Observation of NO\textsubscript{x} enhancement and ozone depletion in the Northern and Southern Hemispheres after the October–November 2003 solar proton events

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Received 7 February 2005; revised 17 June 2005; accepted 22 June 2005; published 30 September 2005.

[1] 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\textsubscript{x} (NO + NO\textsubscript{2}) and O\textsubscript{3} of the period from 25 October to 14 November 2003 are the first global measurements of NO\textsubscript{x} species, covering both the summer (daylight) and winter (dark) polar regions during an SPE. Very large values of NO\textsubscript{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\textsubscript{x} enhancements was found. Arctic mean polar cap (>60°N) NO\textsubscript{x} enhancements of 20 to 70 ppbv between 40 to 60 km lasted for at least 2 weeks, while the Antarctic mean NO\textsubscript{x} enhancement was between 10 and 35 ppbv and was halved after 2 weeks. Ozone shows depletion signatures associated with both HO\textsubscript{x} (H + OH + HO\textsubscript{2}) and NO\textsubscript{x} enhancements but at different timescales. Arctic lower mesospheric (upper stratospheric) ozone is reduced by 50–70% (30–40%) for about 2 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\textsubscript{x} enhancement, large amounts of NO\textsubscript{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\textsubscript{3} depletion was observed inside the polar 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\textsubscript{2} in the upper stratosphere of the northern polar region (mean in-vortex values up to 350 ppbv at ~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

[2] It has been shown that solar proton events (SPEs) have significant effects on the composition of the strato-
sphere 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\textsubscript{x} (H + OH + HO\textsubscript{2}) and NO\textsubscript{x} (NO + NO\textsubscript{2}), followed by large depletions of O\textsubscript{3} in these atmospheric regions. While the direct experimental confirmation of HO\textsubscript{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 40 years [Jackman and McPeters, 2004; Jackman et al., 2005a]. Some of the Geostationary Operational Environmental Satellite (GOES)-11 instruments measured very large fluxes of highly energetic protons (available at http://sec.noaa.gov/Data/goes.htm) (see Figure 1). The protons are guided by the Earth’s magnetic field to both polar regions (geomagnetic latitudes >60\(^\circ\)), where they penetrate down to \(\sim 87\) km, if their energy is >1 MeV, or even down to \(\sim 30\) km, if their energy is >100 MeV [Jackman and McPeters, 2004; Jackman et al., 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 October/November 2003 SPE events by SCIAMACHY [Rohrmann 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\(_2\)O\(_5\), 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 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., 2005; 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 midinfrared from 4.1 to 14.7 μm with high spectral resolution (0.05 cm\(^{-1}\), apodized as described by Norton and Beer [1976]), 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 nonlinear least squares algorithm with Levensberg-Marquardt damping and line by line radiative transfer calculations with the Karlsruhe Optimized and Precise Radiative Transfer Algorithm (KOPRA) [Stiller, 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\(_2\)O, HNO\(_3\), then CH\(_4\) and N\(_2\)O simultaneously, ClONO\(_2\), F-11, ClO, N\(_2\)O\(_5\), 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 \(\nu_2\) 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., 2005]. The retrievals were performed from selected spectral regions (microwindows) 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 microwindows were selected with a tradeoff 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., 2005]. O\(_3\) is retrieved in the 10–68 km altitude range with an accuracy of 10% at 30 km and 20% at 50 km Glathhor et al. [2005]. More details on the O\(_3\) retrieval can be found in the work of Glathhor et al. [2005] and for NO\(_2\) and NO in the work of Funke et al. [2005]. 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 nonlocal thermodynamic equilibrium emission are reported by Funke et al. [2004, also B. Funke et al., Carbon monoxide observations by MIPAS/Envisat during the major warming event in September/October 2002, in preparation for Journal of Geophysical Research, 2005].

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 98.5° inclination at approximately 800 km altitude, MIPAS passes the equator in a southerly direction at 1000 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 10,000 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 Carl 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\(_2\)O, 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 nonlocal 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. 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 Figure 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\textsubscript{x} shows smaller enhancements were all made during daylight. NO\textsubscript{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.

[12] O\textsubscript{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\textsubscript{x} enhancement takes place inside the 60° geomagnetic polar cap and that O\textsubscript{3} loss is mainly caused by the HO\textsubscript{x} catalytic cycle at this altitude [see, e.g., Jackman et al., 2001, 2005b]. The circle O\textsubscript{3} loss structure around the polar night region seems to be caused by the lower background values of HO\textsubscript{x} corresponding to the larger solar zenith angles, which, as shown by Solomon et al. [1983], make the HO\textsubscript{x}–driven ozone loss more efficient. Ozone depletion is largest on 29 October and then decreasing fast on 30 October. This also supports the predominant role of the HO\textsubscript{x} cycle because HO\textsubscript{x} species are very short-lived (lifetime of the order of 1 day). The different way in which solar illumination affects the NO\textsubscript{x} production and the O\textsubscript{3} depletion (HO\textsubscript{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\textsubscript{x} enhancements (visible, e.g., in the polar night region on 30 October, Figure 2a) and could then be the reason for the different spatial distributions observed.

[13] Antarctic O\textsubscript{3} depletion is similar to that in the Northern Hemisphere. It seems larger at some particular locations, e.g., at 100°E–180°E on 29 October, 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 Figure 3 of Jackman et al. [2005b]). For the Southern Hemisphere, O\textsubscript{3} depletion and NO\textsubscript{x} enhancement appear to be quite well spatially correlated. We should note that the longitudinal gradient of O\textsubscript{3} shown on 27 October is mainly due to the illumination conditions of MIPAS measurements. Measurements taken at 80°E–180°E are taken at nighttime, those for 0°–90°W for daytime, and the rest includes both day and nighttime observations. This, however, does not significantly alter the O\textsubscript{3} changes visible in this figure nor the polar cap
averages shown in Figure 4 because the fraction (and location for the first 2 days) of day to nighttime measurements is approximately the same during the 27 October to 14 November period.

15] 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$_3$

16] The zonal mean average of NO$_x$ for the polar caps (latitudes poleward of 70° geographic) shows an enormous increase (of up to 70 ppbv) particularly in the Northern Hemisphere (NH) winter polar region for at least 2 weeks after the major SPE (Figure 4b). The signals of the four major SPEs that occurred on 28 and 29 October and on 2 and 4 November (Figure 1) are visible in the corresponding NO$_x$ abundances (Figure 4b). The rapid increase of NO$_x$ just after the major SPEs hints toward 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 2 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 et al., 2005].

17] During the next 2 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. [2005], respectively.

18] 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 equatorward of 70°S and thus are not captured by the polar cap averages (see Figure 3). The large instantaneous increase in the SH is, however, rather quickly damped, decaying to half the maximum values in about 1 week, and to about a factor of 4 (although still double of typical background levels) in about 2 weeks (Figure 4a).

19] 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 → N$_2$ + O. In addition, NO$_x$ is slowly transported downward 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 photochemically 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 (Figure 4b), which is closely correlated with the descending of CO, 0.2 ppmv contour (Figure 4f), a species which is normally used as a tracer of the meridional circulation in the polar region [e.g., López-Puertas et al.: NO$_x$ and O$_3$ changes after solar proton events].
since daily means were affected by artefacts due to the observed. 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.

Valverde et al., 1996; Allen et al., 2000). NOx 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 (Figure 4f). Instead, this seems to be due to a displacement and extension of the polar vortex outside the 70–90°N polar cap (see Figure 1 of López-Puertas et al. [2005]). The two effects above can also be illustrated when comparing the NOx and CO evolution at given altitudes (Figure 5). The figure clearly shows the good correlation between the two species for the studied period.

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 NOx. 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 NOx.

Overall, the effects of both dark conditions and subsidence of air are responsible for the high and persistent NOx abundance in the polar winter region. In contrast, in the southern polar summer region, the absence of downward (or even weak upwelling) transport (see Figure 4e) and the longer illumination continuously destroy NO2 through NO photolysis at altitudes above ~50 km. This is consistent with the smaller NOx values measured in the summer pole.

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 2 weeks after the SPEs. This decrease is explained by models to be due to the increase of NOx [Jackman et al., 1995, 2001; Jackman and McPeters, 2004] and is also supported by the good temporal correlation between O3 depletion and NOx enhancement in the NH polar cap observed by MIPAS (Figures 4b and 4d), both in the shape of the change, and in the lowering with time of the lower edge contour. Overall, O3 is reduced between 20–80%, depending on the time and altitude. The O3 reduction, as well as the NOx enhancement, is also larger toward the poles. In the SH polar cap (Figure 4c) the decrease in O3 is smaller and is mainly associated with the short-lived HOx production. The O3 depletion by NOx is rather weak in this hemisphere since, as explained above, the increase of NOx is much smaller (Figure 4a).

5. Midterm Effects of SPE on NOx and O3

Models predict that significant NOx enhancement and O3 depletion can persist during the whole winter season after the SPEs until next spring [Jackman et al., 1995, 2001; Jackman and McPeters, 2004]. Seppäälä et al. [2004] have reported from GOMOS/Envisat data, that the effects of the SPEs on NO2 and O3 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 NOx 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 NOx 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 HNO3 and NO3 in November and December 2003.

Figures 6a, 6b, and 6c show the time series for in-vortex Northern Hemisphere abundances of NO2, O3, and CH4, respectively. The equivalent latitudes needed for calculating the in-vortex abundances were computed using the ECMWF analysis data.

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 NO2 is quickly photochemically destroyed in sunlight, a variable vortex region would lead to a significant variability in the in-vortex NO2 not attributed to downward transport or midterm chemical processes. Also, with a 65° equivalent latitude we assure that the vortex at lower altitudes is fully included (see Figure 1 of Orsolini et al. [2005]).

MIPAS observations show clear enhancements in the NO2 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) (Figure 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. NO2 mixing ratios then start to decrease, reaching typical values by the end of December. It is clearly seen that the maxima of NO₂ 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

Figure 6. Temporal evolution at selected potential temperatures of in-vortex (see text for details) Northern Hemisphere abundances of (a) NO₂, (b) O₃, and (c) CH₄ for the pre-SPEs 2002–2003 and post-SPEs 2003–2004 arctic winters. The major SPEs occurred 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 NO₂, have been displaced only for the first period (until 2 January). 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 section 2 for more details).
altitude range of 40–50 km is ~0.5 km/day which is qualitatively consistent with typical wintertime downward 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 20 November, 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 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.

[29] The decline in the NO$_2$ 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$_4$ (Figure 6c). CH$_4$ abundances start increasing around mid-December, a few days earlier at lower altitudes, thus showing that midlatitude air masses have been transported into the polar region.

[30] 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 Figure 6a) were measured on 17 February 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 Figure 9 of Angell et al. [2004]). This cold middle and upper-stratosphere air would favor 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$_4$ (Figure 6c). CH$_4$ concentrations are very low in the middle 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).

[31] 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$_2$ 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 downward transport facilitated by the strong upper stratospheric vortex during February and March. MIPAS NO$_2$ data, version 4.62, which 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 (M. López-Puertas et al., The variability of stratospheric and mesospheric NO$_x$ in the arctic and antarctic 2002–2004 polar winters, in preparation for Space Science Reviews, 2005, hereinafter referred to as López-Puertas et al., submitted manuscript, 2005). This enhancement persisted for about 1 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 October/November 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., 2005a, 2005b]. 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 section 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 Figure 2). However, 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 index, $A_p$, the production of NO$_2$ from 11 November until mid-December was twice that produced during the October/November solar storm. All this then suggests that the major part of the NO$_3$ observed in the second half of January in the lower mesosphere was originated during the winter after the October/November solar storm. This is more in favor of Randall et al. [2005] suggestions than those reported by Natarajan et al. [2004].

[33] The O$_3$ abundances are closely anticorrelated with those of NO$_3$ (Figure 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 ($\Theta = 2500$ 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$_2$ abundances. The dynamical contribution to this loss, i.e., downwelling of O$_3$-poor air, seems to be small since CH$_4$ abundances show nearly constant values ($\Theta = 1000, 1750$ K), or significantly increase ($\Theta = 1250$ K) during this period.

[34] 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 midlatitude air significantly recovered much of the O$_3$ loss.

[35] In comparison with the previous winter, the in-vortex NH O$_3$ abundances in early November at $\Theta = 1000$ 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 $\Theta = 1250$ K, for the whole period from early November until mid-December at $\Theta = 1750$ K, and for a shorter period just after the SPEs at the higher altitudes of $\Theta = 2500$ K. Only at lower altitudes ($\Theta = 1000$ 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.

[36] 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 $\Theta = 1750$ 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 $\sim 1500$ K were not observed by MIPAS because it stopped taking measurements before the NO$_x$ enhancements reach these levels.

[37] 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 downward 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 (Figure 6a and López-Puertas et al. (submitted manuscript, 2005)), 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

[38] 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 midterm 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.

[39] 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 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 $\sim 50$ km) where it is not easily photochemically destroyed in the presence of sunlight. The opposite occurs in the SH summer polar region, where NO is photolyzed above the stratosphere and also the locally produced NO is slowly moved upward (above about 50 km) where it is more easily photolyzed.

[40] An increase in mean NO$_x$ abundance between 20 to 70 ppbv occurred in the NH polar cap, lasting for at least 2 weeks. In the SH the NO$_x$ enhancement is between 10 and 35 ppbv and it is halved after 2 weeks.

[41] 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 2 weeks after the SPEs due to enhanced NO$_x$. In the SH polar region, the
maximum percentage depletion, associated with HOx 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.

[41] The MIPAS data of NO2, O3, and CH4 in the upper stratosphere arctic region for the November 2003 to March 2004 period were also analyzed. 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 NOx were produced in the middle and upper stratosphere and in the lower mesosphere, first locally and later by downward transport. This period terminated with the stratospheric warming that occurred in mid-December and redistributed the NOx to midlatitudes. In this period, a significant depletion of O3 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 NO2 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 NOx 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.

[42] Overall, MIPAS has captured, with global coverage, both short-term and midterm effects of NOx and O3 abundance changes caused by the SPEs. MIPAS also measured an additional number of NOy species, which also showed significant enhancements during and after the SPEs, and are reported in a companion paper [López-Puertas et al., 2005]. 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 NOy 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 downward transport in the polar winter regions.

[43] Acknowledgments. The IAA team has been supported by Spanish Ministerio de Educacion y Ciencia under projects RE001-3249/CLI and ESP2004–01556, EC FEDER funds, and by the European Community Marie Curie Host Fellowship HPMD-CT-2000-40 (SIESTA). IMK was partially supported by German projects SACADA (07ATF53) and KODYACS (07ATF43).

[44] Arthur Richmond thanks Miriam Sinnhuber and another reviewer for their assistance in evaluating this paper.

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