thermosphere during the solar storm in late October/early November might have also contributed to that extraordinary enhancement, although to a lesser extent. In-vortex ozone was observed to significantly decline in the mid-February to late March period above the 1750 K potential temperature level.

6. Conclusions

In this paper we have presented the effects of the large solar storms in October-November 2003 on the NO_x ($NO+NO_2$) and O_3 abundances in the Northern and Southern polar regions as measured by the MIPAS instrument on board Envisat. We have shown both short-term as well as mid-term effects on the abundances of these species in the altitude range from 30 to 60 km, for NO_x, and 30 to 68 km for O_3. To our best knowledge, it is the first time that the NO_x species have been measured globally, covering both the summer (daylight) and winter (dark) polar regions during an SPE. Very high values of NO_x abundances in the upper stratosphere of 180 ppbv (parts per billion by volume) have been measured just after the SPEs.

A large asymmetry in the enhanced NO_x abundances in the Northern and Southern hemisphere polar caps (>70° geographic) has been observed, with high and persistent values of NO_x in the upper stratosphere and lower mesosphere in the NH polar winter region. The reason for this asymmetry is thought to be a combined effect of solar illumination conditions and the meridional circulation. In the NH polar winter region the darker conditions diminish the photolysis destruction of the SPE-produced NO. Also, NO is transported from the mesosphere down to lower regions (below ~50 km) where it is not easily photo-chemically destroyed in the presence of sunlight. The opposite occurs in the SH summer polar region, where NO is photolyzed above the stratopause and also the locally produced NO is slowly moved upwards (above about 50 km) where it is more easily photolysed.

An increase in mean NO_x abundance between 20 to 70 ppbv occurred in the NH polar cap, lasting for at least two weeks. In the SH the NO_x enhancement is between 10 and 35 ppbv and it is halved after two weeks.

Ozone has also been measured, showing depletion signatures associated with both HO_x ($H+OH+HO_2$) and NO_x enhancements. Ozone depletion correlated with NO_x enhancement also exhibits a hemispheric asymmetry. In the NH polar region, ozone is depleted by 50–70 % in the lower mesosphere shortly after the SPEs due to enhanced HO_x and by about 30–40 % in the upper stratosphere, being depleted as low as 35 km and lasting for about two weeks after the SPEs due to enhanced NO_x. In the SH polar region, the maximum percentage depletion, associated with HO_x enhancement, took place in the lower mesosphere just after the major SPEs and is about 50%. After the major SPEs, ozone is depleted about 5–10% at altitudes between ~35 and 68 km.

The MIPAS data of NO_2, O_3 and CH_4 in the upper stratosphere arctic region for the November 2003-March 2004 period were also analysed. In this unusual 2003–2004 Arctic winter we could distinguish two differentiated periods. The first period commenced with the very strong SPE events that occurred in late October/early November, when large amounts of NO_x were produced in the middle and upper stratosphere and in the lower mesosphere, first locally and later by downwards transport. This period terminated with the stratospheric warming that occurred in mid-December and redistributed the NO_x to mid-latitudes. In this period, a significant depletion of O_3 inside the polar vortex was observed in a wide altitude range and extended period. The second period, from mid-

January until the end of March 2004, is characterized by extraordinary high values of NO_2 in the upper stratosphere, which seems to be caused by the unusually strong vortex and downward transport together with a continuous unusually large auroral activity in November-December of 2003. The NO_x produced by electrons in the upper mesosphere/lower thermosphere during the solar storm in late October/early November might have also contributed to that extraordinary enhancement, although to a lesser extent. In-vortex ozone was observed to significantly decline in the mid-February to late March period above the 1750 K potential temperature level.

Overall, MIPAS has captured, with global coverage, both short term and mid-term effects of NO_x and O_3 abundance changes caused by the SPEs. MIPAS also measured an additional number of NO_y species, which also showed significant enhancements during and after the SPEs, and are reported in a companion paper [*López-Puertas et al.*, 2005a]. The simultaneous measurements of such a large number of atmospheric species obtained by MIPAS, with global coverage and very good spatial and temporal resolutions, constitute an unprecedented opportunity to test theories of composition changes induced by SPEs, in particular with respect to NO_y species. An in-depth analysis of the data set with the help of chemistry-transport models would greatly improve our knowledge of the atmospheric effects of solar proton events and would allow a better quantification of the mesospheric/stratospheric downwards transport in the polar winter regions.

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References

Allen, D.R., J.L. Stanford, N. Nakamura, M.A. López-Valverde, M. López-Puertas, F.W. Taylor, and J.J. Remedios, Antarctic polar descent and planetary wave activity observed in ISAMS CO from April to July 1992, *Geophys. Res. Lett., 27*, 665–668, 2000.

Angell, J.K. et al., Northern hemisphere winter 2003–2004 summary, NOAA, 2004. (http://www.cpc.ncep.noaa.gov/products/stratosphere/winter_bulletins/nh_03-04/index.html)

Crutzen P.J., Isaksen I.S.A. and Reid, G.C., Solar proton events: stratospheric sources of nitric oxide, *Science, 189*, 457–458, 1975.

European Space Agency, Envisat, MIPAS An instrument for atmospheric chemistry and climate research, ESA Publications Division, ESTEC, P. O. Box 299, 2200 AG Noordwijk, The Netherlands, SP-1229, 2000.

Fischer, H., and H. Oelhaf, Remote sensing of vertical profiles of atmospheric trace constituents with MIPAS limb-emission spectrometers, *Appl. Opt.*, *35*(16), 2787–2796, 1996.

Funke, B. et al., CO in the middle atmosphere measured with MIPAS/ENVISAT, *Geophys. Res. Abstracts, 6*, 04358, SRef-ID: 1607-7962/gra/EGU04-A-04358, 2004.

Funke, B. et al., Retrieval of stratospheric NO_x from 5.3 and 6.2 μm non-LTE emissions measured by MIPAS on ENVISAT, *J. Geophys. Res.*, in press, 2005a.

Funke, B. et al., Carbon monoxide observations by MIPAS/Envisat during the major warming event in September/October 2002, *J. Geophys. Res.*, in preparation, 2005b.

Garcia, R.R., and S. Solomon, The effect of breaking gravity waves on the dynamics and chemical composition of the mesosphere and lower thermosphere, *J. Geophys. Res., 90*, 3850–3868, 1985.

Glatthor, N., et al., Mixing processes during the Antarctic vortex split in September/October 2002 as inferred from source gas and ozone distributions from MIPAS/ENVISAT, *J. Atmos. Sci.*, *Special issue on Antarctic Vortex 2002*, accepted 7 January 2004, 2005.

Heath, D.F., Krueger, A.J. and Crutzen, P.J., Solar proton events: influence on stratospheric ozone, *Science*, *197*, 886–889, 1977.

Jackman, C.H. et al., Two-dimensional and three-dimensional model simulations, measurements and interpretation of the influence of the October 1989 solar proton events on the middle atmosphere, *J. Geophys. Res., 100*, 11641–11660, 1995.

Jackman, C.H., McPeters, R.D., Labow, G.J., Fleming E.L., Praderas, C.J., and Russell, J.M., Northern hemisphere atmospheric effects due to the July 2000 solar proton event, *Geophys. Res. Lett., 28*, 2883–2886, 2001.

Jackman, C.H. and R.D. McPeters, The effects of solar proton events on ozone and other constituents, Solar variability and its Effects on climate, *Geophys., Mon., 141*, 305–319, 2004.

Jackman, C. H. et al., The influence of the several very large solar proton events in years 2000-2003 on the neutral middle atmosphere, *Adv. Space Res.*, in press, 2005a.

Jackman, C. H. et al., Neutral atmospheric influences of the solar proton events in October-November 2003, *J. Geophys. Res.*, in press, 2005b.

López-Valverde, M. A., M. López-Puertas, J.J. Remedios, C.D. Rodgers, F.W. Taylor, E.C. Zipf, and P.W. Erdman, Validation of Measurements of Carbon Monoxide from the Improved Stratospheric and Mesospheric Sounder, *J. Geophys. Res., 101*, 9929–9955, 1996.

López-Puertas, M., et al., HNO_3, N_2O_5 and $ClONO_2$ enhancements after the October-November 2003 solar proton events, *J. Geophys. Res., submitted*, 2005a.

López-Puertas, M., et al., The variability of stratospheric and mesospheric NO_y in the arctic and antarctic 2002-2004 polar winters, *Space Sci. Rev., submitted*, 2005b.

Manney, G.L., K. Krüger, J.L. Sabutis, S.A. Sena, and S. Pawson, The remarkable 2003-2004 winter and other recent warm winters in the Arctic stratosphere since the late 1990s, *J. Geophys. Res., 110*, doi:10.1029/2004JD005367, 2005.

McPeters, R.D., Jackman, C.H., Stassinopoulus, E.G., Observations of ozone depletion associated with solar proton events, *J. Geophys. Res., 86*, 12071–12081, 1981.

McPeters, R.D., and Jackman, C.H., The response of ozone to solar proton events during solar cycle 21: the observations, Observations of ozone depletion associated with solar proton events, *J. Geophys. Res., 90*, 7945–7954, 1985.

McPeters, R.D., A nitric oxide increase observed following the July 1982 solar proton event, *Geophys. Res. Lett., 13*, 667–670, 1986.

Nash, E.R., P.A. Newman, J.E. Rosenfield, and M.R. Schoeberl, An objective determination of the polar vortex using Ertel's potential vorticity, *J. Geophys. Res., 101*, 9471–9478, 1996.

Natarajan, M., E.E. Remsberg, L.E. Deaver, and J.M. Russell, III, Anomalously high levels of NO_x en the polar upper stratosphere during April 2004: Photochemical consistency of HALOE observations, *Geophys. Res. Lett., 31*, L15113, doi:10.1029/2004GL020566, 2004.

Nett, H., G. Perron, M. Sanchez, A. Burgess, and P. Mosner, MIPAS in-flight calibration and processor verification, in *ENVISAT Calibration Review - Proc. of the European Workshop, 9–13 September 2002, ESTEC, Noordwijk, The Netherlands, CD-ROM*, SP–520, edited by H. Sawaya-Lacoste, ESA Publications Division, ESTEC, Postbus 299, 2200 AG Noordwijk, The Netherlands, 2002.

Norton, R.H. and R. Beer, New apodizing functions for Fourier spectrometry, *J. Opt. Soc. Am., 66(3)*, 259–264, 1976.

Orsolini, Y., G.L. Manney, M. L. Santee, and C.E. Randall, An upper stratospheric layer of enhanced HNO_3 following exceptional solar flares, *Geophys. Res. Lett.*, in press, 2005.

Randall, C.E., Siskind, D.E. and Bevilacqua, R.M., Stratospheric NO_x enhancements in the southern hemisphere polar vortex in winter and spring of 2000, *Geophys. Res. Lett., 28*, 2385–2388, 2001.

Randall, C.E., et al., Stratospheric effects of energetic particle precipitation in 2003-2004, *Geophys. Res. Lett., 32*, L05802, doi:10.1029/2004GL022003, 2005.

Rohen et al., Ozone depletion during the solar proton events of Oct./Nov. 2003 as seen by SCIAMACHY, submitted to JGR, 2005.

Reid, G.C., Solomon, S. and Garcia, R.R., Response of the middle atmosphere to the solar proton events of August-December 1989, *Geophys. Res. Lett., 18*, 1019–1022, 1991.

Seppälä, A. et al. Solar proton events of October-November 2003: Ozone depletion in the Northern hemisphere polar winter as seen by GOMOS/Envisat, *Geophys. Res. Lett., 31*, L19107, doi:10.1029/2004GL02142, 2004.

Solomon, S., Rusch, D. W., Gerard, J.-C., Reid, G. C. and Crutzen, P. J., The effect of particle precipitation events on the neutral and ion chemistry of the middle atmosphere, II. Odd hydrogen, *Planet. Space Sci., 29*, 885–892, 1981.

Solomon, S., Reid, G.C., Rusch, D.W., and Thomas R.G., Mesospheric ozone depletion during the solar proton event of July 13, 1982, 2, Comparison between theory and measurements, *Geophys. Res. Lett., 10*, 257–260, 1983.

Stiller, G. P., *The Karlsruhe Optimized and Precise Radiative Transfer Algorithm (KOPRA)*, Wiss. Ber. FZKA 6487, Forschungszentrum, Karlsruhe, Germany, 2000.

Thomas, R.J. et al., Mesospheric ozone depletion during the solar proton event of July 13, 1982, 1, Measurements, *Geophys. Res. Lett., 10*, 253–255, 1983.

von Clarmann, T. and G. Echle, Selection of optimized microwindows for atmospheric spectroscopy, *Appl. Opt., 37*, 7661–7669, 1998.

von Clarmann, T., et al., Remote sensing of the middle atmosphere with MIPAS, in *Remote Sensing of Clouds and the Atmosphere VII*, vol. 4882, edited by K. Schäfer, O. Lado-Bordowsky, A. Comerón, and R. H. Picard, pp. 172–183, SPIE, Bellingham, WA, USA, 2003a.

von Clarmann, T., et al., Retrieval of temperature and tangent altitude pointing from limb emission spectra recorded from space by the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS), *J. Geophys. Res.*, *108*(D23), 4736, doi:10.1029/2003JD003602, 2003b.

von Clarmann, T., et al., Stratospheric HOCl measurements provide evidence of increased stratospheric odd hydrogen abundances due to solar proton events 2003, *J. Geophys. Res.*, accepted, 2005.

Weeks, L.H., CuiKay, R.S. and Corbin J.R., Ozone measurements in the mesosphere during the solar proton event of 2 November, 1969, *J. Amos. Sci., 29*, 1138–1142, 1972.

Wetzel, G., et al., Validation of MIPAS/Envisat version 4.61 operational data: NO_2, *Proc. 2nd Workshop Atmospheric Validation of ENVISAT (ACVE-2)*, ESA SP-562, 2004.

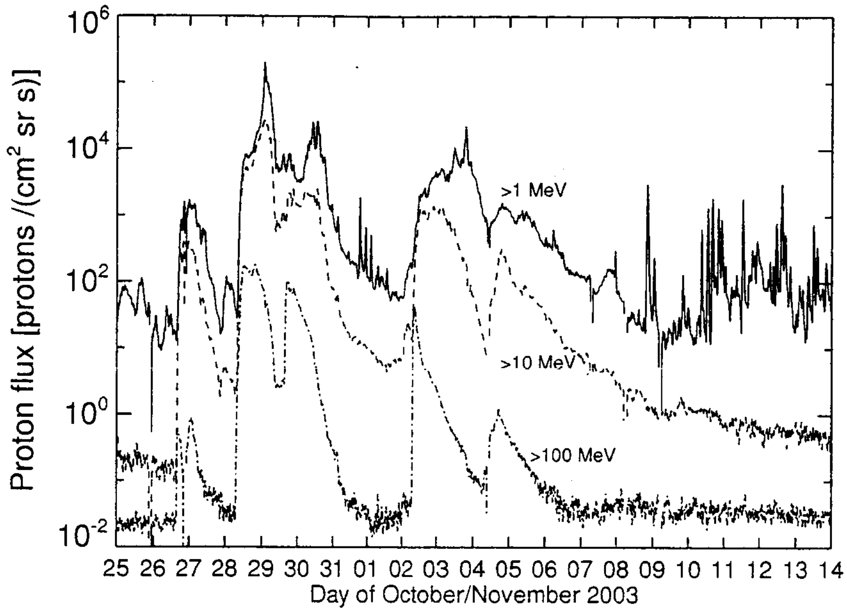

Figure 1. Flux of solar protons as measured by the GOES-11 satellite. These data have been provided by the NOAA Space Environment Center at their website (http://sec.noaa.gov/Data/goes.htm). The curves show the fluxes for protons with shown energy thresholds.

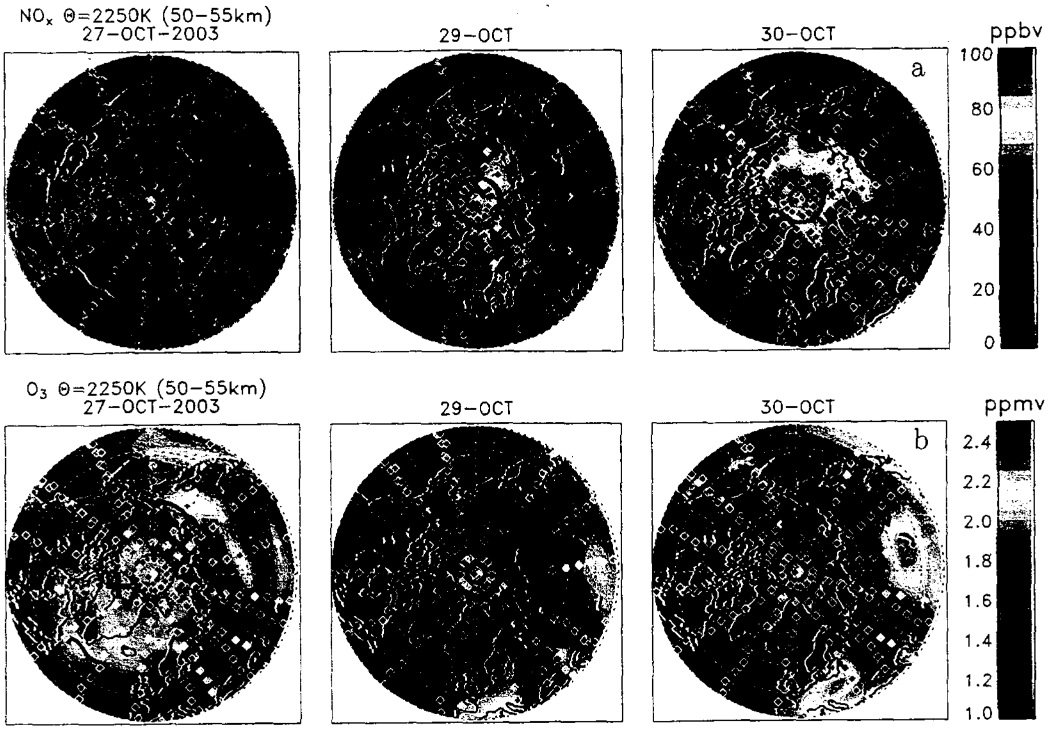

Figure 2. Northern hemisphere polar atmospheric abundances of NO_x (top panels, a) (in ppbv, parts per billion by volume) and ozone (bottom panels, b) (in ppmv, parts per million by volume) for days October 27, 29, and 30 2003, i.e., just before and during the major solar proton events at a potential temperature (Θ) level of 2250 K. Contours are zonally smoothed within 700 km. Individual measurements are represented by diamonds. The vortex edge is plotted with a red curve (see text for details). The geomagnetic pole is marked with a red '+' sign. The circle around the pole represents the polar night terminator.

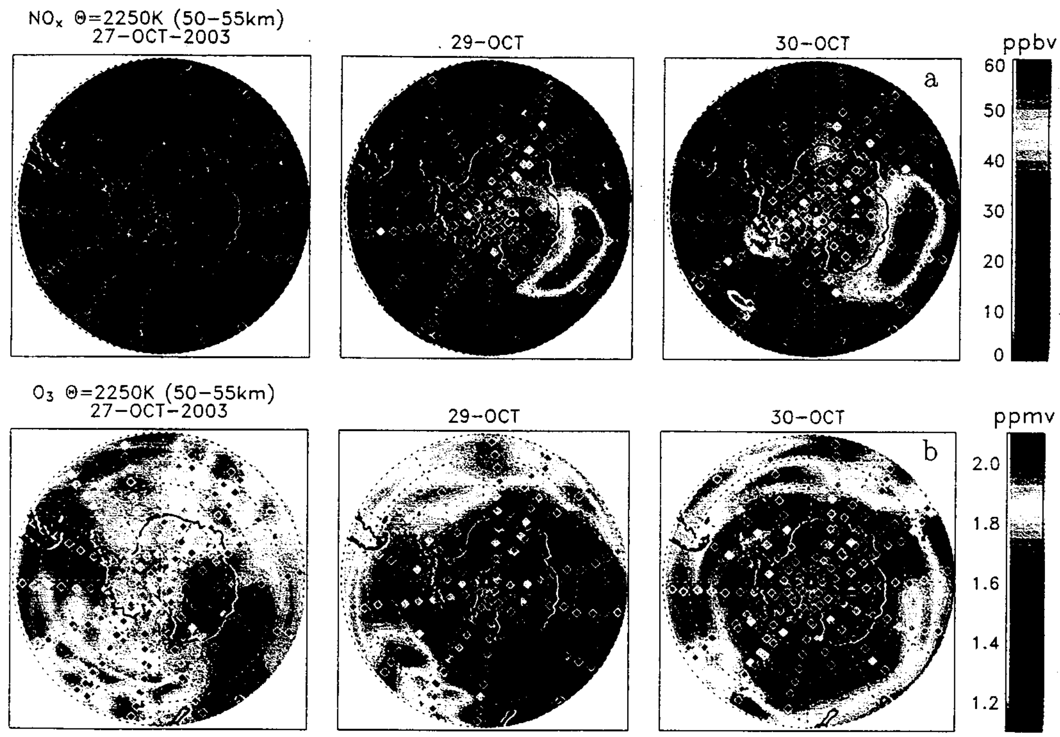

Figure 3. As Fig. 2 but for the Southern hemisphere polar cap. The vortex edge is not plotted because above 1000 K no subsidence was detected neither in CO nor in CH_4 fields.

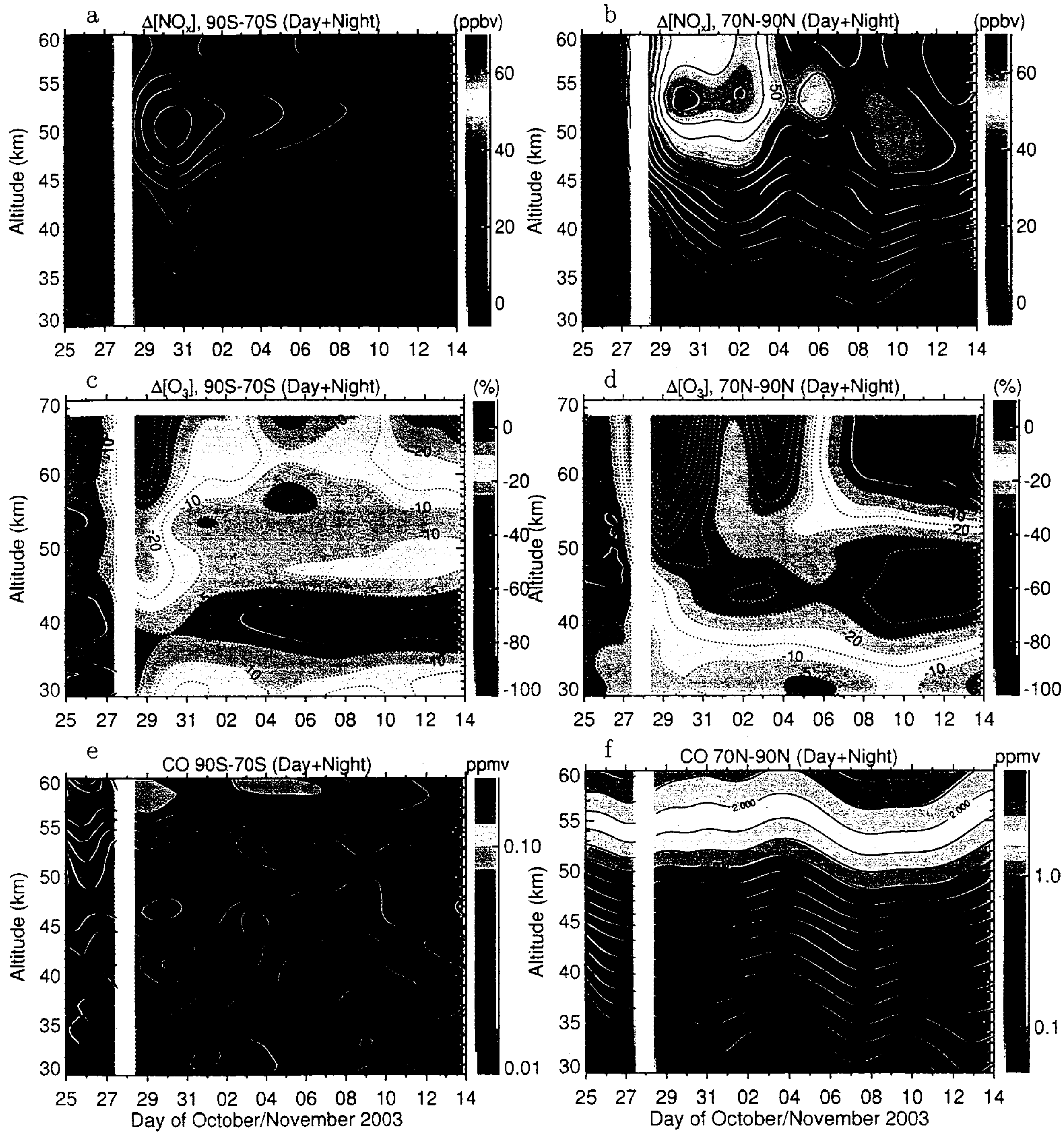

Figure 4.

Temporal evolution of NO_x ($NO+NO_2$) (top panels) and O_3 (middle panels) abundance changes, and CO abundances (lower panels) during and after the October-November 2003 solar proton events for the Southern (SH) (70°S-90°S) (left panels) and Northern (NH) (70°N-90°N) (right panels) polar caps. Changes are shown relative to the mean profile measured on 25 October in absolute values for NO_x, and percentage for O_3. The white band around 28 October represents lack of data due to MIPAS not observing at that time. A triangular smoothing with FWHM of 48 hours has been applied to the measurements sampled at 24 hours since daily means were affected by artefacts due to incomplete sampling. Between 400 and 900 profiles were available for each day. In order to compensate for the different areas represented by each data point, a weighting of the measurements by the cosine of latitude has been applied.

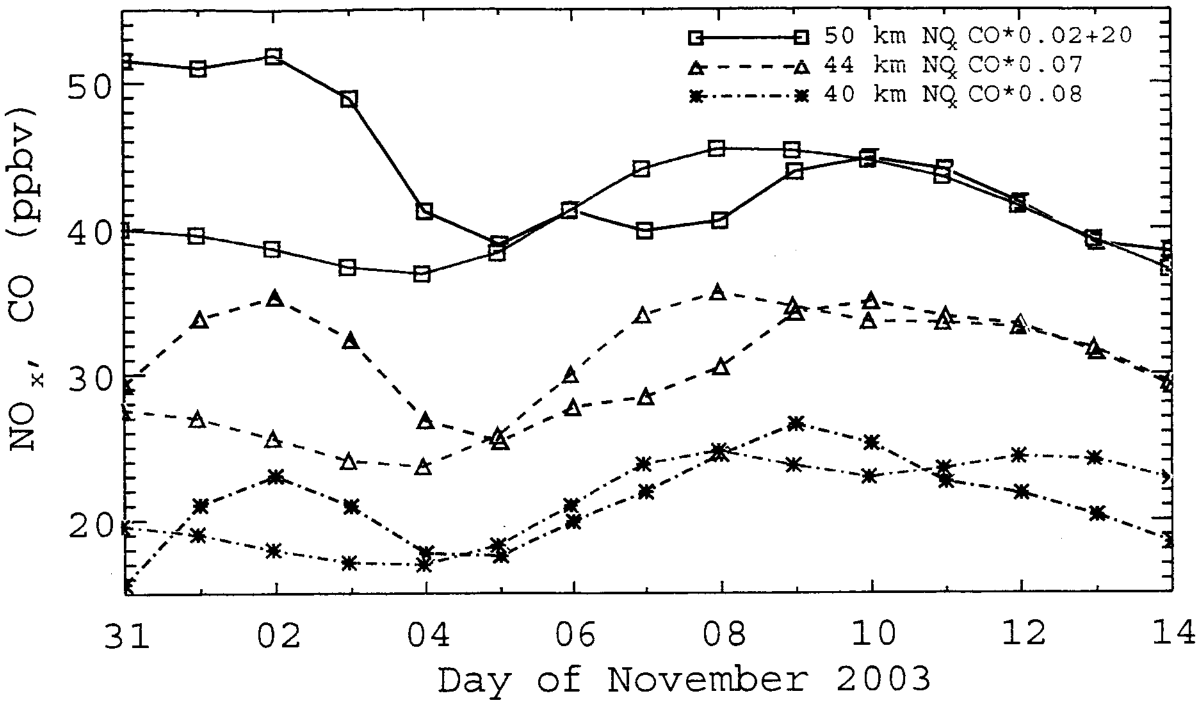

Figure 5. Temporal evolution of NO_x (black) and CO (red) for the Northern (70°N-90°N) polar cap at selected altitudes. The CO measurements have been scaled as shown. A triangular smoothing with FWHM of 48 hours has been applied to the measurements sampled at 24 hours since daily means were affected by artefacts due to incomplete sampling.

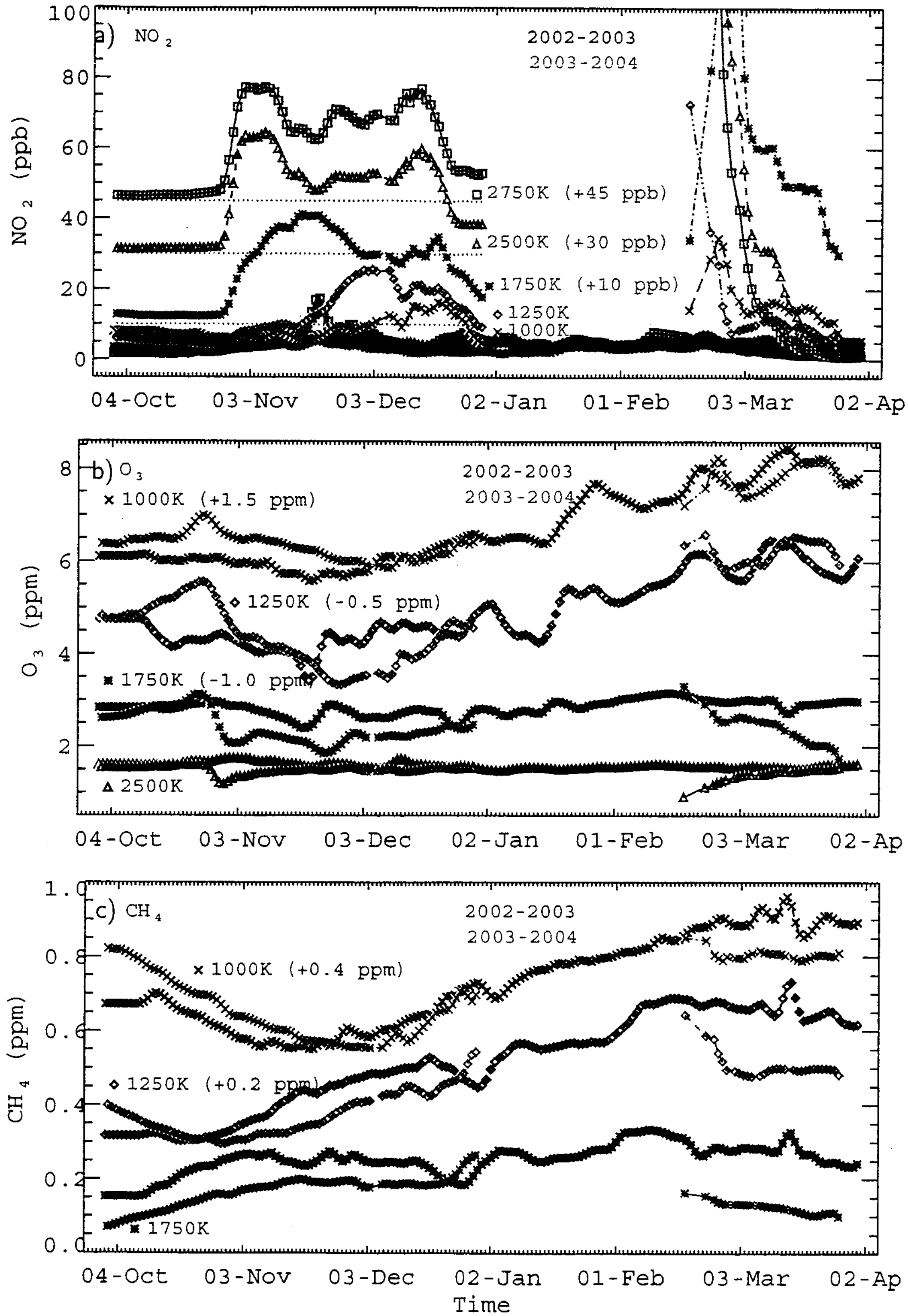
a) NO 2
2002-2003
2003-2004
2750K (+45 ppb)
2500K (+30 ppb)
1750K (+10 ppb)
1250K
1000K
NO 2 (ppb)
04-Oct
03-Nov
03-Dec
02-Jan
01-Feb
03-Mar
02-Ap
b) O 3
1000K (+1.5 ppm)
1250K (-0.5 ppm)
1750K (-1.0 ppm)
2500K
O 3 (ppm)
c) CH 4
1000K (+0.4 ppm)
1250K (+0.2 ppm)
1750K
CH 4 (ppm)
Time

Figure 6.

Temporal evolution at selected potential temperatures of in-vortex (see text for details) Northern hemisphere abundances of NO_2 (a), O_3 (b), and CH_4 (c) for the pre-SPEs 2002–2003 and post–SPEs 2003–2004 arctic winters. The major SPEs ocurred on 28–30 October and 2–4 November 2003. The abundances have been smoothed with a triangle of FWHM of 48 hours and weighted by the cosine of latitude. The gap in the middle of the figures for 2003-2004 represent a period with no data available. Some time series have been displaced, as shown, for clarity. Those in the upper panel, for NO_2, have been displaced only for the first period (until January 2). The data in this figure are from the MIPAS off-line 4.61 version retrieved by ESA [*Ridolfi et al.*, 2000; *Carli et al.*, 2004 (see Sec. 2 for more details)].