Atmos. Chem. Phys., 8, 3805–3815, 2008
www.atmos-chem-phys.net/8/3805/2008/

Atmospheric Chemistry and Physics

Enhancement of N_2O during the October–November 2003 solar proton events

B. Funke[1], **M. García-Comas**[1], **M. López-Puertas**[1], **N. Glatthor**[2], **G. P. Stiller**[2], **T. von Clarmann**[2], **K. Semeniuk**[3], **and J. C. McConnell**[3]

[1]Instituto de Astrofísica de Andalucía, CSIC, Granada, Spain
[2]Forschungszentrum Karlsruhe und Universität Karlsruhe, Institut für Meteorologie und Klimaforschung, Karlsruhe, Germany
[3]Department of Earth and Space Science and Engineering, York University, Toronto, Ontario, Canada

Received: 4 January 2008 – Published in Atmos. Chem. Phys. Discuss.: 4 March 2008
Revised: 18 June 2008 – Accepted: 19 June 2008 – Published: 17 July 2008

Abstract. In this paper we present evidence of enhanced N_2O concentrations in the upper stratosphere/lower mesosphere polar regions after the solar proton events that occurred during October–November 2003. The observations were performed by the MIPAS instrument on the Envisat satellite. Simulations performed using the Canadian Middle Atmospheric Model (CMAM) show that such enhancements are most likely produced by the reaction of $N(^4S)$ with NO_2, both of which species are largely enhanced just after the solar proton events in the winter polar night.

1 Introduction

Nitrous oxide is the main precursor of active nitrogen in the middle atmosphere. Its major sources, both natural and man-made, originate at the surface, and it is transported into the stratosphere, where photo-dissociation by solar UV is its major sink and where its reaction with $O(^1D)$ leads to the formation of chemically active nitrogen species like NO_2 and NO. Hence it indirectly plays a major role in controlling atmospheric ozone abundance through the NO_x (NO_x=NO+NO_2) ozone-destroying catalytic cycle (Brasseur and Solomon, 2005).

It has been widely reported that solar proton events (SPEs) have significant effects on the composition of the stratosphere and mesosphere in the polar regions (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.

In recent years, there have been two large solar proton events (October–November 2003 and January 2005) (Jackman et al., 2008) which have been intensively observed by several instruments on different satellite platforms, including, for example, NOAA 16 SBUV/2 and HALOE data (Jackman et al., 2005a,b; Randall et al., 2005); MIPAS, GOMOS and SCIAMACHY on Envisat (Seppälä et al., 2004; López-Puertas et al., 2005a,b; von Clarmann et al., 2005; Orsolini et al., 2005; Rohen et al., 2005); and MLS on AURA (Verronen et al., 2006). In particular, 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., 2005a, 2008). Some of the Geostationary Operational Environmental Satellite (GOES)-11 instruments measured very large fluxes of highly energetic protons (e.g., López-Puertas et al., 2005a). The protons are guided by the Earth's magnetic field to both polar regions (geomagnetic latitudes $>60°$), 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 et al., 2005a).

During and after this solar proton event, the MIPAS instrument observed global changes (e.g. in both the Northern and Southern polar regions, during day and nighttime) in the stratospheric and lower mesospheric composition. This includes enormous enhancements in NO_x, e.g., in NO and NO_2, and large depletions in O_3 (López-Puertas et al., 2005a) as well as significant changes in other NO_y species, such as HNO_3, N_2O_5, $ClONO_2$ (López-Puertas et al., 2005b). In

Correspondence to: M. López-Puertas
(puertas@iaa.es)

addition, there also have been observed changes in ClO and HOCl, as evidence of perturbations by solar protons on the HO_x and chlorine species abundances (von Clarmann et al., 2005).

However, to our knowledge, no solar-proton-event induced changes in N_2O concentration have so far been reported. A paper on the production and transport of N_2O by auroral electron precipitation seen by the Fourier transform spectrometer on SCISAT-1 has just been submitted by Semeniuk et al. (2008). One should expect this species to be enhanced also if sufficient atomic nitrogen and NO_2 is available after the solar proton event in the polar night upper stratosphere and lower mesosphere. The aim of this paper is to report the enhanced N_2O concentration observed by MIPAS during the October–November 2003 solar proton event and to explain the reason for it using modeling calculations by the Canadian Middle Atmospheric Model (CMAM).

2 MIPAS measurements

MIPAS is a limb emission Fourier transform spectrometer designed for the measurement of trace species from space (Fischer and Oelhaf, 1996; ESA, 2000; Fischer et al., 2008). It is part of the instrumentation of the Environmental Satellite (ENVISAT) which was launched into its sun-synchronous polar orbit of 98.55° inclination at about 800 km altitude on 1 March 2002. MIPAS operated from July 2002 to March 2004 at full spectral resolution of $0.035\,cm^{-1}$ (unapodized) in terms of full width at half maximum and with reduced resolution since August 2004. MIPAS observes the atmosphere during day and night with global coverage from pole to pole. Within its standard observation mode at full spectral resolution, MIPAS covers the altitude range from 68 down to 6 km with tangent altitudes at 68, 60, 52, 47, and then at 3 km steps from 42 to 6 km. Occasionally, MIPAS also operates in several upper atmospheric modes scanning up to 170 km. The field of view of MIPAS is 30 km in horizontal and approximately 3 km in vertical direction. MIPAS passes the equator in southerly direction at 10.00 am local time, 14.3 times a day. During each orbit up to 72 limb scans are recorded. The Level-1b processing of the data (version 4.61/62 was used here), including processing from raw data to calibrated phase-corrected and geolocated radiance spectra, is performed by the European Space Agency (ESA) (Nett et al., 1999, 2002).

The retrieval of N_2O 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, and then CH_4 and N_2O simultaneously. The results of the species retrieved first are then used in the retrievals of the subsequent species.

The N_2O vmr was retrieved from the MIPAS spectra around $1284.9\,cm^{-1}$, where the ν_1 band of N_2O is located (Glatthor et al., 2005). 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. The retrieval noise error in the N_2O vmr for unperturbed conditions (i.e., not during solar proton events) is typically 3% at 10–44 km and 22% at 50 km. The errors induced by interfering species uncertainties (mainly CH_4) are implicitly taken into account in the noise error of N_2O and are smaller than 1% (Glatthor et al., 2005). The systematic errors for N_2O comprise the uncertainties in temperature, interfering species abundances, pointing, spectral data, and calibration; and are about 10-30%. The total error has been computed by the square root sum of all systematic and random error components plus model errors (non-LTE). It varies between 10 and 20% at 10–35 km and is about 30% between 35–50 km (Glatthor et al., 2005).

The resulting vertical resolution was typically about 4 km in the altitude range 15–40 km and decreased to more than 10 km below and above this region. More details on the N_2O retrieval strategy can be found in Glatthor et al. (2005). For a profile of the enhanced N_2O during the SPE (typical of the data shown here) the noise error is about 0.2 ppbv (smaller than 5%) at 50–75 km. However, the vertical resolution is rather sparse with values of 8-15 km above 52 km. This study is focussed mainly on MIPAS data from 25 October to 22 November 2003, which were retrieved by the IMK-IAA processor (data version V3O_N2O_12) from Level-1b data version 4.61/62.

In addition to N_2O we also use MIPAS data for NO_2. MIPAS IMK/IAA retrievals are performed generally for selected episodes of scientific interest and the NO_2 data analyzed here span over two of those periods, (26 and 29 October, 1, 2, 5, 11, 18 and 21 November) and (30 and 31 October, 3, 4, 8, 9, 10, 15, 16, 17, 20 and 22 November), with versions V3O_NO2_9 and V3O_NO2_11, respectively. The differences between these two versions are very small in the regions studied, however, they are significantly improved compared to the previously published data in López-Puertas et al. (2005a).

2.1 N_2O Enhancement in polar regions

Figure 1 shows the temporal evolution of the N_2O distribution at an approximate altitude of 58 km in the Northern polar Hemisphere (40°N–90°N) for the period of 26 October to 11 November 2003, i.e., from two days before the major solar proton events (SPEs) until about ten days after them (note that some days are not shown). We have included only nighttime data because the production mechanism proposed (see below) operates only at nighttime and this is when we observed the larger enhancements.

A large increase in the N_2O abundance is observed at polar latitudes reaching values of about 9 ppbv at 58 km after the SPEs. This coincides with the latitudes where solar protons penetrate into the atmosphere, that is, in the polar cap regions (approximately at $>60°$ geomagnetic latitude). Note the contrast between the distribution on 26 October, before the SPEs, and on 29 October and following days, during and after the SPEs. Maximum N_2O abundances are observed during the first few days of the SPEs (on 30 October until 2 November), when the larger proton fluxes took place (see Fig. 1 in López-Puertas et al., 2005a). We also observe that the enhancement in N_2O concentration lasts until 22 November (see Fig. 6a) when the enhancement is still above 2 ppbv and moved to lower altitudes.

The energetic charged particles (protons and associated secondary electrons) collide with and dissociate N_2, thus producing atomic nitrogen and, subsequently, odd nitrogen in the forms of NO and NO_2 through reactions:

$$N + O_2 \rightarrow NO + O, \quad \text{(R1)}$$

and the further oxidation of nitric oxide through

$$NO + O_3 \rightarrow NO_2 + O_2. \quad \text{(R2)}$$

The generation of $N(^4S)$ can also lead to a reduction in odd nitrogen (NO_y) via

$$N(^4S) + NO \rightarrow N_2 + O. \quad \text{(R3)}$$

This NO_y loss mechanism thus limits the buildup of NO_x and is important especially during large SPEs, when a huge amount of NO_y is produced in a short time (Rusch et al., 1981). However, as a net effect, SPEs will result in an increase in NO_y constituents.

For reasons discussed below, we think that the N_2O enhancement shown in Fig. 1 is produced from the enhancements in $N(^4S)$ and in NO_2 followed by the reaction

$$N(^4S) + NO_2 \rightarrow N_2O + O, \quad \text{(R4)}$$

which is effective only during nighttime conditions since NO_2 is rapidly dissociated in the sunlight, e.g.,

$$NO_2 + h\nu \rightarrow NO + O. \quad \text{(R5)}$$

Thus, the condition required for producing N_2O in the upper stratosphere is to have sufficient amounts of atomic nitrogen N and NO_x under dark conditions, which is well fulfilled when solar proton events occur in the dark polar winter region.

To verify this hypothesis we have investigated the spatial correlation between N_2O and NO_2, which indeed is very pronounced for the period under investigation (Figs. 1 and 2) and thus supports our explanation. As a further check for the relationship between N_2O and NO_2 enhancements, Fig. 3 shows correlation plots for both species for a few days, covering all latitudes in the Northern Hemisphere for altitudes spanning approximately 40 to 60 km. These figures clearly show two different groups of data. One very compact cloud (see Fig. 3a), with a steep slope, spanning over all latitudes, which corresponds to the N_2O/NO_2 correlation before the SPEs; and a second one, less compacted and with a smaller slope, comprising data from high latitudes only, which corresponds to the region and time affected by the SPEs (Fig. 3b–c). Note that the latter figures also show the compact N_2O/NO_2 cloud which corresponds to the mid- and low-latitude data measured during these days. These results then suggests that N_2O during SPEs is produced from NO_2, and the mechanism is of different nature than for non-SPE conditions.

The altitude/latitude distribution of the enhancement is shown in Fig. 4 for four days, one just before the SPEs and three days after these events. The sudden appearance of the N_2O enhancement after the SPE on 29 October, delimited to latitudes northward of 60° and at altitudes above around 40 km, is clearly evident in the top right panel. The other panels of the figure show that the enhancement persists for the following few days, being slightly diluted and descended downwards. Note that these distributions of N_2O are also very closely correlated with those for NO_2 (see Fig. 5), thus further supporting the production mechanism discussed above.

There is also an indication of enhanced N_2O on 26 October (Fig. 4a), just before the SPEs. This seems to be related to energetic electron precipitation (EEP) and is consistent with a corresponding enhancement in NO_2 (see Fig. 5a). This small enhancement in N_2O, as well as that appearing in late November (see next section), are not the focus of this work but are discussed in detail by Funke et al. (2008).

2.2 Temporal evolution of the N_2O enhancement

Figure 6a shows the temporal evolution of zonal mean N_2O in the Northern polar cap (latitudes polewards of 70° geographic) for nighttime conditions. The maximum enhancement took place at 50–55 km on 30–31 October (day of year (doy) 303–304) just after the first major SPE that came about on 29 October. Another enhancement occurred on 3–4 November (doy 307–308), following another major increase in the high-energy solar proton flux (see Fig. 1 in López-Puertas et al., 2005a). A weaker enhancement is also observed around 60 km near the end of this period (18–22 November, doy 324–326). This enhancement seems not to be related to solar proton events. Although a smaller

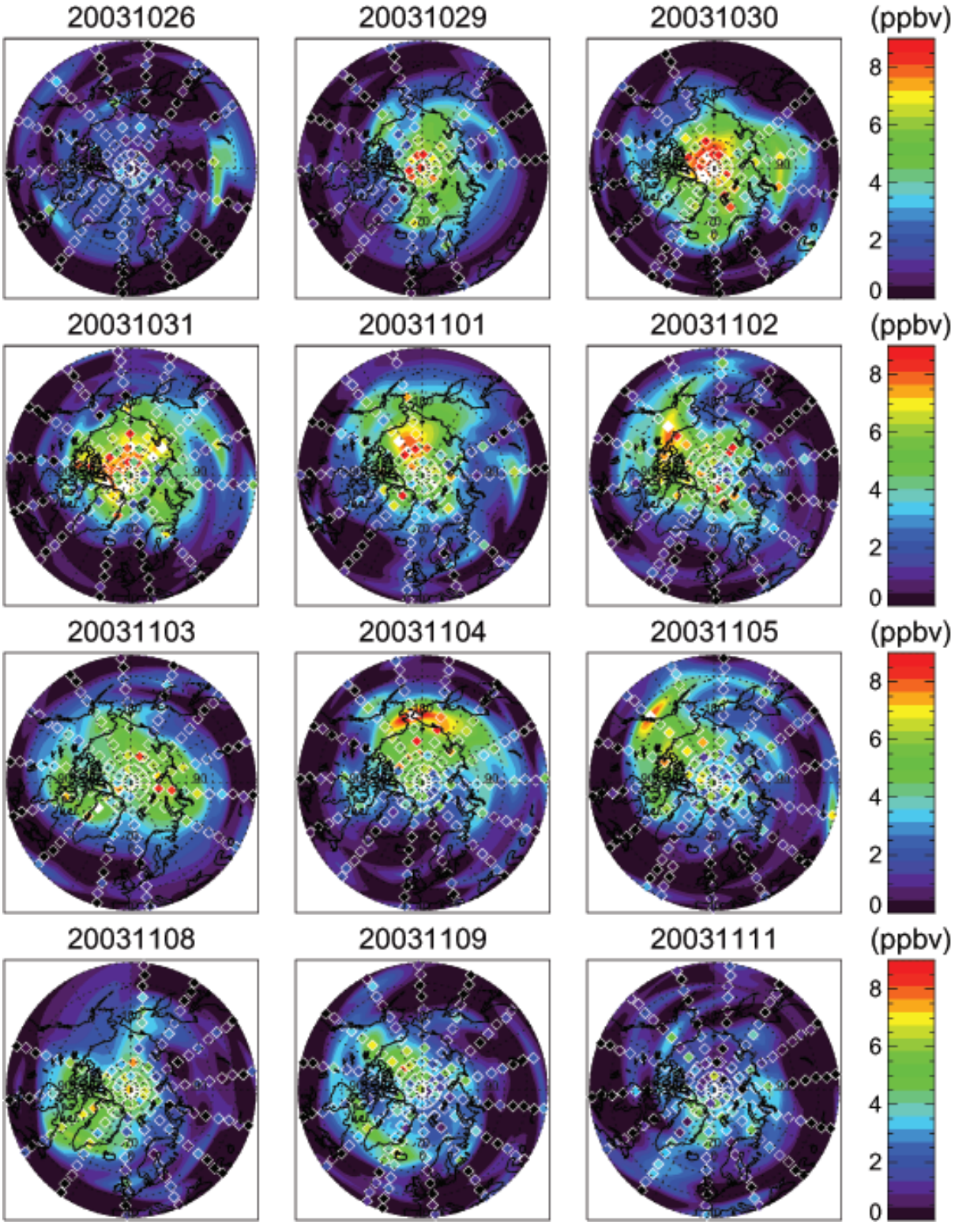

Fig. 1. Northern Hemisphere distributions of N_2O (in ppbv, parts per billion by volume) for days from 26 October to 11 November 2003 at an altitude of 58 km. Only nighttime data is included. Contours are zonally smoothed within 700 km. Individual measurements are represented by white symbols.

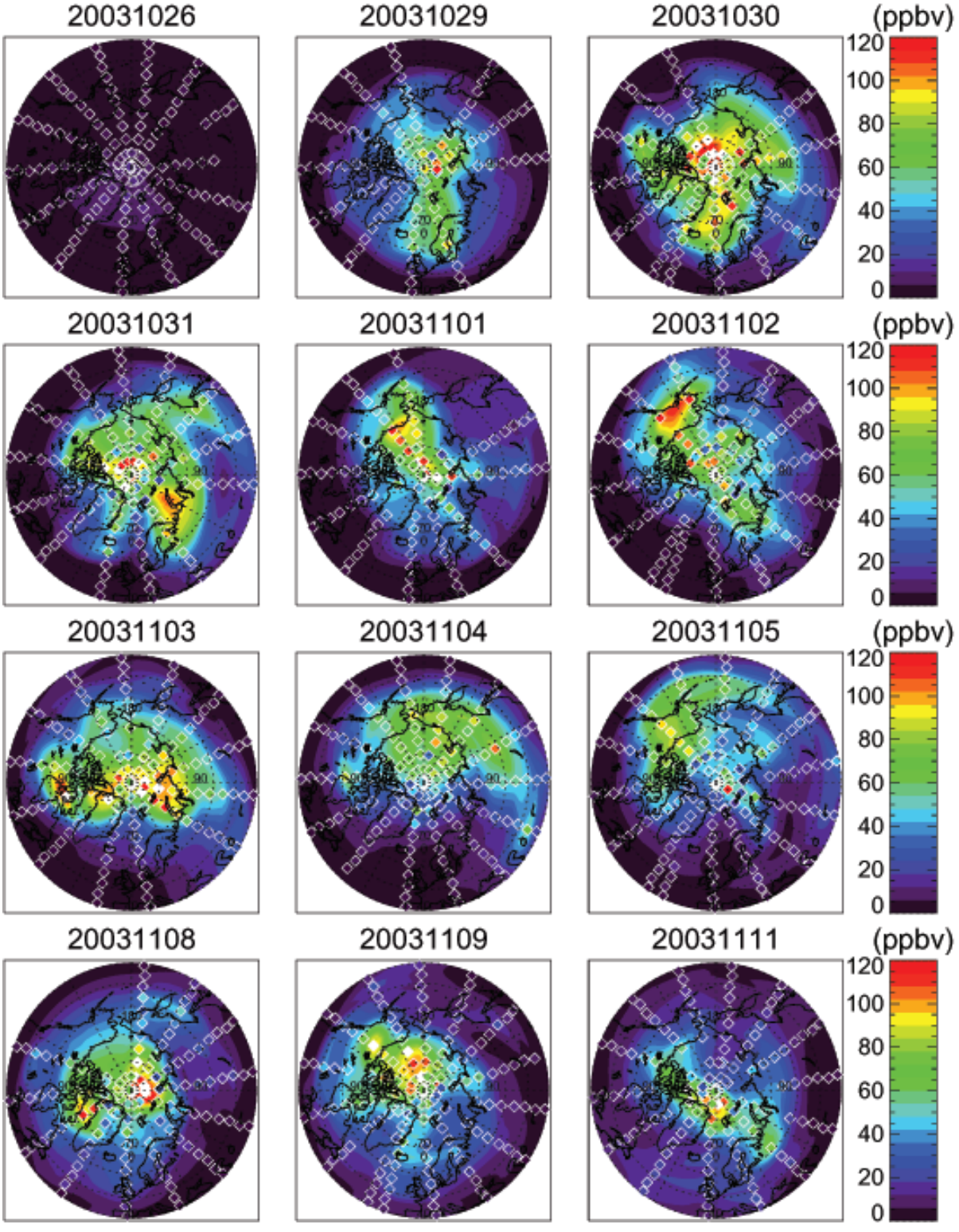

Fig. 2. As Fig. 1 but for NO_2.

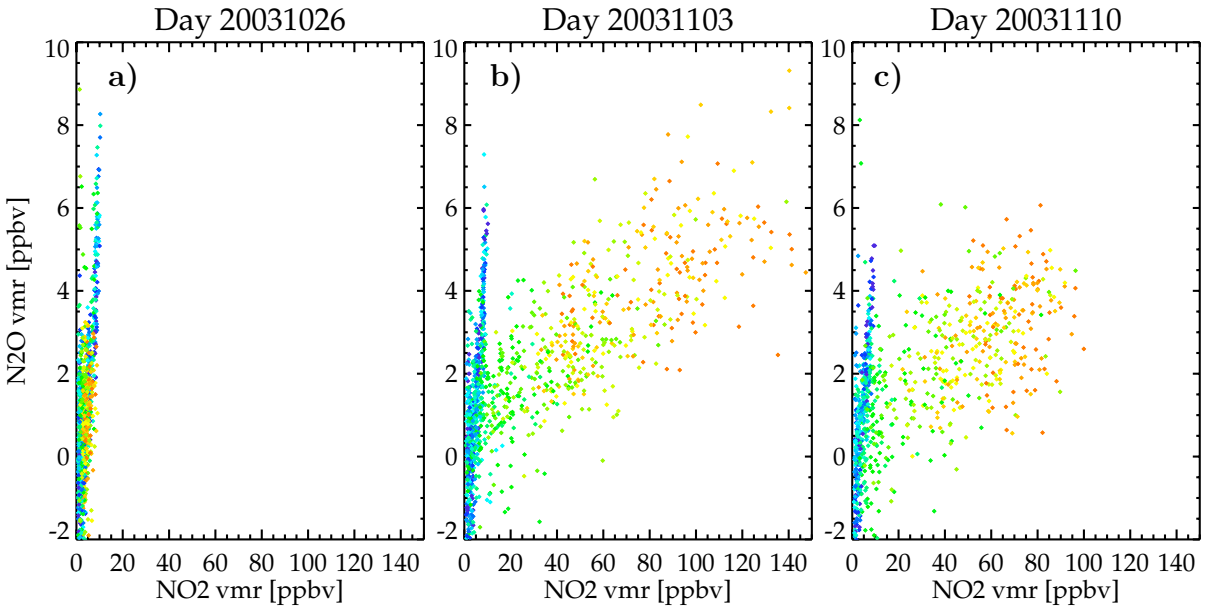

Fig. 3. Correlation plots of N_2O versus NO_2 for the Northern Hemisphere for days 26 October (before the SPE) and 3 and 10 November (after the SPE). The color code indicates the latitudes, ranging from the equator (dark blue) until North pole (orange). The data included comprise altitudes from a potential temperature of 2000 K (∼40 km) to 3000 K (∼60 km). Only nighttime data is included.

SPE took place on 22–25 November the ionization rates due to protons calculated by Jackman (2007b) for these days were about three orders of magnitude lower than for 30–31 October. Also, this N_2O enhancement already started on 18 November, a few days before this secondary SPE occurred. This weaker enhancement, however, seems to be correlated with the onset of the polar winter descent of NO_x from the mesosphere-lower thermosphere (MLT) region which took place in the second half of November and made available sufficient NO_2 during nighttime below approximately 70 km (see Fig. 7a). Atomic nitrogen, also required for N_2O formation, has a too short chemical lifetime to be transported downward from the MLT region, but it could be produced by the high-energy electron precipitation (EEP) taking place at that time. Indeed, fluxes of electrons with energies >100 keV (able to penetrate down to 70 km) measured by the MEPED instrument on NOAA 16 (http://poes.ngdc.noaa.gov/data/avg/) were significantly increased on 16 and 20 November.

The temporal evolution of N_2O in the Northern Hemisphere (Fig. 6a) shows also that N_2O-rich air masses were descending from around 50 km to ∼43 km during November. This descent is also observed in the temporal evolution of NO_2 (Fig. 7a) and is related to the polar winter descent of the meridional circulation.

Smaller N_2O enhancements have also been observed in the Southern Hemisphere (not shown here) but with significantly lower mixing ratios (just ∼1–1.2 ppbv). These smaller enhancements in the sunlit Southern Hemisphere polar cap are expected due to less available NO_2 during daytime conditions (see Fig. 4a in López-Puertas et al., 2005a). The temporal evolution of N_2O in the Southern Hemisphere shows, in contrast to the Northern Hemisphere, a small upward motion which can also be explained by the meridional circulation pattern in this period.

3 Modelling

We have also investigated N_2O production by the 2003 SPEs using the Canadian Middle Atmosphere Model (CMAM). CMAM is a chemistry climate model with a comprehensive set of physical parameterizations and chemistry package. The model chemistry takes into account 102 gas phase, 37 photolysis and 12 heterogeneous reactions on type Ib and II polar stratospheric clouds (de Grandpré et al., 2000). For the simulations conducted here the model chemistry was extended to include Reaction (R4) and the additional branches:

$$N(^4S) + NO_2 \rightarrow NO + NO \quad \text{(R6)}$$

$$N(^4S) + NO_2 \rightarrow N_2 + O_2. \quad \text{(R7)}$$

Based on multiple simulations, it was decided to ascribe 50% of the reaction rate to the primary branch (R4) and 25% to each of the secondary branches (R6 and R7). This split is not excluded by the laboratory work used to determine the reaction rate (Wennberg et al., 1994) and without it the N_2O production is too high for a given amount of NO_2.

The October–November 2003 SPEs production of NO_x, HO_x and atomic oxygen based on vertical profiles of hourly

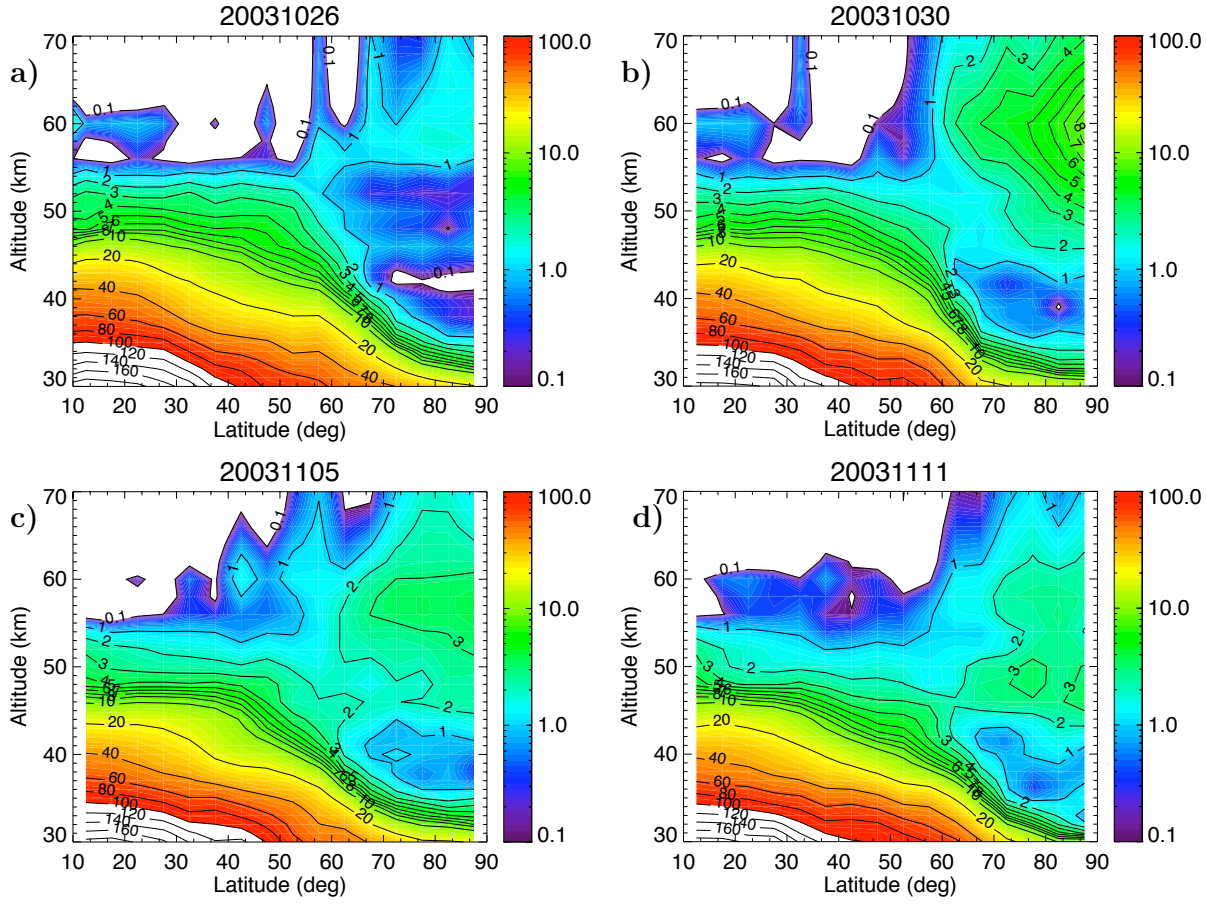

Fig. 4. Zonal mean cross sections of N_2O (in ppbv) in the Northern Hemisphere for the days 26 and 30 October **(a, b)** and 5 and 11 November **(c, d)** 2003 measured in nighttime conditions. The enhancement of N_2O at high latitudes above 40 km is evident in panels b-d. White areas at highest altitudes represent MIPAS measurements with no information and those at the lowest altitudes near the tropics denote values outside of the color scale range.

ion pair production rates derived from NOAA GOES-11 observations of proton fluxes was implemented as in Semeniuk et al. (2005). However, here we use a new chemistry solver that is fully implicit without any approximation to the Jacobian matrix. Ground state atomic nitrogen is not assumed to be in photochemical steady state. We carried out one simulation where Reaction (R4) and its branches were turned off and one simulation where they were active.

The run performed without including Reaction (R4) shows very little N_2O above ∼40 km (due to descent during this time of the year). When this reaction is included, however, the model predicts a significant enhancement for N_2O (see Fig. 6b and c). The values computed by the model (Fig. 6b) look, in a first instance, significantly larger than those measured by MIPAS (Fig. 6a) and with the peak values situated at about 5–10 km higher. We mentioned before that MIPAS measurements have a rather sparse vertical resolution at these altitudes. Hence, for meaningful comparisons, the MIPAS averaging kernels have to be applied to model results. This is shown in Fig. 6c, where we show the model predictions as would have been measured by MIPAS. In general, there is a good agreement with the measurements (panel a), both in the magnitude of the enhancement and in the altitude of its peak; with the model overestimating the measurements in only about 1–2 ppbv (20–30%) in the 55–70 km region. The model also simulates well the double peak in the temporal evolution of the enhancement, corresponding to the two major SPEs on 29 October and 3–4 November, and the dilution and slow descent of the N_2O increase during the following days. This then confirms our hypothesis about the origin of the N_2O enhancement. The model does not show the weaker enhancement on 18–20 November at about 60 km, since this is likely produced by EEPs, and subsequent downward transport, which are not modeled in the results shown here.

As a further check of the mechanism, we compared the measured and modeled values for NO_2, one of the precursors of the N_2O, during this period. The results are shown in Fig. 7a and b for MIPAS and the model, respectively. As

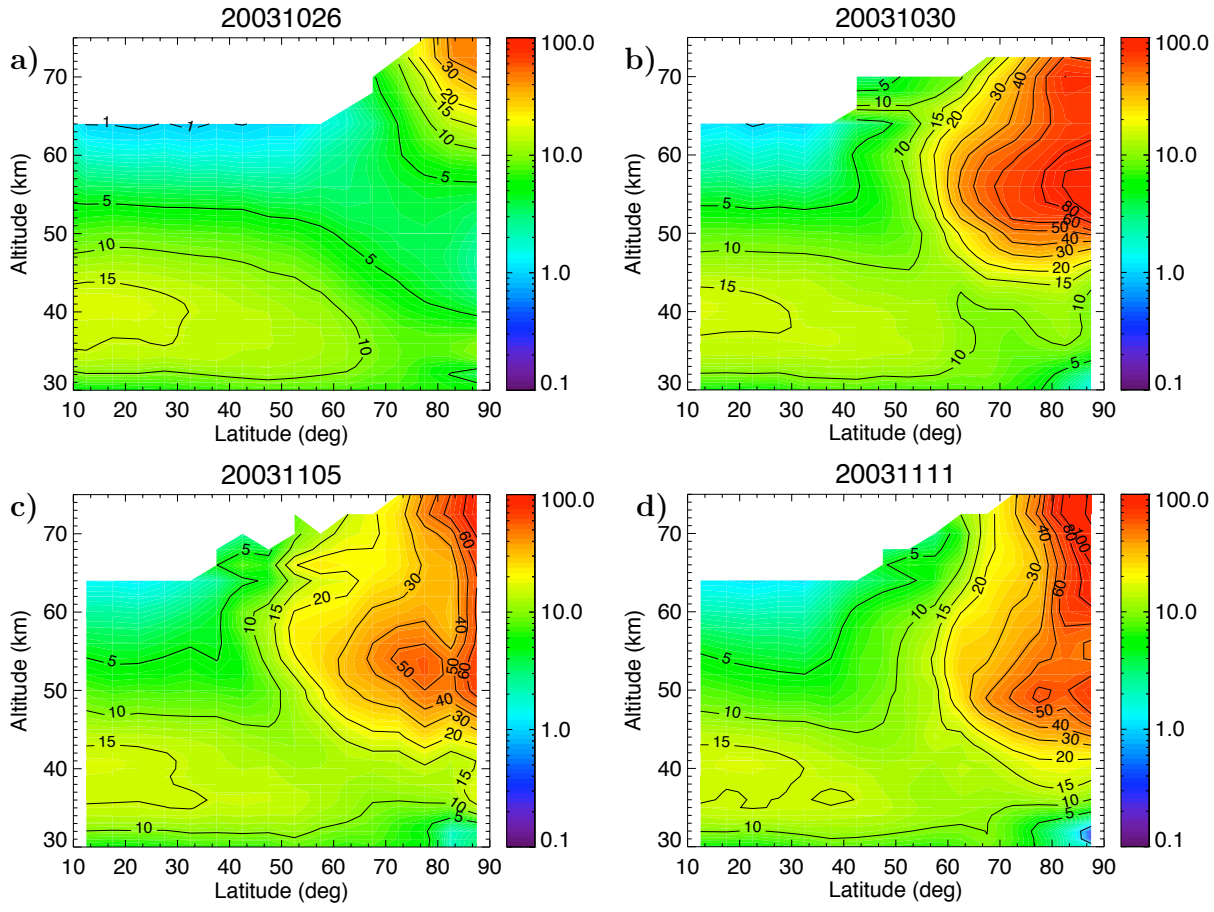

Fig. 5. As Fig. 4 but for NO_2.

has been discussed in the introduction, and shown in Figs. 2 and 5, NO_2 increased significantly during these SPEs. Focusing on the first few days after the SPEs, the figure shows that measured and modeled NO_2 are in rather good agreement. The model predictions for NO_2 are generally smaller than the measurements by about 10–30% below about 55 km, and larger by a similar amount in the 55–70 km region. This model overestimation in the 55–70 km region for NO_2 is similar to that for N_2O of about 20–30% (see above) and suggests that this is the reason for the overestimation of N_2O. The fact that model-measurements differences are similar in both species and take place in the same regions further supports the proposed production mechanism for N_2O.

Large values of NO_2 seen by MIPAS above 60 km are noticeable in Fig. 7a starting on 8 November (doy 312) and mainly after 16 November (doy 320). This enhancement is attributed to a strong descent of mesospheric air, very rich in NO_x, which was produced by energetic electron precipitation in the mesosphere and with some possible local contribution by EEPs (see, e.g., López-Puertas et al., 2006). This NO_x-production mechanism is not included in the current model runs. Note that MIPAS N_2O also exhibits a weak enhancement in this region and time (see Fig. 6a), which is not present in the model run because of insufficient NO_2 and lack of high-energy electron precipitation. The detailed study of these N_2O and NO_2 enhancements are, however, beyond the scope of this paper.

As a final remark, we should note that the small enhancement of 1–1.2 ppbv in the Southern Hemisphere is also consistent with the N_2O production mechanism proposed here. Peak averaged NO_2 values in the Northern Hemisphere are about 80 ppbv (Fig. 7a) while the enhancement in the SH (not shown here) is about 15 ppbv. The NH/SH ratio for NO_2 is about a factor of 5–6, very similar to the NH/SH ratio for N_2O of (6–7)/(1–1.2). In that sense, CMAM predictions for the Southern Hemisphere are also very similar to those measured with peak averaged enhancements ranging from 1 to 1.5 ppbv.

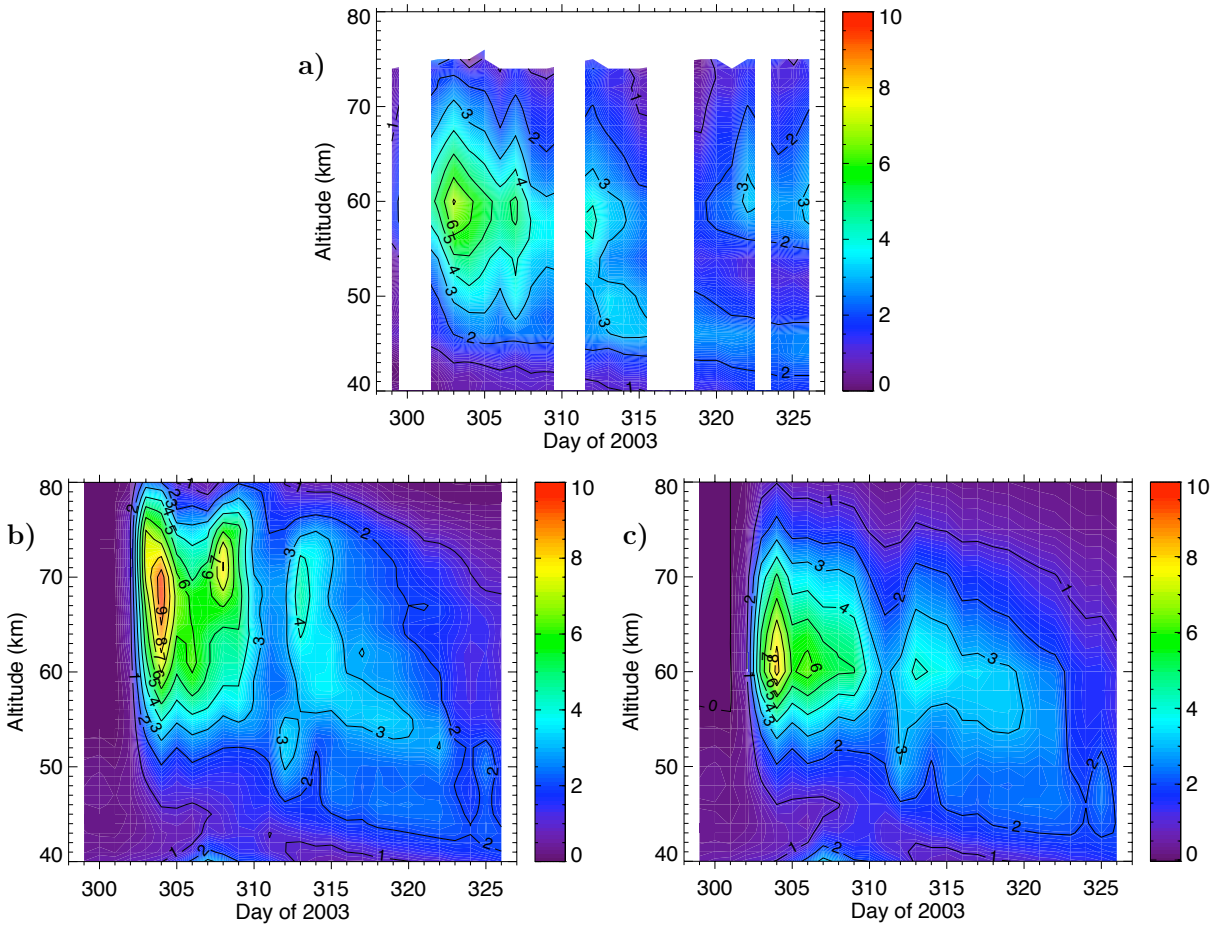

Fig. 6. Time series of N_2O abundance (in ppbv) after the solar proton events of October–November 2003 for the Northern Hemisphere polar cap (70–90° N) during nighttime conditions. **(a)** MIPAS measurements; where white areas at highest altitudes represent MIPAS measurements with no information and the vertical white bands represent days with no processed data. Lower panels: Simulations by the Canadian Middle Atmosphere Model without **(b)** and with **(c)** application of the averaging kernels of the MIPAS retrievals.

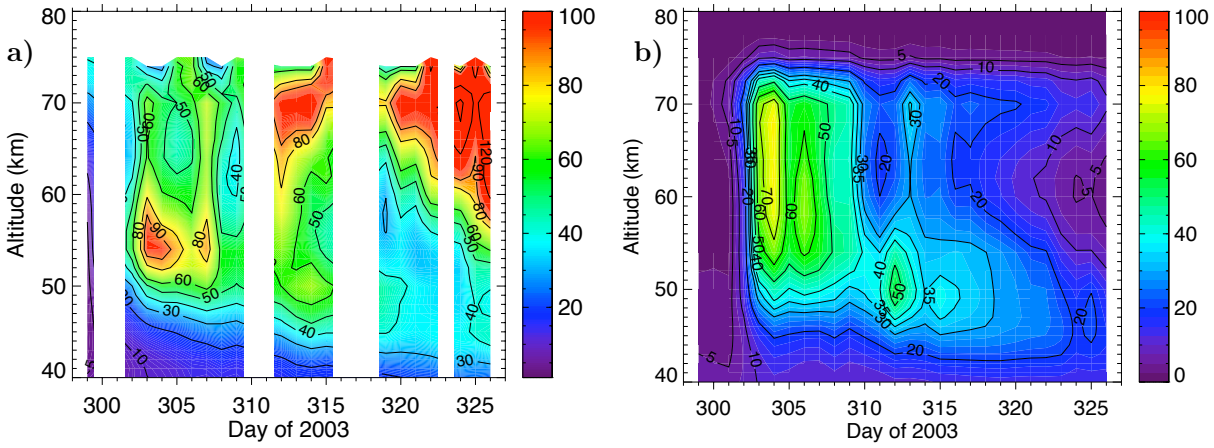

Fig. 7. Time series of NO_2 abundances (in ppbv) after the solar proton events of October–November 2003 for the Northern Hemisphere polar cap (70–90° N) at nighttime conditions as measured by MIPAS **(a)** and modeled by the Canadian Middle Atmosphere Model (CMAM) **(b)** with application of the averaging kernels of MIPAS retrievals. The vertical white bands in panel (a) represent days with no processed data.

4 Summary and conclusions

We have shown in this paper the first evidence of enhanced N_2O concentrations in the upper stratosphere/lower mesosphere polar regions after solar proton events. In particular we show the enhanced N_2O in the Northern Hemisphere polar cap after the SPEs that occurred during October–November 2003. The observations were performed with the MIPAS instrument on the Envisat satellite and show that N_2O was enhanced by about 5 ppbv in the upper stratosphere/lower mesosphere Northern polar cap. Simulations performed using the Canadian Middle Atmospheric Model (CMAM) show that such enhancements can be produced by the reaction of $N(^4S)$ with NO_2, both of which species are largely increased just after the solar proton events in the polar night.

Such N_2O enhancement requires a condition which is rarely present in the upper stratosphere: the simultaneous presence of atomic nitrogen, N, and high amounts of NO_2, a condition which is met when solar proton events come up under polar night conditions. High-energy electron precipitation is also capable of producing atomic nitrogen in the middle mesosphere, and might then represent a continuous source of atmospheric N_2O in the polar night regions in the upper mesosphere, which can occasionally descend to the stratopause region (Semeniuk et al., 2008**??**; Funke et al., 2008).

N_2O is almost completely produced at the surface by both natural and anthropogenic sources. The mechanism presented here represents an additional natural atmospheric source of N_2O. Its investigation in the future is therefore of high importance.

Acknowledgements. The IAA team was supported by the Spanish project ESP2004-01556 and EC FEDER funds. The authors acknowledge ESA for providing MIPAS spectra. The IMK team was supported by the Priority Program CAWSES of the German science foundation (DFG) under the project MANOXUVA. J. C. McConnell and K. Semeniuk would like to thank the Natural Sciences and Engineering Research Council of Canada, the Canadian Foundation for Climate and Atmospheric Sciences and the Canadian Foundation for Innovation.

Edited by: V. Fomichev

References

Brasseur, G. and Solomon, S.: Aeronomy of the middle Atmosphere, 3rd revised and enlarged ed., Springer, Dordrecht, 644, 327–358, 2005.

de Grandpré, J., Beagley, S. R., Fomichev, V. I., Griffioen, E., McConnell, J. C., Medvedev, A. S., and T. G. Shepherd: Ozone climatology using interactive chemistry: Results from the Canadian Middle Atmosphere Model, J. Geophys. Res., 105, 26 475–26 491, 2000.

European Space Agency, Envisat, MIPAS An instrument for atmospheric chemistry and climate research, ESA Publications Division, ESTEC, The Netherlands, SP-1229, 1–123, 2000.

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

Fischer, H., Birk, M., Blom, C., Carli, B., Carlotti, M., von Clarmann, T., Delbouille, L., Dudhia, A., Ehhalt, D., Endemann, M., Flaud, J. M., Gessner, R., Kleinert, A., Koopmann, R., Langen, J., López-Puertas, M., Mosner, P., Nett, H., Oelhaf, H., Perron, G., Remedios, J., Ridolfi, M., Stiller, G., and Zander, R.: MIPAS: An Instrument for Atmospheric and Climate Research, Atmos. Chem. Phys., 8, 2151–2188, 2008, http://www.atmos-chem-phys.net/8/2151/2008/.

Funke, B., López-Puertas, M., Gil-López, S., Clarmann, T., Stiller, G., Kellmann, S., and Fischer, H.: Downward transport of upper atmospheric NO_x into the polar stratosphere and lower mesosphere during the Antarctic 2003 and Arctic 2002/2003 winters, J. Geophys. Res., 110, D24308, doi:10.1029/2005JD006463, 2005.

Funke, B., López-Puertas, M., Garcïa-Comas, M., Stiller, G. P., von Clarmann, T., and Glatthor, N.: Mesospheric N_2O enhancements as observed by MIPAS on Envisat during the polar winters in 2002-2004, Atmos. Chem. Phys. Discuss., 8, 10 561–10 596, 2008.

Glatthor, N., von Clarmann, T., Fischer, H., Funke, B., Grabowski, U., Höpfner, M., Kellmann, S., Kiefer, M., Linden, A., Milz, M., Steck, T., Stiller, G. P., Mengistu Tsidu, G., and Wang, D.-Y.: Mixing processes during the Antarctic vortex split in September–October 2002 as inferred from source gas and ozone distributions from ENVISAT-MIPAS, J. Atmos. Sci., 62, 787–800, 2005.

Jackman, C. H. and McPeters, R. D.: 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., DeLand, M. T., Labow, G. J., Fleming, E. L., Weisenstein, D. K., Ko, M., Sinnhuber, M. K. W., and Russell, J. M.: Neutral atmospheric influences of the solar proton events in October–November 2003, J. Geophys. Res., 110, A09S27, doi:10.1029/2004JA010888, 2005a.

Jackman, C. H., DeLand, M. T., Labow, G. J., Fleming, E. L., Weisenstein, D. K., Ko, M., Sinnhuber, M. K. W., Anderson, J., and Russell, J. M.: The influence of the several very large solar proton events in Years 2000–2003 on the neutral middle atmosphere, Adv. Space Res., 35, 445–450, 2005b.

Jackman, C. H., Marsh, D. R., Vitt, F. M., Garcia, R., Fleming, E. L., Labow, G. J., Randall, C., López-Puertas, M., and Funke, B.: Short- and medium-term atmospheric effects of very large solar proton events, Atmos. Chem. Phys., 8, 765–785, 2008, http://www.atmos-chem-phys.net/8/765/2008/.

Jackman, C. H.: Ionization rates for 1963–2007 from Solar Proton events, www.geo.fu-berlin.de/en/met/ag/strat/research/SOLARIS/Input_data/SOLARIS_Jackman_SPEs.pdf, 2007.

López-Puertas, M., Funke, B., Gil-López, S., von Clarmann, T., Stiller, G. P., Höpfner, M., Kellmann, S., Fischer, H., and Jackman, C. H.: Observation of NO_x enhancement and ozone depletion in the Northern and Southern Hemispheres after the October–November 2003 solar proton events, J. Geophys. Res., 110, A09S43, doi:10.1029/2005JA011050, 2005a.

López-Puertas, M., Funke, B., Gil-López, S., Mengistu Tsidu,

G., Fischer, H., and Jackman, C. H.: HNO_3, N_2O_5, and $ClONO_2$ enhancements after the October–November 2003 solar proton events, J. Geophys. Res., 110, A09S44, doi:10.1029/2005JA011051, 2005b.

López-Puertas, M., Funke, B., Clarmann, T., Fischer, H., and Stiller, G.: The Variability of Stratospheric and Mesospheric NO_y in the Arctic and Antarctic 2002–2004 Polar Winters, Space Sci. Rev., 125, 403–416, doi:10.1007/s11214-006-9073-2, 2006.

Nett, H., Carli, B., Carlotti, M., et al.: MIPAS ground processor and data products, Proc. IEEE 1999 Inter. Geosci. and Remote Sensing Symp., Hamburg, Germany, 1692–1696, 1999.

Nett, H., Perron, G., Sanchez, M., Burgess, A., and Mosner, P.: 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, 1–10, 2002.

Orsolini, Y. J., Manney, G. L., Santee, M. L., and Randall, C. E.: An upper stratospheric layer of enhanced HNO_3 following exceptional solar storms, Geophys. Res. Lett., 32, L12S01, doi:10.1029/2004GL021588, 2005.

Randall, C. E., Harvey, V. L., Manney, G. L., et al.: Stratospheric effects of energetic particle precipitation in 2003–2004, Geophys. Res. Lett., 32, L05802, doi:10.1029/2004GL022003, 2005.

Rohen, G., von Savigny, C., Sinnhuber, M., Llewellyn, E. J., Kaiser, J. W., Jackman, C. H., Kallenrode, M.-B., Schroter, J., Eichmann, K.-U., Bovensmann, H., and Burrows, J. P.: Ozone depletion during the solar proton events of Oct./Nov. 2003 as seen by SCIAMACHY, J. Geophys. Res., 110, A09S39, doi:10.1029/2004JA010984, 2005.

Rusch, D. W., Gerard, J.-C., Solomon, S., Crutzen, P. J., and Reid, G. C.: The effect of particle precipitation events on the neutral and ion chemistry of the middle atmosphere, 1, Odd nitrogen, Planet. Space Sci., 29, 767–774, 1981.

Semeniuk, K., McConnell, J. C., Jin, J. J., Jarosz, J. R., Boone, C. D., and Bernath, P. F.: N_2O production by high energy auroral electron precipitation, J. Geophys. Res., doi:10.10.29/2008JD010634, in press, 2008.

Semeniuk, K., McConnell, J. C., and Jackman, C. H.: Simulation of the October–November 2003 solar proton events in the CMAM GCM: Comparison with observations, Geophys. Res. Lett., 32, L15S02, doi:10.1029/2004GL022392, 2005.

Seppälä, A., Verronen, P. T., Kyrölä, E., Hassinen, S., Backman, L., Hauchecorne, A., Bertaux, J. L., and Fussen, D.: 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:10.1029/2004GL021042, 2004.

Stiller, G. P.: The Karlsruhe Optimized and Precise Radiative Transfer Algorithm (KOPRA), Wiss. Ber. FZKA 6487, Forschungszentrum, Karlsruhe, Germany, 521–540, 2000.

Verronen, P. T., Seppälä, A., Kyrölä, E., Tamminen, J., Pickett, H. M., and Turunen, E.: Production of odd hydrogen in the mesosphere during the January 2005 solar proton event, Geophys. Res. Lett., 33, L24811, doi:10.1029/2006GL028115, 2006.

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

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

von Clarmann, T., Glatthor, N., Grabowski, U., 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., Glatthor, N., Höpfner, M., et al.: Stratospheric HOCl measurements provide evidence of increased stratospheric odd hydrogen abundances due to solar proton events 2003, J. Geophys. Res., 110, A09S45, doi:10.1029/2005JA011053, 2005.

Wennberg, P. O., Anderson, J. G., and Weisenstein, D. K.: Kinetics of reactions of ground state nitrogen atoms ($^4S_{3/2}$) with NO and NO_2, J. Geophys. Res., 99, 18 839–18 846, 1994.