

## HNO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, and ClONO<sub>2</sub> enhancements after the October–November 2003 solar proton events

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Received 7 February 2005; revised 17 June 2005; accepted 29 June 2005; published 30 September 2005.

[1] The large solar storm in October–November 2003 produced enormous amounts of high-energy protons which reached the Earth and penetrated into the middle atmosphere in the polar regions. At this time, the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) on board the Environmental Satellite (ENVISAT) was observing the atmosphere in the 6–68 km altitude range. MIPAS observed significant enhancements of the NO<sub>y</sub> components HNO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, and ClONO<sub>2</sub> in the northern polar stratosphere after the intense solar proton events. Two distinct HNO<sub>3</sub> enhancements were observed. An instantaneous increase of 1–2 ppbv was observed immediately after the SPEs and is attributed to gas-phase chemistry: NO<sub>2</sub> + OH + M → HNO<sub>3</sub> + M, accelerated by SPE-produced excess OH. A very large second increase of 1–5 ppbv started around 10 November and lasted until the end of December. It is attributed to NO<sub>x</sub> (NO + NO<sub>2</sub>) produced in the mesosphere during the major SPEs in late October/early November and then transported downward during November and December, partially converted to N<sub>2</sub>O<sub>5</sub> in the upper stratosphere, which finally formed HNO<sub>3</sub> via ion cluster reactions. N<sub>2</sub>O<sub>5</sub> was observed to increase by 0.1–0.4 ppbv 1–3 days after the major SPEs and reached down to 30 km altitude. A second, more pronounced N<sub>2</sub>O<sub>5</sub> enhancement of up to 1.2 ppbv at 40 km appeared about 12–13 days after the major SPEs. With a delay of 1–2 days after the major SPEs ClONO<sub>2</sub> increased by up to 0.4 ppbv (40%) at 32 km altitude. NO<sub>y</sub> enhancements in the Southern Hemisphere were generally less pronounced.

**Citation:** López-Puertas, M., B. Funke, S. Gil-López, T. von Clarmann, G. P. Stiller, M. Höpfner, S. Kellmann, G. Mengistu Tsidu, H. Fischer, and C. H. Jackman (2005), HNO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, and ClONO<sub>2</sub> enhancements after the October–November 2003 solar proton events, *J. Geophys. Res.*, 110, A09S44, doi:10.1029/2005JA011051.

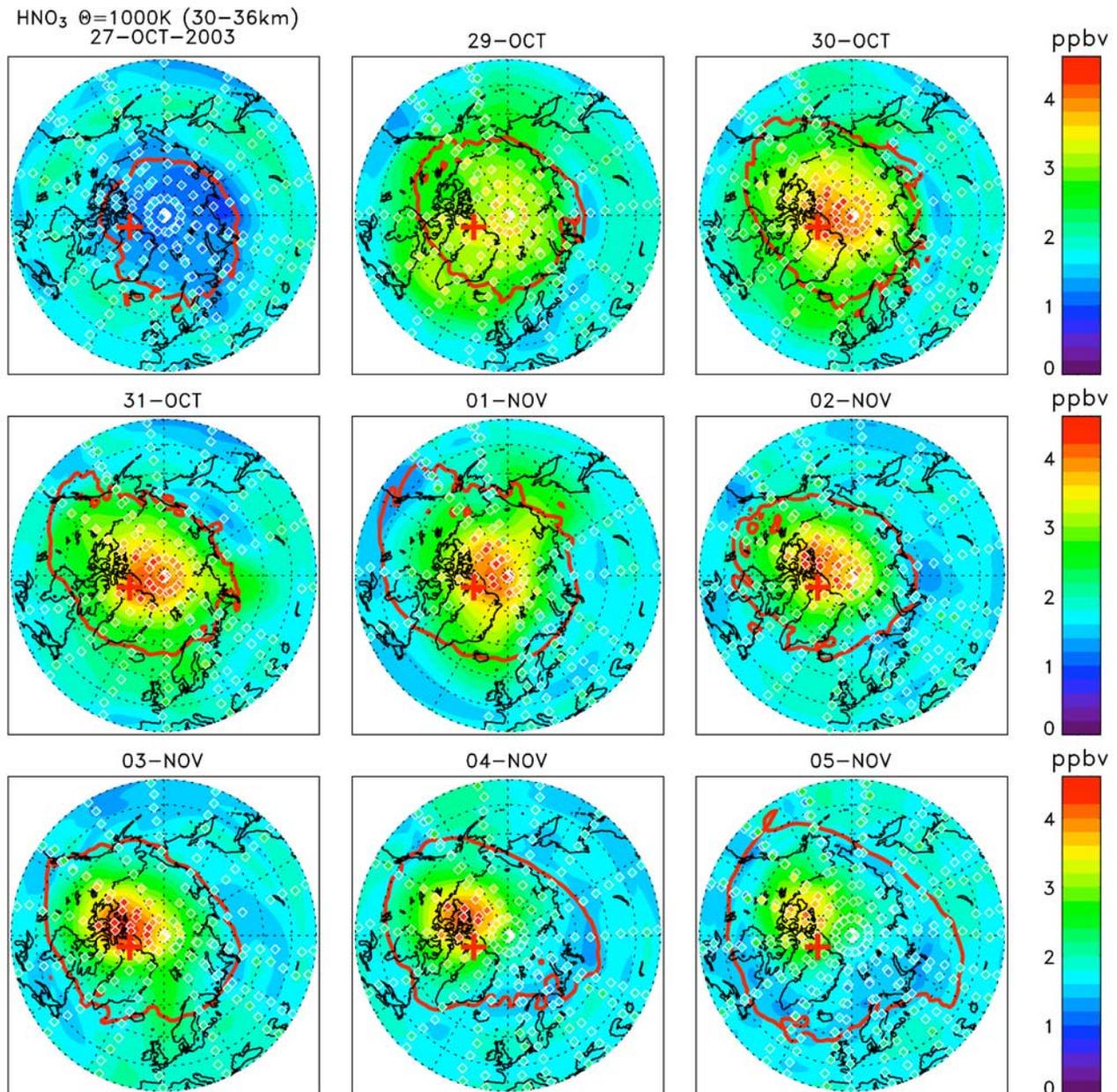
### 1. Introduction

[2] Solar proton events (SPEs) have important effects on the composition of the stratosphere and mesosphere in the polar regions (see, e.g., Jackman and McPeters [2004] for a recent review).

[3] Models predict that besides perturbations of NO<sub>x</sub> (NO + NO<sub>2</sub>), also other NO<sub>y</sub> species as, for example, nitric acid (HNO<sub>3</sub>), dinitrogen pentoxide (N<sub>2</sub>O<sub>5</sub>), and chlorine nitrate (ClONO<sub>2</sub>), should be enhanced in the stratosphere after strong solar proton events [Solomon *et al.*, 1981; Brasseur and Solomon, 1986; Solomon, 1999; Jackman and McPeters, 2004]. These species are part of the reservoir

of the reactive nitrogen oxides in the stratosphere. They are photochemically linked among themselves and with NO and NO<sub>2</sub> and hence play a very important role in the processes controlling the ozone abundance [see, e.g., Solomon, 1999]. It is therefore important to know their distributions in the stratosphere as well as to understand their sources and sinks. Enhancements in these species are predicted to occur after SPEs because of the increase in NO<sub>x</sub> and also through catalytic cycles involving ion chemistry in the absence of sunlight.

[4] During late October and early November 2003, three active solar regions produced solar flares and solar energetic particles of extremely high intensity, the fourth largest event observed in the past 40 years [Jackman *et al.*, 2005a, 2005b]. Some of the Geostationary Operational Environmental Satellite (GOES)-11 instruments measured very



**Figure 1.** Northern Hemisphere distributions of HNO<sub>3</sub> (in ppbv, parts per billion by volume) for days from 27 October to 14 November 2003 at a potential temperature ( $\Theta$ ) level of 1000 K ( $\sim$ 35 km). 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 plus sign.

large and energetic proton fluxes (<http://sec.noaa.gov/Data/goes.html>; see also Figure 1 of López-Puertas *et al.* [2005]), which can penetrate the atmosphere down to the lower stratosphere in the polar regions [Jackman *et al.*, 2005a, 2005b].

[5] Global changes in many NO<sub>y</sub> species were observed by MIPAS over both the North and South Poles. While in a companion paper [López-Puertas *et al.*, 2005] we discuss perturbations in NO, NO<sub>2</sub>, and O<sub>3</sub>, we focus here on the alterations observed in HNO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, and ClONO<sub>2</sub> abundances during and after the major SPEs of this period, from

25 October to 14 November 2003. To our best knowledge, these measurements constitute the first experimental evidence of enhancements in these NO<sub>y</sub> species caused by solar proton events. Only Orsolini *et al.* [2005] has very recently reported HNO<sub>3</sub> enhancements also using MIPAS measurements. HNO<sub>3</sub> enhancements have also been reported by Kawa *et al.* [1995], de Zafrá *et al.* [1997], and Santee *et al.* [2004] but not in the context of SPEs. This paper is focused on the description of the changes of those species and discusses possible processes originating the changes. In subsequent studies, the data set presented here

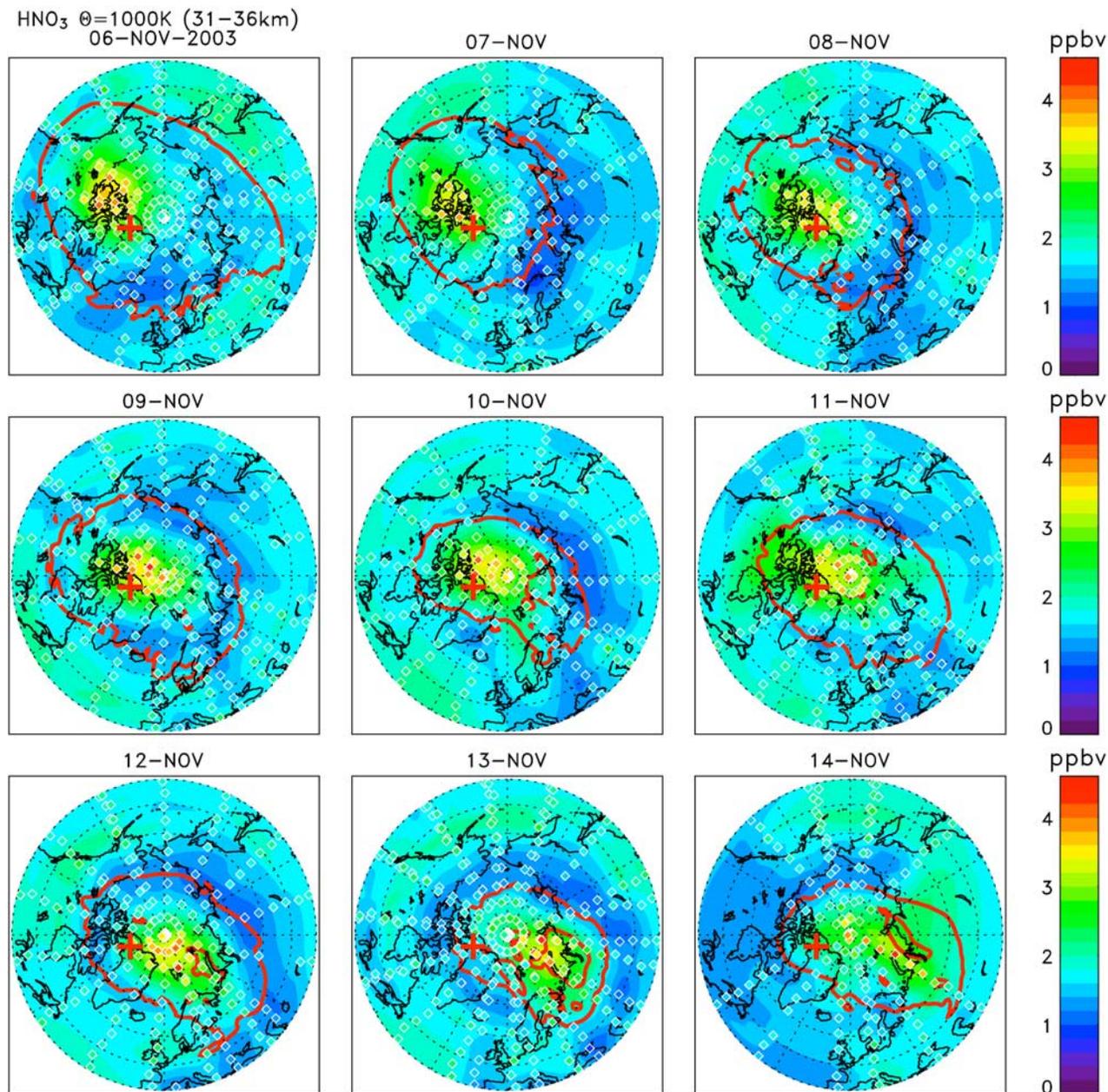


Figure 1. (continued)

is intended to be used for sensitivity studies with chemical transport models in order to better quantify the relative importance of the various reaction pathways.

## 2. MIPAS Data

[6] Details about the satellite orbit, the instrument, and the observation scenario are given in the companion paper [López-Puertas *et al.*, 2005]. MIPAS measured limb radiance spectra with high spectral resolution ( $0.05\text{ cm}^{-1}$ ) in a wide spectral range (4.1 to  $14.7\text{ }\mu\text{m}$ ), thus offering the opportunity to infer abundances of many species, including those of HNO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, and ClONO<sub>2</sub> analyzed here. The retrieval of these species was performed with the IMK-IAA data processor [von Clarmann *et al.*, 2003]. Details of the retrieval approach are given by von Clarmann *et al.* [2003].

In the following we summarize aspects relevant to the retrieval of HNO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, and ClONO<sub>2</sub>.

[7] Details of the retrieval of HNO<sub>3</sub> are described by Mengistu Tsidu *et al.* [2005]. HNO<sub>3</sub> was retrieved from its infrared emission originating from its  $\nu_5$  and  $2\nu_9$  bands in the 10–56 km region with a vertical resolution of about 3.5 km. Noise errors are smaller than 10% below about 35 km increasing up to about 50% at 45 km. Errors in ancillary information are of similar magnitude to the noise errors and are dominated by the uncertainties in the spectroscopic data and in pointing information.

[8] The retrieval method and characteristics of N<sub>2</sub>O<sub>5</sub> inverted from MIPAS are described by Mengistu Tsidu *et al.* [2004]. N<sub>2</sub>O<sub>5</sub> is retrieved from its infrared emission in the  $\nu_{12}$  band in the spectral range from  $1239\text{--}1236\text{ cm}^{-1}$ . The vertical resolution is 4 km at 30–40 km and 6–8 km

below 30 km and at 40–50 km. The noise error is better than 5% in the altitude range of 10–35 km, while steadily rising to above 40% at 50 km for unperturbed conditions, but better in our case. The systematic errors are within 10–30% at 20–35 km and increase up to 50% outside this region.

[9] The retrieval of ClONO<sub>2</sub> from MIPAS spectra has been described by Höpfner *et al.* [2004]. ClONO<sub>2</sub> has been retrieved from the infrared emission in the Q branch of its  $\nu_4$  band in the 779.5–781.0 cm<sup>-1</sup> spectral region. It is derived in the 15–40 km region with a vertical resolution varying from 3.5 km below 30 km and steadily increasing to 7 km at 40 km. Noise error is better than 10% below 30 km and below 15% at other altitudes. The systematic errors are between 3% and 9% and are dominated by spectroscopic uncertainties.

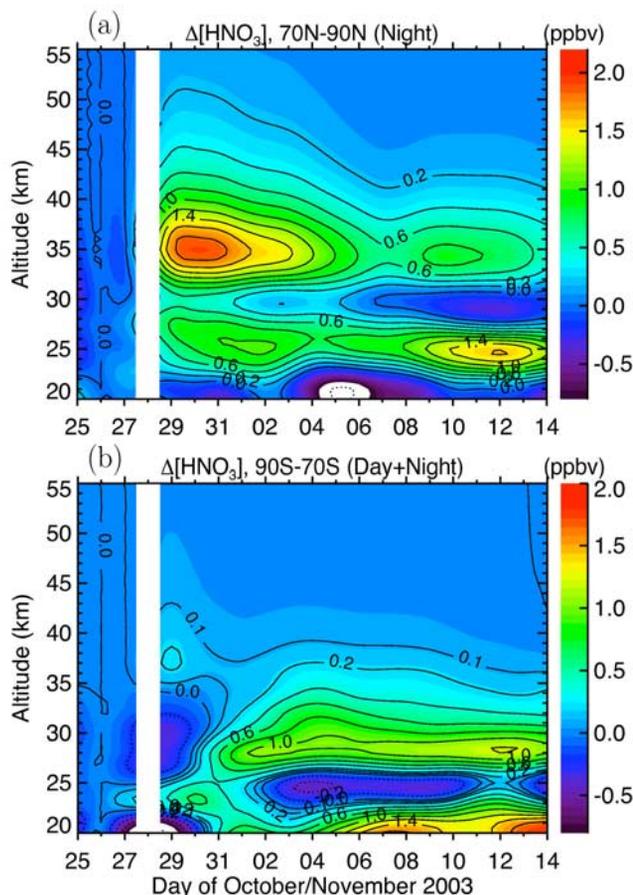
[10] IMK-IAA MIPAS data of 25 October to 14 November have been used in this work, including nearly 10,000 elevation scans. In addition, the off-line (reprocessed) MIPAS data (version 4.61) for HNO<sub>3</sub> vmr profiles for the arctic polar winters of 2002–2003 and 2003–2004 were used since, contrary to the episode-based scientific MIPAS-IMK-IAA data, these data were available for a longer period. For more details on the data sets and the improvements of the IMK-IAA data with respect to ESA operational MIPAS data set, see section 2 in the companion paper [López-Puertas *et al.*, 2005].

### 3. HNO<sub>3</sub> Enhancement

[11] Figure 1 shows the temporal evolution of the HNO<sub>3</sub> distribution at a potential temperature level of  $\Theta = 1000$  K for the period of 27 October to 14 November 2003, i.e., from the day before the major solar proton event (SPE) to about 2 weeks after (see Figure 1 of López-Puertas *et al.* [2005]). The effects on HNO<sub>3</sub> abundances are clearly seen. The enhancement commences on 29 October, just after the major SPE (see Figure 1 of López-Puertas *et al.* [2005]), and it is centered around the north geomagnetic pole. The maximum HNO<sub>3</sub> abundance is reached on 30 October when values above 4 ppbv are observed. This represents enhancements of  $\sim 2$  ppbv, that is, a 100% increase. HNO<sub>3</sub> abundances remain at high values until around 3–4 November (significant SPEs occurred until 2 November) and then slowly decline with time.

[12] Although the changes in HNO<sub>3</sub> are well correlated in time with the occurrence of SPEs, thus suggesting they were caused by the SPEs, the evolution of the incipiently formed polar vortex was checked with MIPAS CH<sub>4</sub> data in order to discard that abrupt changes in its evolution caused the HNO<sub>3</sub> perturbations. No evidence of a sudden change in the polar vortex on 29 October or close days is observed in the CH<sub>4</sub> fields [see also López-Puertas *et al.*, 2005]. Hence we conclude that the changes observed in HNO<sub>3</sub> are caused by the advents of SPEs.

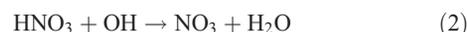
[13] Figure 2a shows the time evolution of HNO<sub>3</sub> changes as a function of altitude during this period for the 70°N–90°N (geographic) polar cap. It is observed that the maximum absolute change occurs at around 35 km and that significant enhancements also take place in the region between 30 and 50 km. This time series shows more clearly the correlation of HNO<sub>3</sub> abundance perturbation and the occurrence of SPEs. HNO<sub>3</sub> enhancements take place just after the SPEs. The large

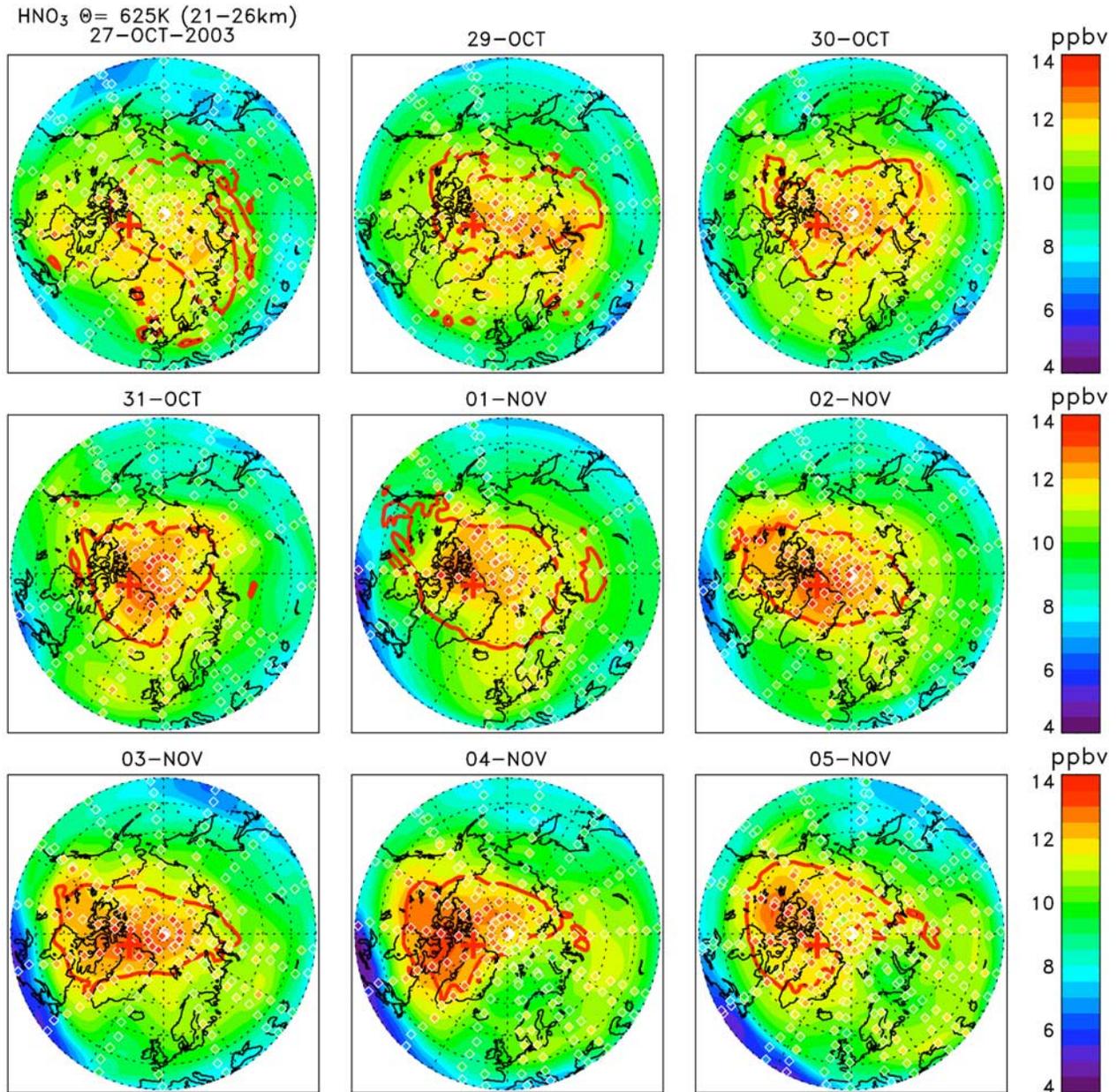


**Figure 2.** Temporal evolution of MIPAS HNO<sub>3</sub> abundance changes during and after the October–November 2003 solar proton events for the (a) Northern Hemisphere (70°N–90°N) and (b) Southern Hemisphere (70°S–90°S) (geographic) polar caps. Changes are shown relative to the mean profile measured on 26 October. The white band around 28 October represents lack of data due to MIPAS not observing at the 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. The number of profiles measured for each day varies between 400 and 900. An area-weighting factor (cosine of latitude) has been applied.

HNO<sub>3</sub> changes observed from 29 October through 1 November are correlated with the two large SPEs on 28 and 29 October (see Figure 1 of López-Puertas *et al.* [2005]). Also the small increase in HNO<sub>3</sub> on 3 November is correlated with the large SPE that occurred early on 2 November. From these days, HNO<sub>3</sub> at these altitudes (around 35 km) slowly returns to background values.

[14] This sudden enhancement in HNO<sub>3</sub> abundance after the SPEs suggests that it is produced by gas-phase chemistry. The major gas phase reactions where HNO<sub>3</sub> is involved are



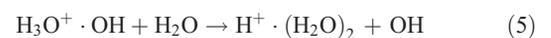
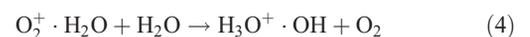


**Figure 3.** As Figure 1 but for a potential temperature level of altitude of  $\Theta = 625\text{ K}$  ( $\sim 25\text{ km}$ ).

Reaction (1) is the major production process. It is fast enough to produce an HNO<sub>3</sub> enhancement similar to that observed and faster than the loss processes (reactions (2) and (3)). Since loss of HNO<sub>3</sub> by reaction with OH (reaction (2)) is slower than photodissociation, some of the HNO<sub>3</sub> enhancement could be caused by an increase of OH, NO<sub>2</sub>, or both. The solar proton events can produce enhancements of both OH and NO<sub>2</sub> [see, e.g., *Jackman and McPeters, 2004*]. Indirect evidence of the increase in OH during this SPE through O<sub>3</sub> depletion and through enhancement of HOCl have been reported by *López-Puertas et al. [2005]* and *von Clarmann et al. [2005]*, respectively. *López-Puertas et al. [2005]* have shown that NO<sub>2</sub> decreases by about 2–3 ppbv in the 30–40 km region on 29 and 30 October, i.e., the first 2 days after the major SPEs, the region and time where HNO<sub>3</sub> shows its major increase of

about 1–2 ppbv. It then seems that at least some of the HNO<sub>3</sub> increase is produced through reaction (1) caused by an increase of OH in the 30–40 km region during 29 and 30 October. As a consequence of this process, NO<sub>2</sub> is depleted in this region and time, opposite to the enormous increase that occurs at higher altitudes and subsequent times [*López-Puertas et al., 2005*].

[15] HNO<sub>3</sub> might also be enhanced after SPEs through ion chemistry. *Solomon et al. [1981]* proposed the following pathway for producing HO<sub>x</sub> through ion recombination in the stratosphere,



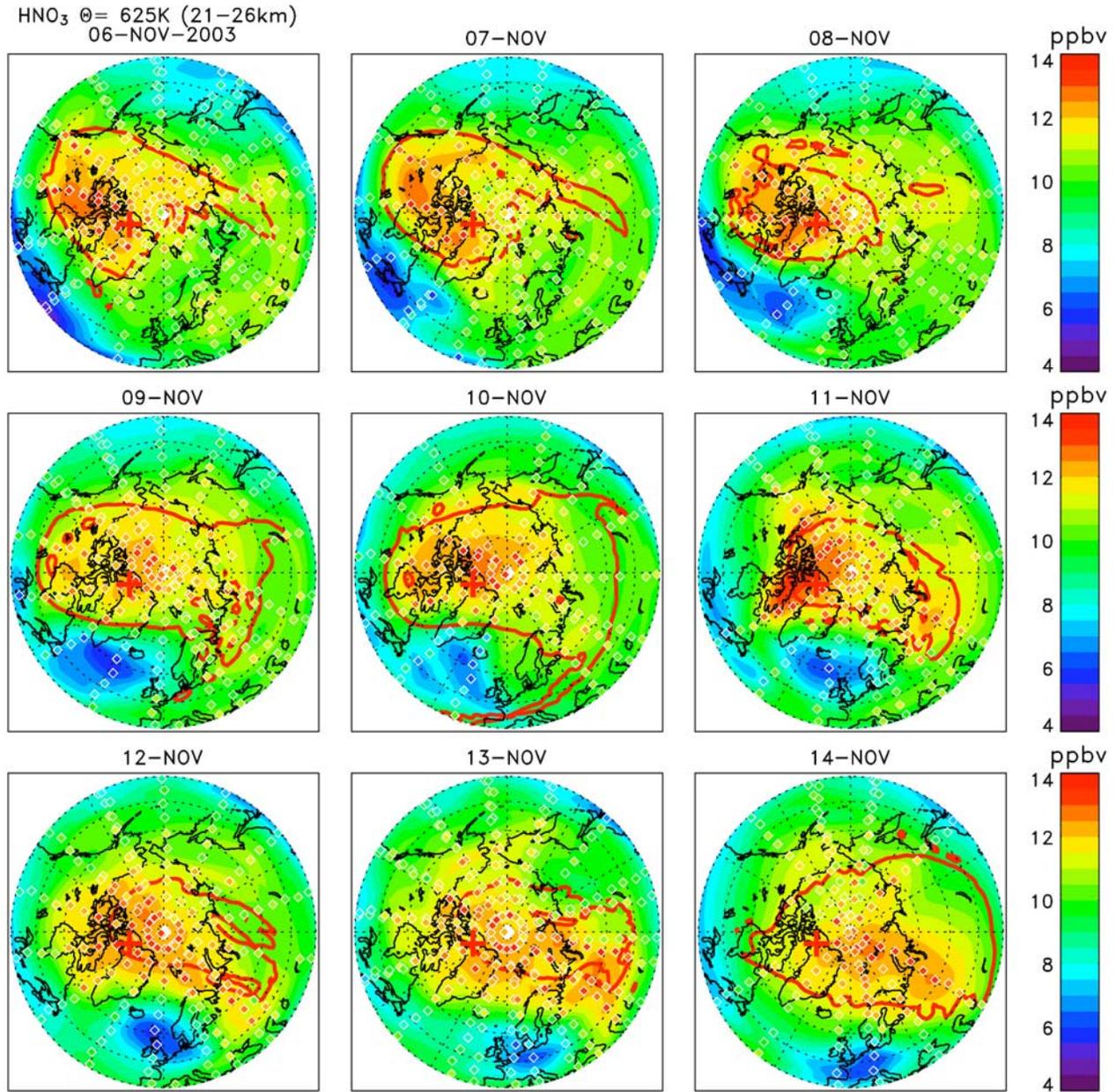
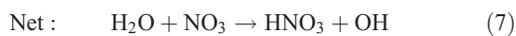


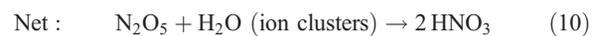
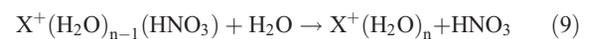
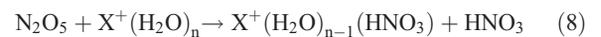
Figure 3. (continued)



where net HNO<sub>3</sub> is produced under dark conditions. This process requires the production of NO<sub>3</sub><sup>-</sup>. The dominant process for the production of NO<sub>3</sub><sup>-</sup> in the stratosphere is through CO<sub>3</sub><sup>-</sup> + NO<sub>2</sub> → NO<sub>3</sub><sup>-</sup> + CO<sub>2</sub> [Brasseur and Solomon, 1986], which also constitutes a loss of NO<sub>2</sub>.

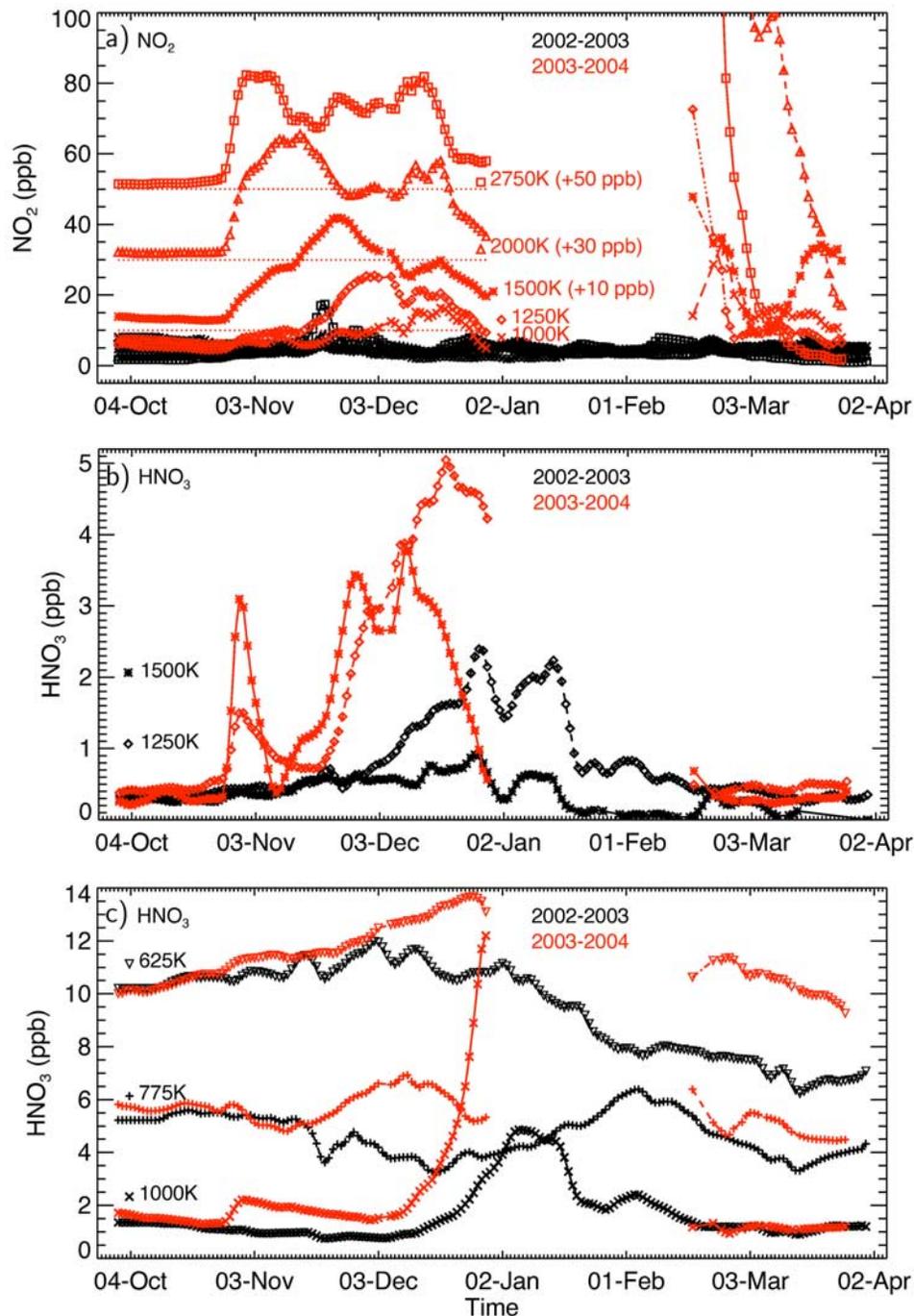
[16] Still another mechanism for producing HNO<sub>3</sub> involving ion chemistry was first proposed by Böhlinger *et al.* [1983] and was applied in modeling and data analysis

studies [e.g., Kawa *et al.*, 1995; de Zafra and Smshtyaev, 2001]. This mechanism involves N<sub>2</sub>O<sub>5</sub> and is given as



This mechanism requires HNO<sub>3</sub> to be formed at the expense of N<sub>2</sub>O<sub>5</sub>. Our observations indicate, however, a slow enhancement of N<sub>2</sub>O<sub>5</sub> after the SPEs (see Figure 5).

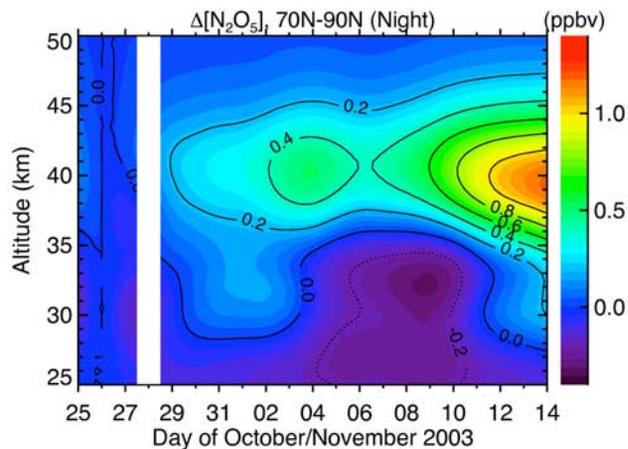
[17] Hence the scheme above involving ion chemistry (equations (4)–(7)) and reaction (1) will both lead to HNO<sub>3</sub>



**Figure 4.** Temporal evolution at selected potential temperatures of in-vortex (see text for details) Northern Hemisphere abundances of (a) NO<sub>2</sub> and (b and c) HNO<sub>3</sub> for the pre-SPEs 2002–2003 and post-SPE 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 represents a period with no data available at this time. Some of the time series for NO<sub>2</sub> for 2003–2004 in the period of October/January have been displaced, as shown, for clarity. The data in this figure are from the MIPAS off-line (reprocessed) 4.61 version retrieved by ESA [Ridolfi *et al.*, 2000; Carli *et al.*, 2004]. See section 2 in the companion paper of López-Puertas *et al.* [2005] for more details.

production and NO<sub>2</sub> depletion, as has been observed in the 30–40 km region during the first 2 days after the major SPEs. Whether this ion chemistry scheme contributes significantly to HNO<sub>3</sub> enhancement or process 1 alone can explain the

observed enhancement is still an open question. Production via ion cluster chemistry (equations (8)–(10)) is unlikely since the conversion from N<sub>2</sub>O<sub>5</sub> to HNO<sub>3</sub> through this mechanism will take at least 2 weeks (G. P. Stiller *et al.*, An



**Figure 5.** Temporal evolution of N<sub>2</sub>O<sub>5</sub> in the northern (70°N–90°N) polar cap. See caption of Figure 2 for more details.

enhanced HNO<sub>3</sub> second maximum in the Antarctic mid-winter upper stratosphere 2003, submitted to *Journal of Geophysical Research*, 2005, hereinafter referred to as Stiller et al., submitted manuscript, 2005). In addition, N<sub>2</sub>O<sub>5</sub> should quickly decrease, while MIPAS observed even a slow enhancement (see section 5 below).

[18] Once HNO<sub>3</sub> is produced just after the SPEs, it is expected to only slowly decrease. The major HNO<sub>3</sub> loss occurs through photolysis (reaction (3)) but this is rather slow (photolysis lifetime is about 1 week for noontime midlatitude conditions) and most of the 70–90°N (geographic) polar cap is in the dark during this period. The smaller enhancement on 7 November could be due to dynamical effects or nonuniform sampling, since the time series for the CO vmr also shows a significant decrease at this day (see Figure 4f of López-Puertas et al. [2005]).

[19] Changes in HNO<sub>3</sub> just after the major SPEs and in the subsequent days are also observed below 30 km with a maximum change around 25 km. The surface plot at a potential temperature level of  $\Theta = 625$  K ( $\sim 25$  km) (Figure 3) shows a rather good spatial correlation with the enhancement at  $\Theta = 1000$  K ( $\sim 35$  km) (Figure 1), at least during the first days after the major SPEs, suggesting that these changes are caused by the SPEs. A comparison of HNO<sub>3</sub> in this period inside the vortex with the values measured by MIPAS in the previous winter, when no significant SPEs had appeared, is shown in Figures 4b and 4c. The enhancement over the 2002–2003 winter just after the SPEs is very clear at the 1500 K ( $\sim 42$  km), 1250 K ( $\sim 38$  km), and 1000 K ( $\sim 35$  km) potential temperatures, the latter persisting at least until the end of December. At the 775 K level ( $\sim 30$  km) a small increase is also seen after the SPEs, although only lasting a few days. At lower altitudes, 625 K ( $\sim 25$  km), we observe an increase just after the solar storms and HNO<sub>3</sub> vmrs remaining always larger than in the previous winter at least until the end of December. Current models estimate that most energetic protons do not have energy enough to penetrate below 30 km [Jackman et al., 2005b]. Also the temporal evolution at 625 K is rather different from that at 1000 K. We cannot unambiguously show that the changes at the 625 K level are caused by the SPEs.

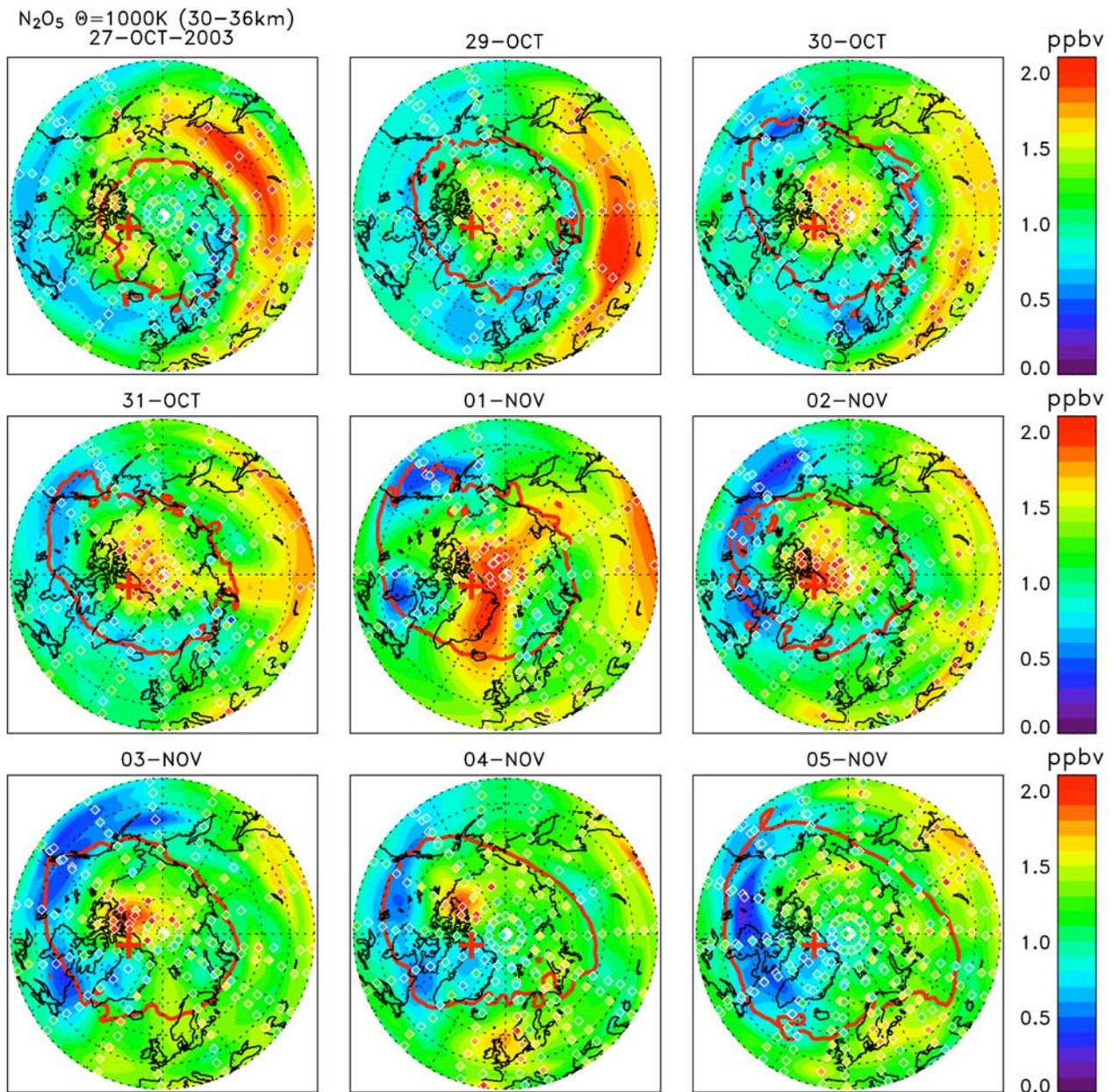
[20] The changes observed in NO<sub>x</sub> and O<sub>3</sub> in the Southern Hemisphere are much smaller than in the Northern Hemisphere [López-Puertas et al., 2005]. We would then expect also smaller changes, if any, in the NO<sub>y</sub> species studied here. Figure 2b shows the temporal evolution for HNO<sub>3</sub> in the Southern Hemisphere. The major change is observed in the region between 27 and 40 km. An inspection of the surface plots at these altitudes has shown that the polar vortex was very weak and at least part of the enhancement observed between 25 and 35 km are due to intrusion of HNO<sub>3</sub>-rich air from midlatitudes. Thus maximum changes due to SPEs are around 0.2 ppbv and confined to above  $\sim 35$  km, which are much smaller than those observed in the Northern Hemisphere.

#### 4. Midterm HNO<sub>3</sub> Enhancements

[21] Enhancements in HNO<sub>3</sub> from late November 2003 to 7–8 January 2004 in the northern polar region from MIPAS near-real time data have been reported by Orsolini et al. [2005]. In this section we describe the in-vortex HNO<sub>3</sub> measured by MIPAS during the post-SPE Arctic winter 2003–2004 (November 2003 to March 2004) and compare with the previous 2002–2003 arctic winter, when no significant SPEs took place. In this study we discuss the instantaneous increase of HNO<sub>3</sub> in the context of the whole winter and compare the HNO<sub>3</sub> development with the previous northern winter 2002–2003.

[22] Figures 4b and 4c show the time series for in-vortex Northern Hemisphere abundances of HNO<sub>3</sub> (b and c) as measured by MIPAS (off-line data, version 4.61). The time series for in-vortex NO<sub>2</sub> (shown in the work of López-Puertas et al. [2005]) was adapted here to show the strong correlation between NO<sub>2</sub> and HNO<sub>3</sub>. The vortex was assumed as the region where the equivalent latitudes were greater than 65°. For more details on these calculations, see section 5 in the work of López-Puertas et al. [2005]. The sudden increase in HNO<sub>3</sub> on 29 October, following the major SPEs, is apparent at potential temperature levels from 1500 K down to 1000 K. At lower levels a small increase is also noted. As explained in the previous section, this sudden increase is mainly produced by gas-phase chemistry, which is fast enough to produce an HNO<sub>3</sub> enhancement on a timescale of 1 or 2 days after the immediate enhancement of OH produced by the SPEs. NO<sub>2</sub> is also quickly enhanced after the major SPEs by local production. It is produced after N<sub>2</sub> is dissociated by the charged particles, N reacts with O<sub>2</sub> to form NO which then produces NO<sub>2</sub> through the catalytic destruction of O<sub>3</sub> [see, e.g., Jackman and McPeters, 2004]. (See López-Puertas et al. [2005] for more details on the NO<sub>2</sub> enhancements.)

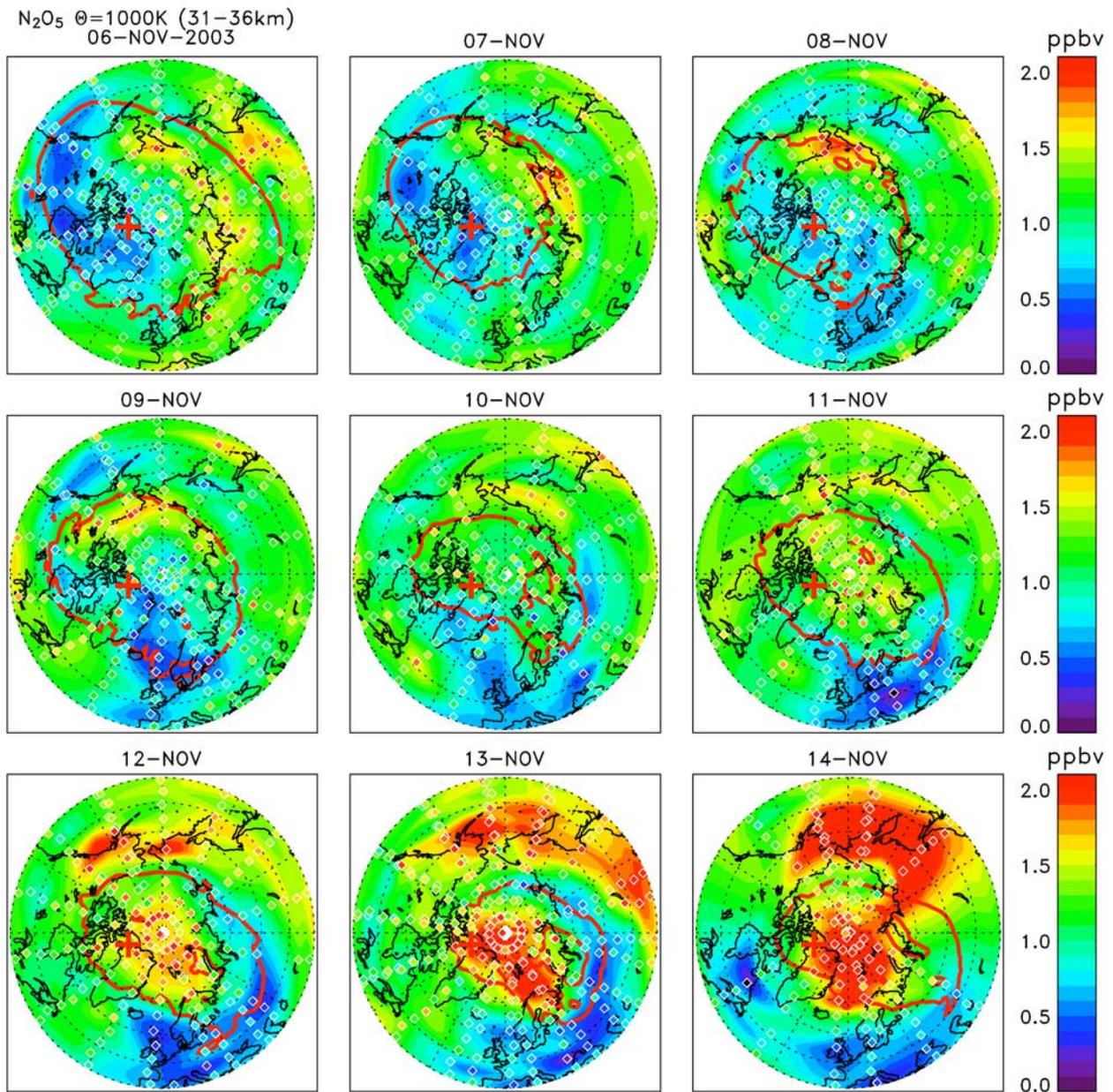
[23] We observe, after some decrease during November at the 1250 K and 1500 K levels, a further significant enhancement in HNO<sub>3</sub> at essentially all levels, during the second half of November and December with maxima around 10 December, 16 December, and 30 December for  $\theta$  levels of 1500 K, 1250 K, and 1000 K, respectively. Orsolini et al. [2005] have studied these enhancements and their correlations with NO<sub>2</sub> and the A<sub>p</sub> index and suggested that they were caused by energetic particles that induced a direct production of NO<sub>x</sub> in the upper stratosphere. From Figures 4 we note a correlation between the maxima in



**Figure 6.** Northern Hemisphere distributions of N<sub>2</sub>O<sub>5</sub> (in ppbv, parts per billion by volume) for days from 27 October to 14 November 2003 at a potential temperature ( $\Theta$ ) level of 1000 K ( $\sim$ 35 km). 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 plus sign.

HNO<sub>3</sub> at the different  $\Theta$  levels (1500, 1250, and 1000 K) and those in NO<sub>2</sub> but shifted approximately by about 2 weeks (maxima in NO<sub>2</sub> at those levels took place around 23 November, 1 December, and 18 December, while those in HNO<sub>3</sub> took place around 10 December, 16 December, and 30 December). This is the estimated time needed for producing HNO<sub>3</sub> from N<sub>2</sub>O<sub>5</sub> through the ion cluster reactions (equations (8)–(10)) (Stiller et al., submitted manuscript, 2005). The maximum at 1500 K that appeared around 28 November is not correlated to any of the two minor SPEs taking place on 20–23 November and 3–5

December. This seems more an apparent maximum caused by the lower abundances measured during 1–8 December in the continuous increase of HNO<sub>3</sub> from early November until mid-December. These lower values are likely produced by dynamically induced changes in the descending NO<sub>x</sub> or by excursions of the vortex to illuminated regions. We therefore think that the major part of these exceptionally high HNO<sub>3</sub> enhancements taking place between around 8 November until the end of December have their origin in the NO<sub>x</sub> produced in the mesosphere during the major SPEs in late October/early November, which was then

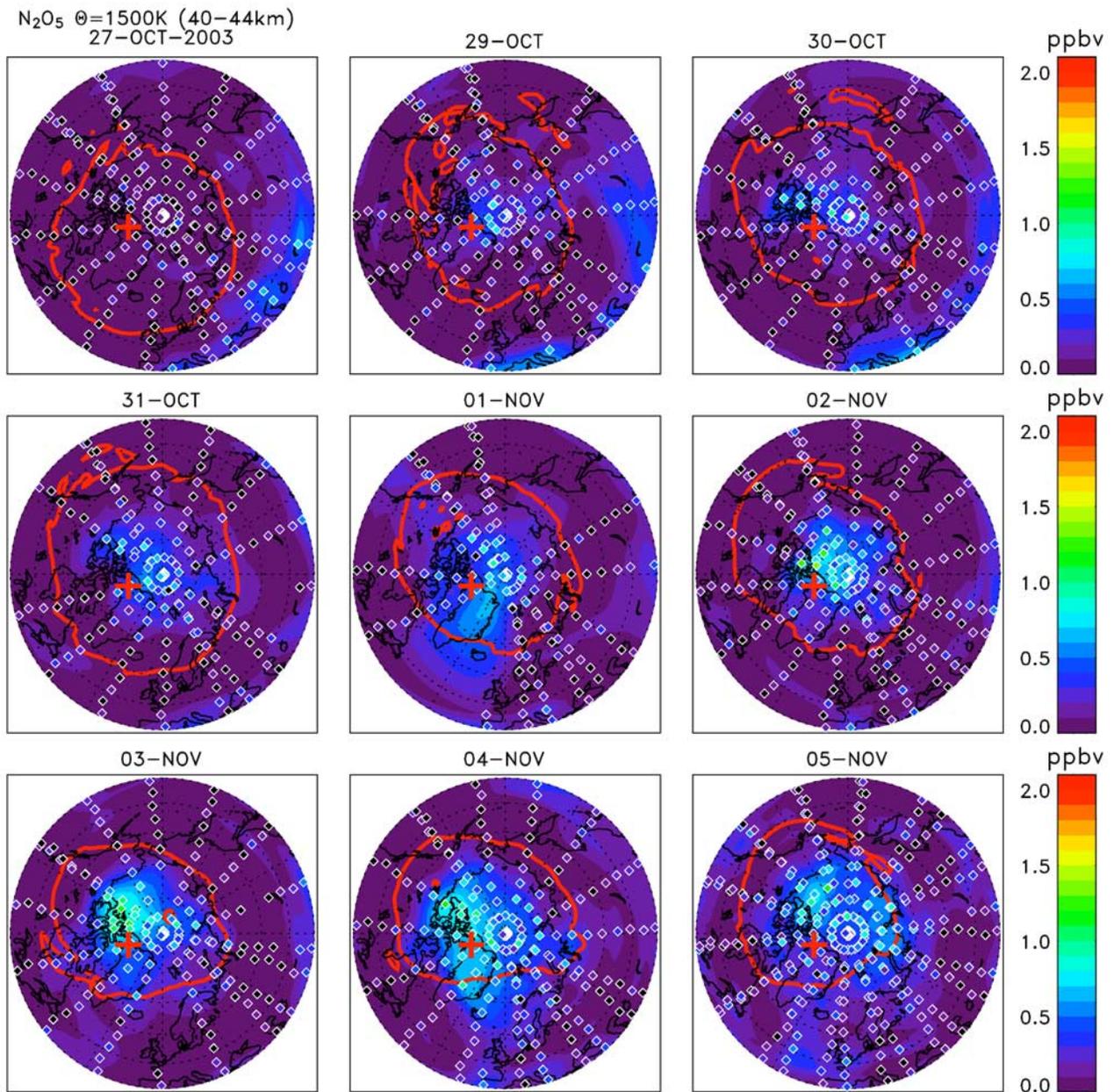


**Figure 6.** (continued)

transported downward through November and December, partially converted into N<sub>2</sub>O<sub>5</sub> in the upper stratosphere, and afterward into HNO<sub>3</sub> by heterogeneous ion-cluster reactions. The direct formation of HNO<sub>3</sub> in this period, e.g., locally by gas-phase chemistry triggered by the smaller SPEs that took place on 20–23 November and on 3–5 December, does not seem plausible: First, no instantaneous response to these minor SPEs over a wide altitude range was observed, in contrast to the October/November SPEs. Second, these SPEs were much weaker and fluxes of protons with energy below 10 MeV (that penetrate only down to 60 km) were two orders of magnitude smaller, and those with energy enough to penetrate into the upper stratosphere, e.g., 30–100 MeV [Jackman and McPeters, 2004] were only negligibly enhanced (<http://sec.noaa.gov/Data/goes.html>).

[24] Starting around 10 December, and depending on the altitude level, we see that the enhancements abruptly drop down (particularly at 1500 and 1250 K). These are in very close correlation with the decline in NO<sub>2</sub> enhancements and seem to be caused by the major stratospheric warming that took place at that time [see, e.g., Angell *et al.*, 2004; Manney *et al.*, 2005].

[25] In the period from mid-February until the end of March, NO<sub>2</sub> increased extraordinarily. HNO<sub>3</sub>, however, is not significantly enhanced at high altitudes (1500–1000 K). At this time substantial parts of the polar vortex were no longer in darkness, which is required to produce HNO<sub>3</sub> from NO<sub>x</sub> with heterogeneous ion-cluster chemistry. This seems to be the reason for the absence of HNO<sub>3</sub> enhancements even though extraordinary high amounts of NO<sub>x</sub> were



**Figure 7.** As Figure 6 but at a potential temperature ( $\Theta$ ) level of 1500 K ( $\sim 42$  km).

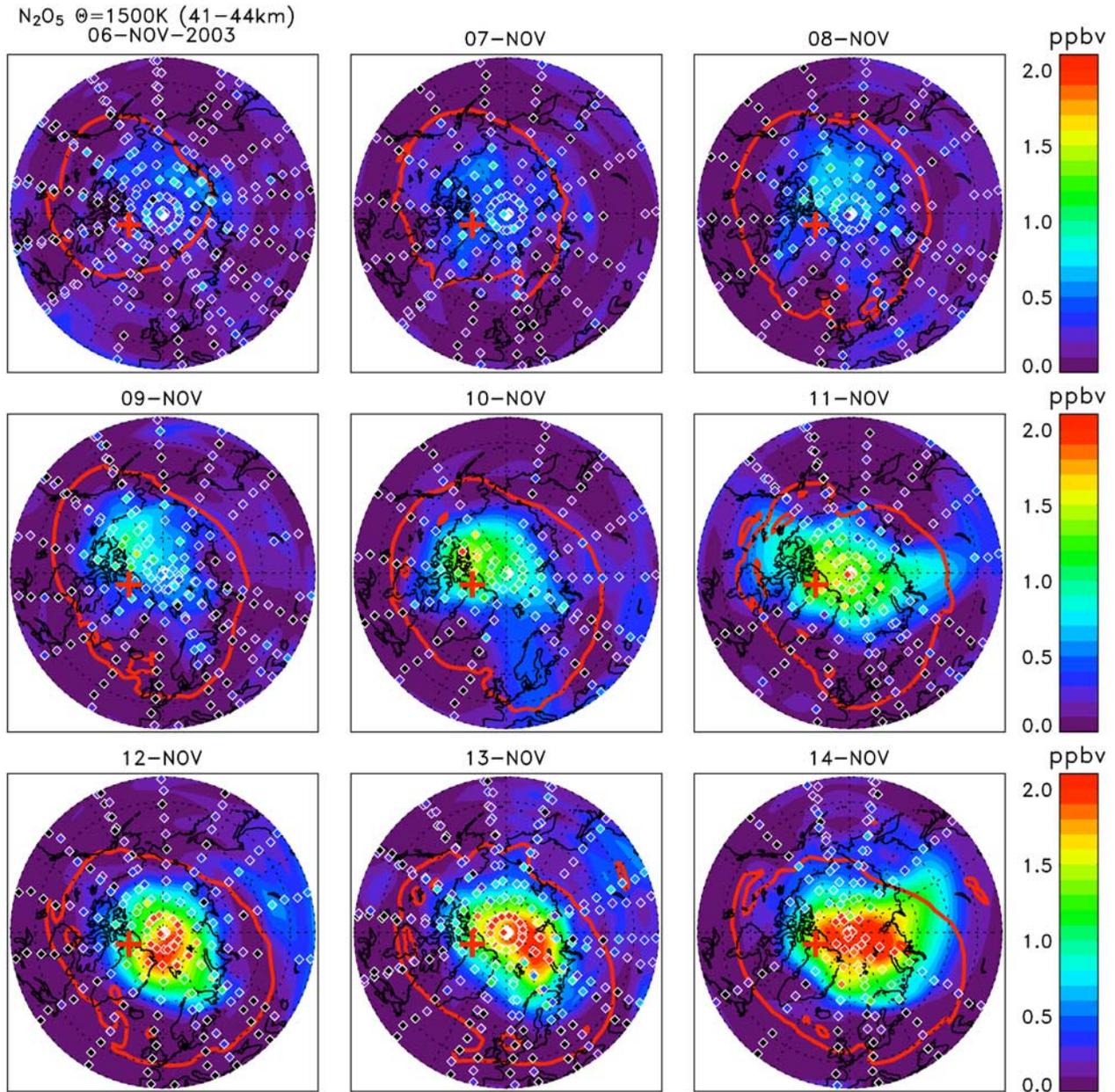
present (see Stiller et al. (submitted manuscript, 2005) for more details).

[26] At lower levels, 775 K and 625 K, we also observe much larger in-vortex HNO<sub>3</sub> values than in the previous winter after mid-November (775 K) and early December (625 K), extending to the end of the winter in late March. These differences are not expected to be caused by the SPEs nor by particle precipitation. Manney et al. [2005] have reported (Figure 1) that the area with temperatures below the NAT (nitric acid trihydrate) formation temperature at the 50 hPa level ( $\sim 20$  km) was much larger in the 2002–2003 NH arctic winter than in 2003–2004. Polar Stratospheric Cloud (PSC) formation obviously was much weaker in 2003–2004, then sequestration of HNO<sub>3</sub> in the PSCs was

smaller, and that would explain the higher midstratospheric HNO<sub>3</sub> abundances.

## 5. N<sub>2</sub>O<sub>5</sub> Enhancement

[27] Nitrogen pentoxide (N<sub>2</sub>O<sub>5</sub>) has also been observed to be affected by the solar proton events of October–November 2003. Figure 5 shows the temporal evolution for this species in the NH polar cap. The increase of N<sub>2</sub>O<sub>5</sub> abundance follows just after the SPE but, contrary to HNO<sub>3</sub>, it increases slowly, reaching its maximum toward the end of this period. The maximum enhancement is located at around 40 km in the whole period and varies with time from 0.5 (29 October) to 1.2 ppbv (14 November), about 20 to 60% of the prestorm



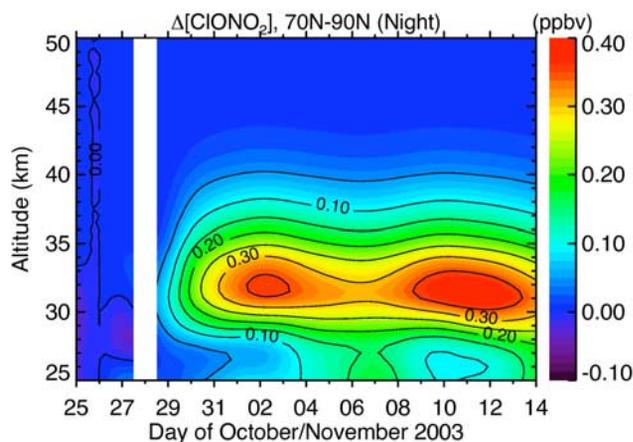
**Figure 7.** (continued)

value, which is well above the N<sub>2</sub>O<sub>5</sub> precision of  $\sim 0.5$ –1% for the mean profiles shown here [Mengistu Tsidu *et al.*, 2004]. The late occurrence of the maximum enhancement was expected on the basis of the currently known chemistry. N<sub>2</sub>O<sub>5</sub> is expected to increase after the NO<sub>x</sub> enhancement, but the subsequent partial conversion of NO<sub>x</sub> to N<sub>2</sub>O<sub>5</sub> through



takes several days. However it is expected from model calculations that the maximum change should appear around 7–8 November, about 1 week before the observed one. Hence the actual development of the enhancement is not completely clear, although it seems that dynamics played a significant role (see below) in its evolution.

[28] N<sub>2</sub>O<sub>5</sub> enhancements are visible in the surface distributions. Figures 6 and 7 show the N<sub>2</sub>O<sub>5</sub> distributions at potential temperature levels of  $\Theta = 1000$  K and 1500 K (approximately 35 and 40 km), respectively. Focusing on  $\Theta = 1000$  K, we note the emergence of a large increase in N<sub>2</sub>O<sub>5</sub> around the North Pole on 29 October, just after the major SPEs, which is rather large until 2–3 November, which then disappears but emerges again on 12 November. Its distribution at  $\Theta = 1500$  K (Figure 7) also shows an enhancement in N<sub>2</sub>O<sub>5</sub> near the North Pole on 29 October, although more incipient than at  $\Theta = 1000$  K. This enhancement increases slowly during the first 4 to 5 days, continues on (or slightly decreases) until 8–9 November, and then it quickly rises on 9–10 November to reach large values in the following days. It looks like there are two distinct enhancements, one appearing early



**Figure 8.** Temporal evolution of CIONO<sub>2</sub> in the northern (70°N–90°N) polar cap. See caption of Figure 2 for more details.

after the major SPEs and penetrating deep in the stratosphere, and a second one, larger, appearing about 12–13 days after.

[29] The first enhancement is consistent with those observed for HNO<sub>3</sub> and HOCl (see von Clarmann *et al.* [2005] for the latter). The data suggest that an increase in OH is produced, giving rise to an HNO<sub>3</sub> enhancement and an NO<sub>2</sub> depletion. The larger amount of HNO<sub>3</sub> in the presence of OH under dark conditions would lead to an increase in NO<sub>3</sub> and hence in N<sub>2</sub>O<sub>5</sub>.

[30] The second enhancement seems to be caused by a slow subsidence of NO<sub>x</sub>-rich air after 8 November since it appears earlier at higher altitudes ( $\Theta = 1500$  K), and about 3–4 days later at  $\Theta = 1000$  K. This is also noted in Figure 5 where the N<sub>2</sub>O<sub>5</sub> enhancement at 35–40 km steadily increases with time on 10–14 November and is consistent with the NO<sub>x</sub> subsidence shown in our companion paper [López-Puertas *et al.*, 2005].

[31] Some small enhancements have been observed for N<sub>2</sub>O<sub>5</sub> in the southern polar cap. An enhancement of 0.07 ppbv is observed in the nighttime profiles between 60–70°S at altitudes of 40–45 km on 29 and 30 October. In this polar cap there is only a small fraction of nighttime profiles compared to those in daytime. Hence the small changes observed in the SH are in consonance with theoretical expectations since the formed NO<sub>3</sub>, required to produce N<sub>2</sub>O<sub>5</sub> (reaction (11)) is very short-lived in the illuminated SH polar cap.

## 6. CIONO<sub>2</sub> Enhancement

[32] Following the chain of chemical processes, a larger abundance of NO<sub>2</sub> would also produce an enhancement in CIONO<sub>2</sub> through the reaction



[see, e.g., Brasseur and Solomon, 1986; Solomon, 1999; Jackman *et al.*, 2000]. MIPAS observations have confirmed these predictions, in particular in the NH polar stratosphere where CIONO<sub>2</sub> is largely enhanced (Figure 8). The maximum enhancement of CIONO<sub>2</sub> is centered in a

layer around 32 km with values of 0.4 ppbv, about 40%. This change is significant since the estimated random error in the daily mean profiles used in Figure 8 is  $\sim 0.5\%$  [Höpfner *et al.*, 2004]. The increase in CIONO<sub>2</sub> is slightly delayed by 1–2 days with respect to the major SPEs. This enhancement is consistent with the observed decrease in NO<sub>2</sub> by about 2–3 ppbv in the 30–40 km region on 29 and 30 October [see López-Puertas *et al.*, 2005]. These enhancements are, qualitatively, in agreement with known chemical processes [see von Clarmann *et al.*, 2005].

[33] To show CIONO<sub>2</sub> enhancements in more detail, we have plotted its surface series close to the altitude where it is more enhanced, 850 K ( $\sim 32$  km) (Figure 9). CIONO<sub>2</sub> starts enhancing significantly on 29 October but its maximum is reached a few days later, consistent with the time series plot (Figure 8). We note that during the first 3 days after the major SPEs, it is enhanced at latitudes lower than  $\sim 80^\circ\text{N}$  but not over the North Pole. This is consistent with the observed NO<sub>2</sub> depletion at these altitudes and times at latitudes very close to the North Pole, as discussed above. For this reason the enhancement during the first few days is smaller. In the following days, the CIONO<sub>2</sub> enhancements extend over all latitudes north of  $\sim 60^\circ\text{N}$ . These enhancements in CIONO<sub>2</sub> also reflect the interference with the chlorine-induced catalytic ozone loss [Jackman and McPeters, 2004; von Clarmann *et al.*, 2005].

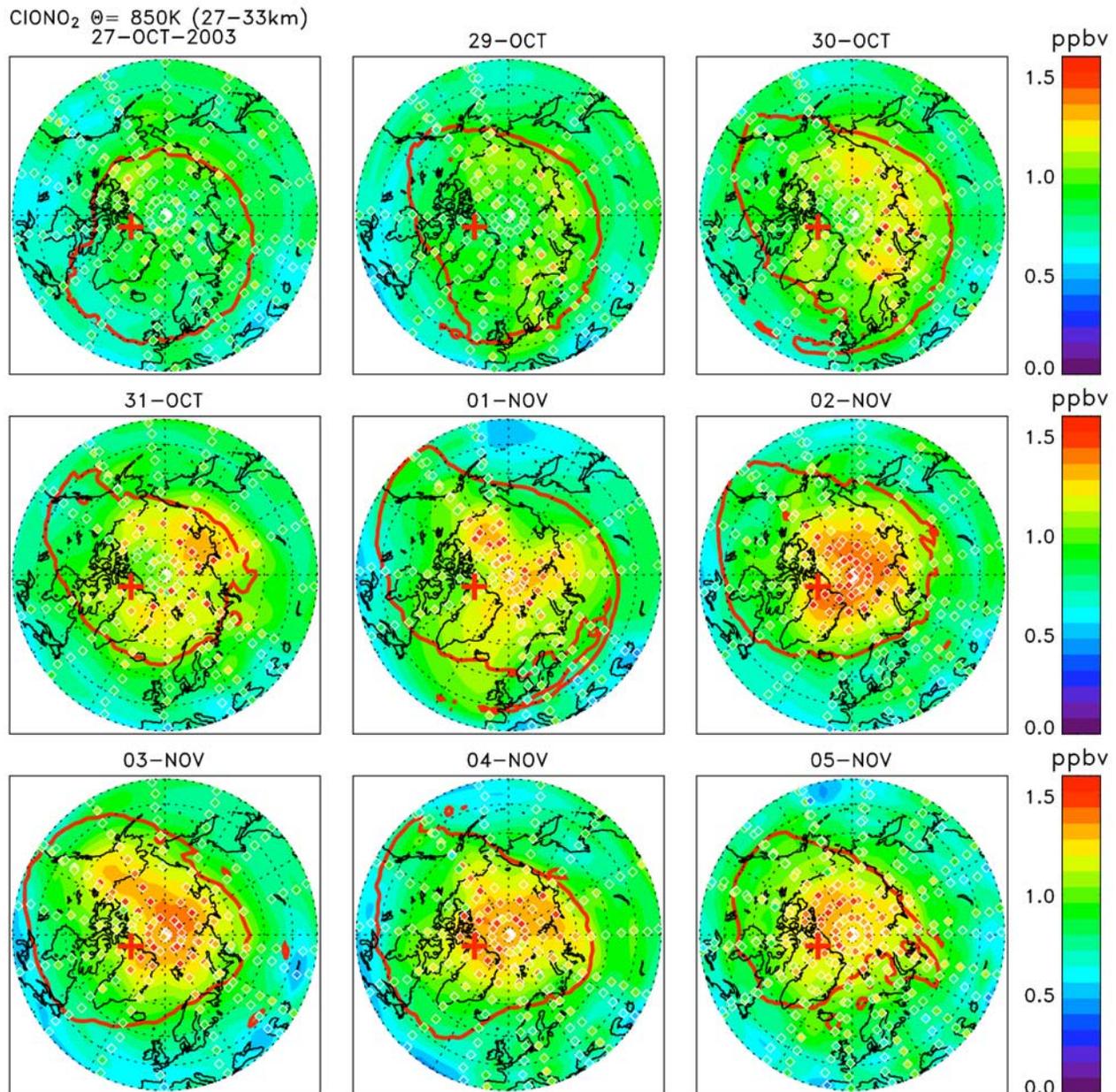
[34] In the Southern Hemisphere, the changes observed are very small. The maximum enhancements are about 0.1 ppbv in the nighttime profiles between 60–70°S at 25–30 km on 31 October. This is in consonance with a much smaller NO<sub>2</sub> enhancement observed in the austral hemisphere, particularly below about 40 km.

## 7. Summary and Conclusions

[35] We have shown in this paper significant enhancements in HNO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, and CIONO<sub>2</sub> in the polar stratosphere produced after the intense solar proton events (SPEs) which occurred in October–November 2003. The measurements of these species were taken by the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) on board the Environmental Satellite (ENVISAT). To our best knowledge, these represent the first simultaneous observations of changes in all these NO<sub>y</sub> species produced by SPEs. Only Orsolini *et al.* [2005] have recently reported HNO<sub>3</sub> enhancements also using MIPAS measurements.

[36] Large HNO<sub>3</sub> enhancements have been observed in the Northern Hemisphere polar cap (70°N–90°N) in the upper stratosphere. Two clearly separated enhancements are observed: an instantaneous increase of 1–2 ppbv following the October–November SPEs, and a very large second enhancement (1–5 ppbv depending on altitude), starting around 10 November and lasting until at least the end of December.

[37] The sudden enhancement just after the SPEs seems to be mainly produced by gas-phase chemistry: NO<sub>2</sub> + OH + M  $\rightarrow$  HNO<sub>3</sub> + M, originated by the instantaneous increase in OH. HNO<sub>3</sub> might also be enhanced after SPEs through ion chemistry involving NO<sub>3</sub><sup>+</sup>. A smaller enhancement (of about 1 ppbv) also occurred at an altitude of  $\sim 25$  km. Although the comparison with the previous winter suggests it was caused



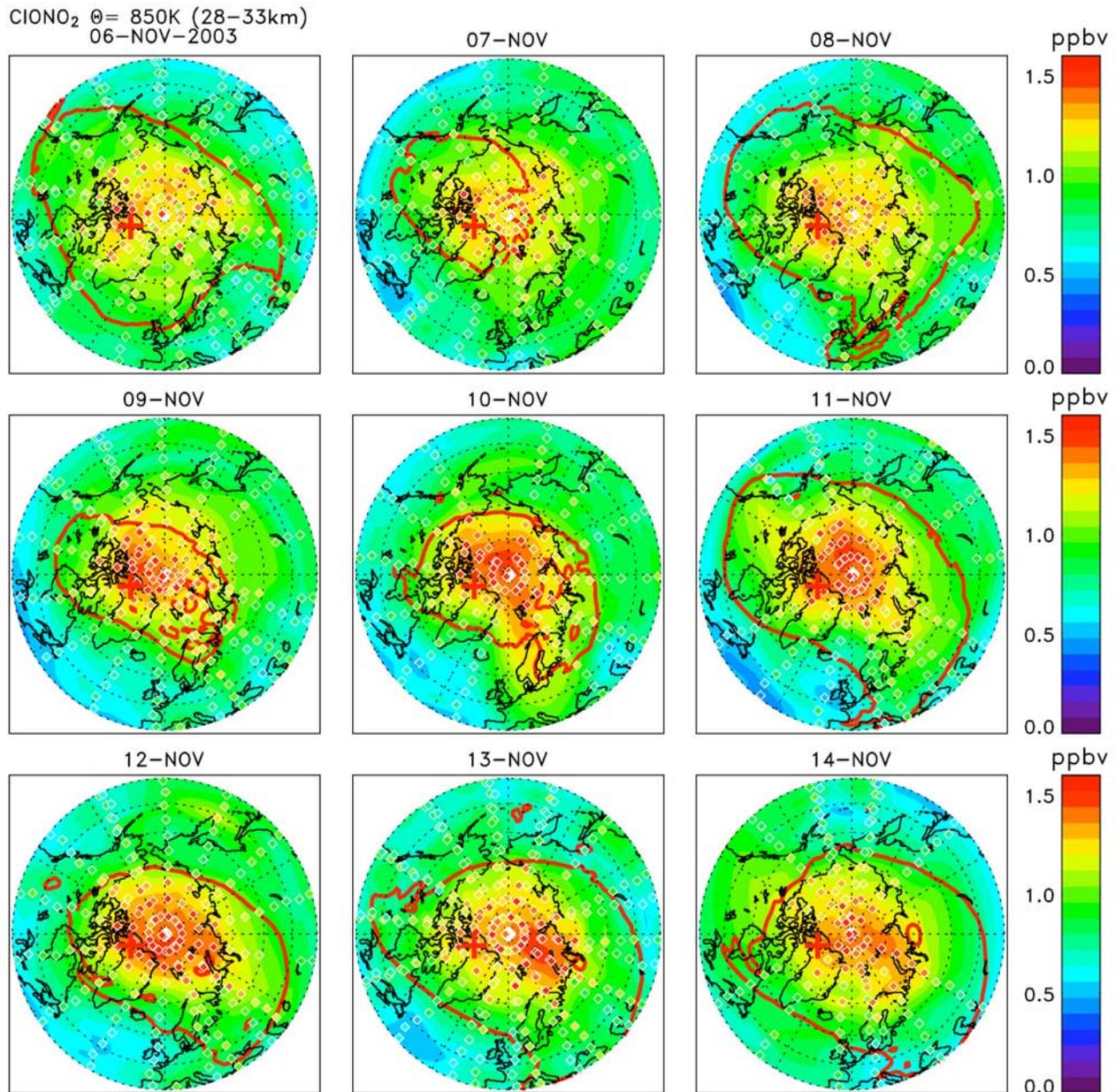
**Figure 9.** Northern Hemisphere distributions of CIONO<sub>2</sub> (in ppbv, parts per billion by volume) for days from 27 October to 14 November 2003 at a potential temperature ( $\Theta$ ) level of 850 K ( $\sim$ 32 km). Contours are zonally smoothed within 700 km. Individual measurements are represented by diamonds. The vortex edge is plotted with a red curve (see text for details). The geomagnetic pole is marked with a red plus sign.

by SPEs, it is not clear yet since the changes are within the expected climatological variability and relatively few solar protons penetrate so deep in the atmosphere.

[38] Enhancements of HNO<sub>3</sub> just after the October–November 2003 SPEs were also observed in the southern polar cap (70°S–90°S) (summer pole), although much smaller than in the northern counterpart. The enhancement in the austral polar cap took place between 30 and 40 km with maximum changes of about 0.2 ppbv.

[39] Orsolini *et al.* [2005] have studied the HNO<sub>3</sub> enhancements from late November 2003 to early January 2004 and their correlations with NO<sub>2</sub> and the A<sub>p</sub> index and

suggested that it was caused by energetic particles that induced a direct production of NO<sub>x</sub> in the upper stratosphere. From our analysis of the correlation of HNO<sub>3</sub> and NO<sub>2</sub> maxima shown here, the analysis of the origin of the NO<sub>2</sub> enhancements observed in this period presented in our companion paper [López-Puertas *et al.*, 2005], and the analysis of HNO<sub>3</sub> enhancement during several winters of Stiller *et al.* (submitted manuscript, 2005), we have concluded that the major part of this exceptionally high HNO<sub>3</sub> enhancement taking place between around 8 November until the end of December has its origin in the NO<sub>x</sub> produced in the mesosphere during the major SPEs in late October/early



**Figure 9.** (continued)

November, which was then transported downward during November and December, partially converted into N<sub>2</sub>O<sub>5</sub> in the upper stratosphere, and then, by heterogeneous ion-cluster reactions (equations (8)–(10)), into HNO<sub>3</sub>.

[40] The local formation of the HNO<sub>3</sub> enhancement in this period by gas-phase chemistry triggered by smaller SPEs which took place on 20–23 November and on 3–5 December does not seem plausible since no instantaneous response to these minor SPEs was observed over a wide altitude range, in contrast to the October/November SPEs. These SPEs were much weaker and unable to produce significant atmospheric changes at upper stratospheric levels.

[41] We also observe much larger in-vortex HNO<sub>3</sub> values in 2003–2004 (November–March) than in the previous winter at lower altitudes, at 775 K and 625 K potential temperature levels. These differences, however, do not seem

to be caused by the SPEs but to the larger area with temperatures below NAT formation temperature that took place in the 2002–2003 winter, which produced more PSCs formation and hence a larger sequestration of HNO<sub>3</sub> in the PSCs.

[42] N<sub>2</sub>O<sub>5</sub> has also been observed to be enhanced after the SPEs in the northern polar cap but, contrary to HNO<sub>3</sub>, it reached the maximum enhancement about 2 weeks after the SPEs. The maximum increase in N<sub>2</sub>O<sub>5</sub> took place at around 40 km and varies from 0.5 to 1.2 ppbv, about 20 to 60%. The N<sub>2</sub>O<sub>5</sub> surface plots reveal that two distinct enhancements appeared. One of about 0.1–0.4 ppbv occurring early after the major SPEs and penetrating deep in the stratosphere, down to 30 km, and a second one, larger, up to 1.2 ppbv, peaking around 40 km and appearing about 12–13 days after the major SPEs. The first enhancement is

assigned to an increase in OH. An OH enhancement gives rise to an HNO<sub>3</sub> increase which, in the presence of OH under dark conditions, leads to an increase in NO<sub>3</sub> and then in N<sub>2</sub>O<sub>5</sub>. The second enhancement seems to be caused by a slow subsidence of NO<sub>x</sub>-rich air after 8 November. Small enhancements (0.07 ppbv) have been observed for N<sub>2</sub>O<sub>5</sub> in the southern polar cap. This is in consonance with theoretical expectations, since NO<sub>3</sub>, which is required to produce N<sub>2</sub>O<sub>5</sub>, is very short-lived in the illuminated SH polar cap.

[43] Finally, ClONO<sub>2</sub> has been observed to be increased in the northern polar cap after the SPEs. The maximum enhancement of ClONO<sub>2</sub> was centered in a layer around 32 km with values of 0.4 ppbv, about 40%. The increase is slightly delayed by 1–2 days with respect to the major SPEs, which is consistent with the observed depletion in NO<sub>2</sub> of about 2–3 ppbv in the 30–40 km region on 29 and 30 October [López-Puertas et al., 2005]. In the Southern Hemisphere, the changes observed in ClONO<sub>2</sub> were much smaller than in the northern polar cap. The maximum enhancements were about 0.1 ppbv in the nighttime profiles between 60°S and 70°S at 25–30 km on 31 October.

[44] In summary, during the first 3 days after the major storm at around 35 km and at latitudes very close to the North Pole, we observed that NO<sub>2</sub> decreased [see López-Puertas et al., 2005], ClONO<sub>2</sub> did not change significantly, but HNO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub> and HOCl increased. The overall picture suggests that the increase in OH [see von Clarmann et al., 2005] produced the increase in HNO<sub>3</sub> and the decrease in NO<sub>2</sub>. Also, larger amounts of HNO<sub>3</sub> in the presence of OH lead to an increase in N<sub>3</sub> and hence in N<sub>2</sub>O<sub>5</sub>. ClONO<sub>2</sub> did not increase significantly in this period since the required NO<sub>2</sub> was even slightly smaller than before the SPEs.

[45] Many features have been discussed on the basis of the currently known chemistry and on observations of other species as NO<sub>x</sub> and HOCl. The quantitative reproduction of the MIPAS observations of temporal and spatial development of the nitrogen reservoirs, reactive species, and ozone will be a challenge to chemistry transport models. New insights both in the dynamic schemes, in particular with respect to subsidence of thermospheric/mesospheric air, and the chemical schemes, in particular with respect to ion cluster chemistry, are expected.

[46] **Acknowledgments.** The IAA team has been supported by Spanish Ministerio de Educación y Ciencia under projects REN2001-3249/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).

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

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