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# Composition changes after the “Halloween” solar proton event: the High-Energy Particle Precipitation in the Atmosphere (HEPPA) model versus MIPAS data intercomparison study

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**Abstract.** We have compared composition changes of NO, NO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>, N<sub>2</sub>O, HNO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, HNO<sub>4</sub>, ClO, HOCl, and ClONO<sub>2</sub> as observed by the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) on Envisat in the aftermath of the “Halloween” solar proton event (SPE) in October/November 2003 at 25–0.01 hPa in the Northern hemisphere (40–90°N) and simulations performed by the following atmospheric models: the Bremen 2D model (B2dM) and Bremen 3D Chemical Transport Model (B3dCTM), the Central Aerological Observatory (CAO) model, FinROSE, the Hamburg Model of the Neutral and Ionized Atmosphere (HAMMONIA), the Karlsruhe Simulation Model of the Middle Atmosphere (KASIMA), the ECHAM5/MESy Atmospheric Chemistry (EMAC) model, the modeling tool for Solar Climate Ozone Links studies (SOCOL and SOCOLi), and the Whole Atmosphere Community Climate Model (WACCM4). The large number of participating models allowed for an evaluation of the overall ability of atmospheric models to reproduce observed atmospheric perturbations generated by SPEs, particularly with respect to NO<sub>y</sub> and ozone changes. We have further assessed the meteorological conditions and their implications on the chemical response to the SPE in both the models and observations by comparing temperature and tracer (CH<sub>4</sub> and CO) fields.

Simulated SPE-induced ozone losses agree on average within 5% with the observations. Simulated NO<sub>y</sub> enhancements around 1 hPa, however, are typically 30% higher than

indicated by the observations which can be partly attributed to an overestimation of simulated electron-induced ionization. The analysis of the observed and modeled NO<sub>y</sub> partitioning in the aftermath of the SPE has demonstrated the need to implement additional ion chemistry (HNO<sub>3</sub> formation via ion-ion recombination and water cluster ions) into the chemical schemes. An overestimation of observed H<sub>2</sub>O<sub>2</sub> enhancements by all models hints at an underestimation of the OH/HO<sub>2</sub> ratio in the upper polar stratosphere during the SPE. The analysis of chlorine species perturbations has shown that the encountered differences between models and observations, particularly the underestimation of observed ClONO<sub>2</sub> enhancements, are related to a smaller availability of ClO in the polar night region already before the SPE. In general, the intercomparison has demonstrated that differences in the meteorology and/or initial state of the atmosphere in the simulations causes a relevant variability of the model results, even on a short timescale of only a few days.

## 1 Introduction

Energetic particle precipitation has important implications on atmospheric chemistry. In particular, protons and associated electrons, generated during solar eruptions, cause sporadically in-situ production of NO<sub>x</sub> and HO<sub>x</sub> radicals involved in catalytic ozone destruction. These solar proton events (SPEs) thus represent an important Sun-Earth connection which contributes to the natural ozone variability. The quasi-instantaneous increase of odd nitrogen and hydrogen

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due to SPEs induces perturbations of the chemical composition of the middle atmosphere on a short-time scale. In this sense, SPE-induced perturbations of the atmospheric composition represent an ideal natural laboratory for studying stratospheric and mesospheric chemistry (see also Jackman and McPeters, 1987).

In recent years, there have been two large SPEs (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 (López-Puertas et al., 2005a,b; von Clarmann et al., 2005; Orsolini et al., 2005; Seppälä et al., 2004; 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., 2005b, 2008). During and after this event, often called “Halloween” storm, 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  $\text{NO}_x$ , e.g., in  $\text{NO}$  and  $\text{NO}_2$ , and large depletions in  $\text{O}_3$  (López-Puertas et al., 2005a) as well as significant changes in other  $\text{NO}_y$  species, such as  $\text{HNO}_3$ ,  $\text{N}_2\text{O}_5$ ,  $\text{ClONO}_2$  (López-Puertas et al., 2005b), and  $\text{N}_2\text{O}$  (Funke et al., 2008). In addition, there also have been observed changes in  $\text{ClO}$  and  $\text{HOCl}$  as evidence of perturbations by solar protons on the  $\text{HO}_x$  and chlorine species abundances (von Clarmann et al., 2005).

Several model studies, aiming at reproducing observed short- and medium-term composition changes after this particular event (Jackman et al., 2008; Verronen et al., 2008; Funke et al., 2008; Baumgaertner et al., 2010; Egorova et al., 2010) and evaluating SPE-induced long-term effects (Jackman et al., 2009) have been carried out in the past.

The High-Energy Particle Precipitation in the Atmosphere (HEPPA) model vs. data intercomparison initiative has brought together scientists involved in atmospheric modeling using state-of-the-art general circulation models (GCMs) and chemistry-transport models (CTMs) on the one hand and scientists involved in the analysis and generation of observational data on the other hand. The objective of this community effort is (i) to assess the ability of state-of-the-art atmospheric models to reproduce composition changes induced by particle precipitation, (ii) to identify and – if possible – remedy deficiencies in chemical schemes, and (iii) to serve as a platform for discussion between modelers and data producers. This is achieved by a quantitative comparison of observed and modeled composition changes after particle precipitation events, as well as by inter-comparing the simulations performed by the different models.

In this study we report results from the intercompari-

son of MIPAS/Envisat data obtained during 26 October – 30 November 2003, before and after the Halloween SPE, at altitudes between 25–75 km (25–0.01 hPa) with simulations performed using the following GCMs and CTMs: the Bremen 2d Model (B2dM) (Sinnhuber et al., 2003b; Winkler et al., 2009), the Bremen 3d Chemical Transport Model (B2dM and B3dCTM) (Sinnhuber et al., 2003a), the Central Aerological Observatory (CAO) model (Krivolutsky and Vyushkova, 2002), FinROSE (Damski et al., 2007b), the Hamburg Model of the Neutral and Ionized Atmosphere (HAMMONIA) (Schmidt et al., 2006), the Karlsruhe Simulation Model of the Middle Atmosphere (KASIMA) (Kouker et al., 1999), the ECHAM5/MESSy Atmospheric Chemistry (EMAC) model (Jöckel et al., 2006), the modeling tool for SOLar Climate Ozone Links studies (SOCOL and SOCOLi) (Egorova et al., 2005; Schraner et al., 2008; Egorova et al., 2010), and the Whole Atmosphere Community Climate Model (WACCM4) (Garcia et al., 2007). Among the species affected by SPEs we focus here on  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{H}_2\text{O}_2$ ,  $\text{O}_3$ ,  $\text{N}_2\text{O}$ ,  $\text{HNO}_3$ ,  $\text{N}_2\text{O}_5$ ,  $\text{HNO}_4$ ,  $\text{ClO}$ ,  $\text{HOCl}$ , and  $\text{ClONO}_2$ . For these species a significant perturbation well above the detection limit has been observed by MIPAS. We have further assessed the meteorological background conditions in both the models and the real atmosphere as observed by MIPAS by comparing temperature and tracer fields ( $\text{CH}_4$  and  $\text{CO}$ ). Although SPE-induced composition changes during the Halloween event have been reported in both hemispheres, we restrict our analysis to the Northern hemisphere (NH) in the latitude range 40–90°N where most pronounced effects have been observed and composition changes can be well distinguished from the background variability.

Apart from the initial particle forcing leading to atmospheric ionization, SPE-induced composition changes are controlled by several other factors such as the neutral and ion chemistry responsible for the repartitioning of primarily generated species, the background composition interfering with the chemical repartitioning, and the meteorological/dynamical conditions. The large number of controlling factors and their interaction introduce a significant spread in the model results and make their analysis difficult. In order to reduce the model variability and to make differences between the simulations more traceable, we have simplified the intercomparison setup such that a common particle-induced ionization source has been used in all models. These ionization rates, accounting for protons (154 eV–500 MeV) and electrons (154 eV–5 MeV) have been provided by the AIMOS model (Wissing and Kallenrode, 2009). Different model responses to the particle forcing are hence reduced to differences of the intrinsic model properties, e.g. chemical and dynamical schemes. A major aim of this paper is the assessment of these differences and their implications on the models’ ability to correctly describe particle precipitation effects which represent an important source of natural, solar-induced climate variability on short and mid-term scales. Additionally, conclusions on the quality of the description of the ex-

**Table 1.** Used MIPAS data versions (indicated by the last digits of the retrieval version) for all species on a daily basis within the period 26 October–30 November 2003.

Day	26	27	28	29	30	31	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	
Temp.	9	10	10	9	9	9	9	9	9	9	9	10	10	10	9	9	9	9	10	10	10	9	9	9	9	9	9	10	10	10	10	10	9	9	9	9	
CH <sub>4</sub>	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	
CO	9	11	11	9	10	10	9	9	10	10	9	11	11	10	10	10	9	11	11	11	10	10	10	9	10	10	11	11	11	11	11	9	10	10	10		
NO	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	14	
NO <sub>2</sub>	14	13	13	14	11	11	14	14	11	11	14	13	13	11	11	11	14	13	13	13	11	11	11	14	11	11	14	11	13	13	13	13	14	11	11	11	
N <sub>2</sub> O	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	
HNO <sub>3</sub>	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	
N <sub>2</sub> O <sub>5</sub>	9	10	10	10	10	10	9	10	10	10	10	10	10	10	10	10	9	10	10	10	10	10	10	10	10	10	9	10	10	10	10	10	10	10	10	10	
HNO <sub>4</sub>	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12	12
O <sub>3</sub>	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	9	
H <sub>2</sub> O <sub>2</sub>	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	4	
ClO	10	11	11	11	11	11	10	11	11	11	11	11	11	11	11	11	10	11	11	11	11	11	11	11	11	10	11	11	11	11	11	11	11	11	11	11	
HOCl	3	4	4	3	3	3	3	3	3	3	3	4	4	4	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	
ClONO <sub>2</sub>	11	12	12	12	12	12	11	12	12	12	12	12	12	12	12	12	11	12	12	12	12	12	12	12	12	11	12	12	12	12	12	12	12	12	12	12	

ternal forcing provided by the ionization model can be drawn from the overall agreement of the short-time response of primarily generated constituents (i.e. NO<sub>x</sub>).

The paper is organized as follows: In Section 2 we give an overview on MIPAS observations and data products used in this study, followed by Section 3 describing the ionization model AIMOS and Section 4 describing the participating global circulation and chemistry transport models. The intercomparison method is described in Section 5, followed by the discussion of the results (Section 6).

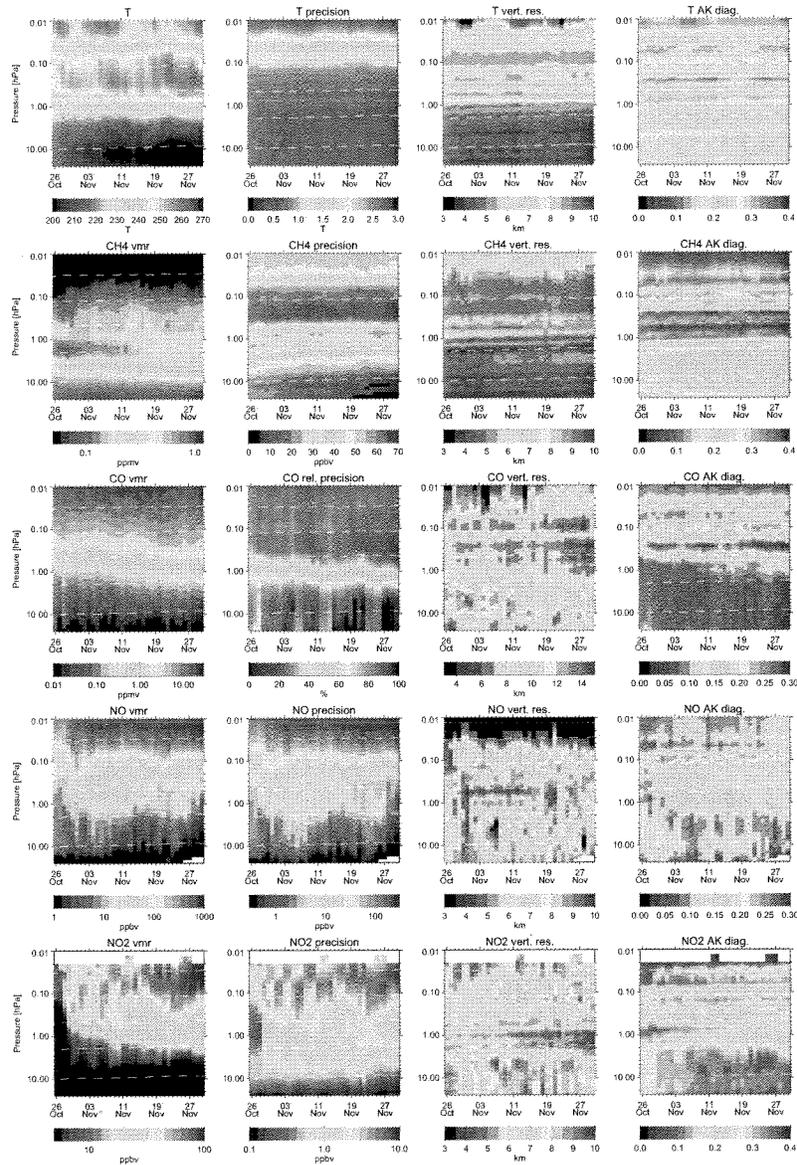
## 2 MIPAS observations

The Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) is a mid-infrared Fourier transform limb emission spectrometer designed and operated for measurement of atmospheric trace species from space (Fischer et al., 2008). It is part of the instrumentation of the European Environmental Satellite (ENVISAT) which was launched into its sun-synchronous polar orbit of 98.55°N inclination at about 800 km altitude on 1 March 2002. MIPAS passes the equator in a southerly direction at 10.00 a.m. local time 14.3 times a day, observing the atmosphere during day and night with global coverage from pole to pole. The instrument’s field of view is 30 km in horizontal and approximately 3 km in vertical direction. MIPAS operated during October/November 2003 at full spectral resolution of 0.035 cm<sup>-1</sup> (unapodized) in terms of full width at half maximum. During this period, MIPAS recorded a rear-viewing limb sequence of 17 spectra each 90 s, corresponding to an along track sampling of approximately 500 km and providing about 1000 vertical profiles per day in its standard observation mode. Tangent heights covered 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.

Trace gas profiles have been retrieved from calibrated geolocated limb emission spectra with the scientific MIPAS level 2 processor developed and operated by the Institute of Meteorology and Climate Research (IMK) in Karlsruhe together with the Instituto de Astrofísica de Andalucía (IAA)

in Granada. The general retrieval strategy, which is a constrained multi-parameter non-linear least squares fitting of measured and modeled spectra, is described in detail in von Clarmann et al. (2003). Its extension to retrievals under consideration of non-LTE (i.e., CO, NO, and NO<sub>2</sub>) is described in Funke et al. (2001). Non-LTE vibrational populations of these species are modeled with the Generic Radiative transfer AnD non-LTE population Algorithm (GRANADA) (Funke et al., 2007) within each iteration of the retrieval.

In contrast to previous work describing MIPAS observations of composition changes during the Halloween SPE (López-Puertas et al., 2005a,b; von Clarmann et al., 2005), we base our analysis here on reprocessed IMK/IAA MIPAS data which have substantially improved with respect to previous data versions. These improvements include updates in the L1B processing (version 4.61/62 instead of 4.59) performed by ESA as well as changes in the L2 processing performed at IMK/IAA. The new data set also offers full temporal coverage over the period of interest (26 October–30 November 2003). In the following, we summarize the improvements of the retrieval setups for each species/parameter and characterize the data used in our analysis in terms of estimated single measurement precision and vertical resolution obtained from the full width at half maximum of the rows of the averaging kernel (AK) matrix (Rodgers, 2000). The AK diagonal elements are also discussed as a measure of the sensitivity of the retrieval at a given profile grid point to the “true” profile. Values close to zero (typically <0.03) indicate that there is no significant sensitivity to the retrieval parameter at the corresponding altitude and hence are excluded from our analysis. This value may appear unreasonably small but since IMK/IAA retrievals are not constrained by optimal estimation (Rodgers, 2000) but by a first order smoothing constraint using a Tikhonov (1963) formalism, low values do not hint at a large a priori content of the retrieval but only at extensive smearing of information over altitude. A detailed discussion of systematic retrieval errors can be found in previous works describing the individual constituent retrievals which are referenced in the following.



**Fig. 1.** Temporal evolution of MIPAS temperature, CH<sub>4</sub>, CO, NO, NO<sub>2</sub>, (from top to bottom) volume mixing ratio, single measurement precision, vertical resolution, and AK diagonal element profiles (left to right) during 26 October - 30 November 2003 averaged over 60–90°N. White dashed lines indicate 30, 40, 50, 60, and 70 km geometric altitude levels. White regions reflect meaningless data (AK diagonal elements smaller than 0.03).

## 2.1 Temperature

245 Temperature data versions used here are V3O\_T\_9 and V3O\_T\_10 (see Table 1), both including as an extension to 250 the original retrieval setup described in von Clarmann et al.

(2003) the joint retrieval of horizontal temperature gradients. Differences between both versions are of minor nature and do not noticeably affect the data characteristics. In the period of interest, observed temperatures range at 60–90°N from around 200 K in the lower stratosphere to around 270 K at

the stratopause (see Figure 1). The single measurement precision ranges from 0.5 K to 1.5–2.5 K above the stratopause. Vertical resolution is 3–4 km below 1 hPa and 5–7 km above. Meaningful data are obtained in the whole vertical range of interest (25–70 km).

## 2.2 CH<sub>4</sub>

We use version V3O.CH4.12 (see Table 1) which has been jointly retrieved with N<sub>2</sub>O (V3O.N2O.12). The retrieval setup is similar to that described in Glatthor et al. (2005). The single measurement precision ranges from 10–20 ppbv in the upper stratosphere to 50–70 K above and below (see Figure 1) Vertical resolution is 3–6 km below 0.03 hPa and slightly higher above. Meaningful data is obtained in the whole vertical range of interest (25–70 km).

## 2.3 CO

CO data versions used here are V3O.CO.9, V3O.CO.10, described in detail in Funke et al. (2009), as well as the most recent version V3O.CO.11 (see Table 1). Improvements implemented in the latter version include an extended set of spectral fitting windows resulting in a better precision and vertical resolution in the lower and middle stratosphere. In the period of interest, the temporal evolution of MIPAS CO abundances at 60–90°N indicate polar winter descent of mesospheric air masses of about 10 km around 1 hPa (see Figure 1). The single measurement precision ranges from 20–30% above 1 hPa to 70–80% in the lower stratosphere. Vertical resolution is 6–12 km below 0.1 hPa. Meaningful data are obtained in the whole vertical range of interest (25–70 km).

## 2.4 NO

We use version V3O.NO.14 (see Table 1), available for the whole time period. This version has substantially improved with respect to the retrieval setup described in Funke et al. (2005) and the data discussed in López-Puertas et al. (2005a) by i) the use of  $\log(\text{vmr})$  instead of  $\text{vmr}$  (volume mixing ratio) in the retrieval vector, ii) a revised correction scheme for line of sight variations of the NO<sub>x</sub> partitioning close to the terminator, and iii) joint-fitted  $\text{vmr}$  horizontal gradients at constant longitudes and latitudes. NO increases of several 100 ppbv have been observed at 60–90°N during the intense proton forcing during 29 October–4 November in the upper stratosphere around 0.2 hPa (see Figure 1). Above, NO increases were mainly produced by polar winter descent of upper atmospheric air masses, resulting in vmrs up to 1 ppmv below 70 km. The single measurement precision is of the order of 10%. Vertical resolution ranges from 4 to 8 km below 70 km. Meaningful data are obtained in the whole vertical range of interest (25–70 km).

## 2.5 NO<sub>2</sub>

NO<sub>2</sub> data versions used here are V3O.NO2.11, V3O.NO2.13, and V3O.NO2.14 (see Table 1). Including the same modifications as described above for NO, these versions have substantially improved with respect to the retrieval setup described in Funke et al. (2005) and the data discussed in López-Puertas et al. (2005a). While differences between the latter two versions do not affect noticeably the data characteristics, a modified regularization scheme and terminator treatment implemented after version V3O.NO2.11 gave rise to non-negligible differences in the newer versions with respect to the previous setup. These differences are visible in the vertical resolution in the mesosphere and middle stratosphere (see Figure 1, third column) and go along with generally smaller vmrs around the terminator at 70°N around 0.1 hPa. Similar to NO, increases of 50–80 ppbv were observed during the proton forcing in the upper stratosphere, descending by approximately 10 km until the end of November. Polar winter descent of NO<sub>x</sub> led to mesospheric NO<sub>2</sub> increases of more than 100 ppbv, particularly in the second half of November. The single measurement precision is of the order of 5–10%. Vertical resolution ranges from 4 to 8 km below 70 km. Meaningful data are obtained in the whole vertical range of interest (25–70 km).

## 2.6 N<sub>2</sub>O

We use version V3O.N2O.12 (see Table 1), available for the whole time period. This version, which has already been used for the previous analysis of N<sub>2</sub>O abundance changes during the Halloween SPE (Funke et al., 2008) and differs from other versions by a relaxed regularization above approximately 40 km which allows for vertically resolving the upper stratospheric and mesospheric enhancements. At 60–90°N, these enhancements of around 5–7 ppbv appeared around 30 October and descended during November to the middle stratosphere (see Figure 2). The single measurement precision ranges from 0.5 ppbv in the upper stratosphere to 2 ppbv in the mesosphere. Vertical resolution is 4–6 km. Meaningful data are obtained in the whole vertical range of interest (25–70 km).

## 2.7 HNO<sub>3</sub>

We use version V3O.HNO3.9 (see Table 1), available for the whole time period, and which is based on the retrieval setup described in Wang et al. (2007). HNO<sub>3</sub> increases of around 3 ppbv up to altitudes of 0.1 hPa during the proton forcing and a further buildup at slightly lower altitudes at the end of November are visible in Figure 2, consistent with previous findings (López-Puertas et al., 2005b). The single measurement precision ranges from 0.1 ppbv in the middle stratosphere to 0.35 ppbv around the stratopause. Vertical resolu-

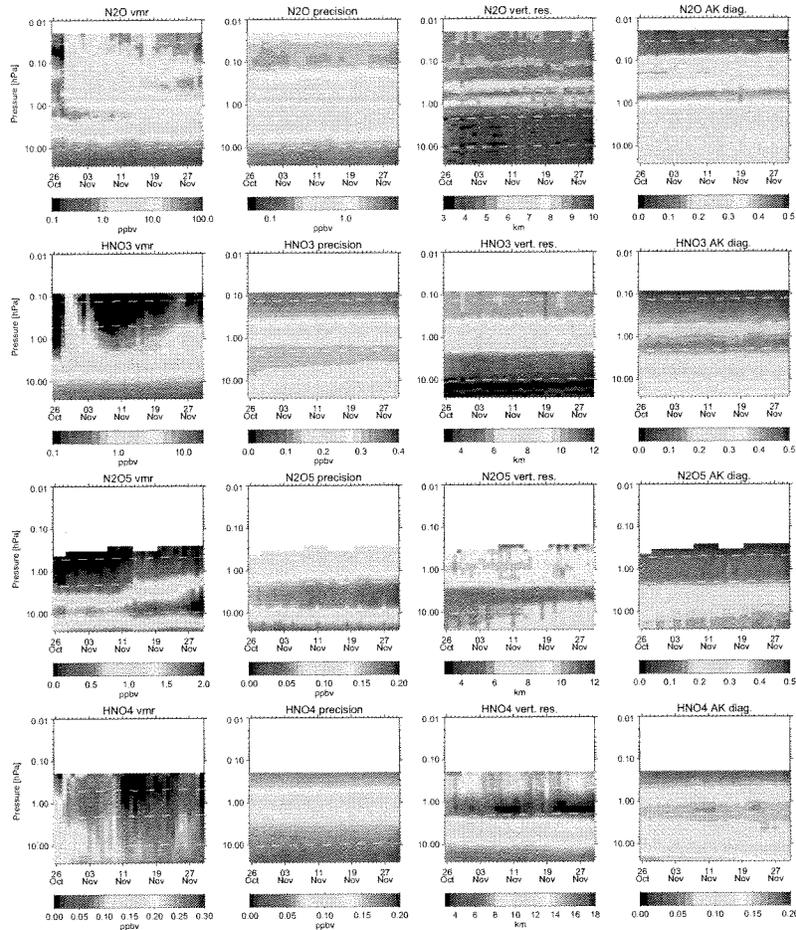


Fig. 2. Same as Figure 1, but for  $\text{N}_2\text{O}$ ,  $\text{HNO}_3$ ,  $\text{N}_2\text{O}_5$ , and  $\text{HNO}_4$ .

350 tion is 3–4 km below 12 hPa and 7–10 km above. Meaningful data are obtained below 0.1 hPa (60 km).

### 2.8 $\text{N}_2\text{O}_5$

355  $\text{N}_2\text{O}_5$  data versions used here are V3O\_N2O5\_9 and V3O\_N2O5\_10 (see Table 1), all based on the retrieval setup described in Mengistu Tsidu et al. (2004). Differences between both versions are of minor nature and do not affect noticeably the data characteristics.  $\text{N}_2\text{O}_5$  increases related to the proton event are mainly visible in Figure 2 in the second half of November around 2–0.5 hPa, consistent with previous findings (López-Puertas et al., 2005b). The single measurement precision ranges from 0.05 ppbv to 0.15 ppbv 375 in the middle stratosphere. Vertical resolution is 5–7 km below 2 hPa and 5–7 km above. Meaningful data are obtained

below approximately 0.3 hPa (52 km).

### 2.9 $\text{HNO}_4$

We use version V3O\_HNO4\_12 (see Table 1) which differs from the original retrieval setup described in Stiller et al. (2007) by the application of a weaker regularization in the middle stratosphere, where most pronounced SPE effects are expected. Unfortunately, this version is sensitive to systematic oscillations in the radiance baseline related to an imperfect gain calibration of the instrument (see also Stiller et al., 2008). In consequence, retrieved  $\text{HNO}_4$  profiles are systematically biased during each gain calibration period (typically a few days) with a randomly changing magnitude from one calibration period to another. The variable bias is noticeable in the temporal evolution of the observed

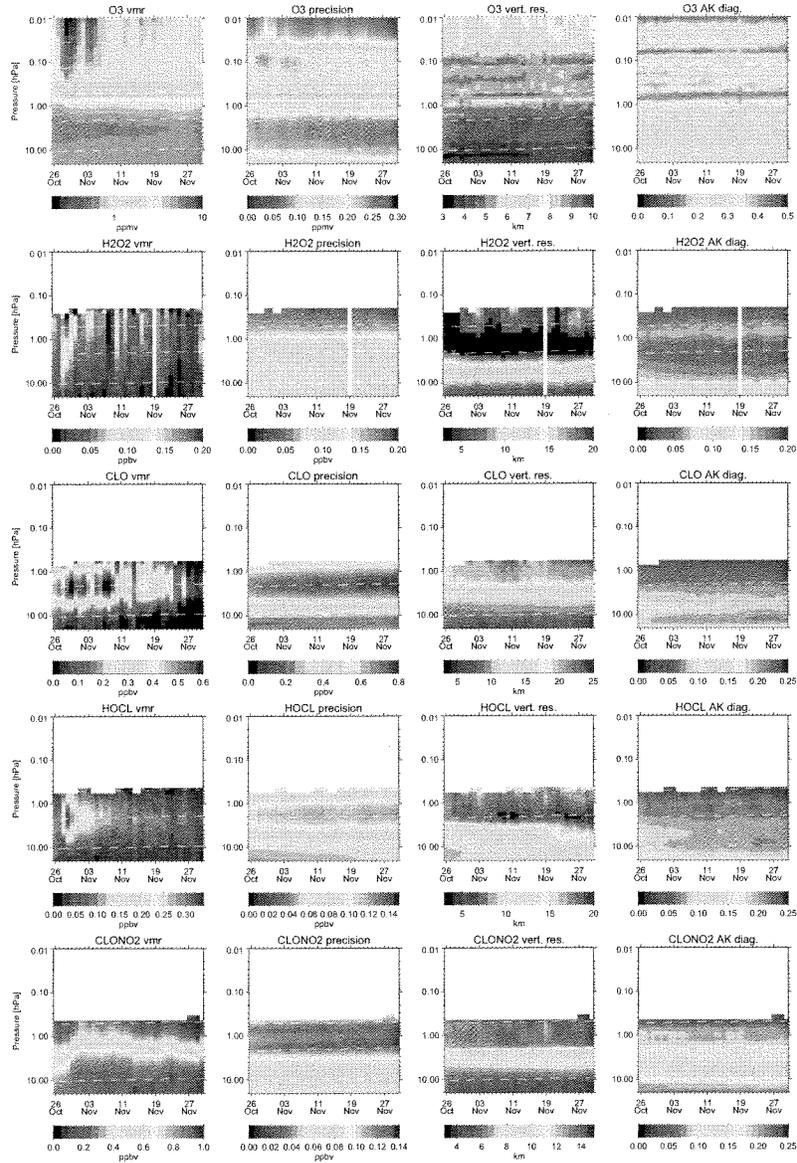


Fig. 3. Same as Figure 2, but for  $O_3$ ,  $H_2O_2$ ,  $ClO$ ,  $HOCl$ , and  $ClONO_2$ .

380  $HNO_4$  distributions at  $60\text{--}90^\circ N$  (see Figure 2) as sharp increases/decreases in the upper stratosphere, coincident with the onsets of new gain calibration periods (i.e., 28 October, 10 November, and 24 November). Therefore, we restrict our analysis of SPE-related  $HNO_4$  increases in Section 6 to data  
 385 observed during one particular gain calibration period, 28 October – 5 November, covering the onset of the proton forcing which led to short-term  $HNO_4$  increases of the order of

0.15 ppbv (hardly visible in Figure 2). The single measurement precision ranges from 0.03 ppbv to 0.15 ppbv around the stratopause. Vertical resolution is 6–10 km below 5 hPa and around 10 km above. Meaningful data are obtained below approximately 0.2 hPa (55 km).

## 2.10 O<sub>3</sub>

We use version V3O.O3\_9 (see Table 1), available for the whole time period. Retrieval setup and characteristics are similar to those described in Steck et al. (2007), except for a slightly different selection of spectral intervals (micro-  
 395 windows) and the inclusion of pre-fitted horizontal temperature gradients. A pronounced O<sub>3</sub> depletion during the intense proton forcing as already reported in López-Puertas et al. (2005a) is visible above the stratopause at 60–90°N, competing in weeks with seasonal mesospheric O<sub>3</sub> buildup (see Figure 3). Also, the previously reported NO<sub>x</sub>-induced losses at lower altitudes are seen on a mid-term scale. The single measurement precision ranges from 0.1 ppmv around the stratopause to 0.25 ppbv above and below. Vertical reso-  
 400 lution is 3–4 km below 1 hPa and 5–7 km above. Meaningful data are obtained in the whole vertical range of interest (25–70 km).

## 2.11 H<sub>2</sub>O<sub>2</sub>

We use version V3O.H2O2\_4, available for the whole time period (see Table 1) which is based on the retrieval setup described in Versick (2010). H<sub>2</sub>O<sub>2</sub> increases up to 0.15 ppbv  
 410 have been observed at 60–90°N during the intense proton forcing on 29 October–4 November in the upper stratosphere around 0.2 hPa (see Figure 3). The single measurement precision in the middle stratosphere ranges from 0.1 to 0.2 ppbv, being thus of the order of the observed enhancements. In consequence, averaging is required for the analysis. Vertical  
 415 resolutions larger than 10 km indicate that no relevant information on the vertical distribution of the middle/upper stratospheric enhancements can be extracted from the measurements. Meaningful data are obtained below approximately  
 420 0.2 hPa (55 km).

## 2.12 ClO

ClO data versions used here are V3O.CLO\_10 and V3O.CLO\_11 (see Table 1), all based on the retrieval setup described in Glatthor et al. (2004). Differences between both versions are of minor nature and do not affect noticeably the data characteristics. As in the case of HNO<sub>4</sub>, ClO data is affected by systematic oscillations in the radiance baseline related to an imperfect gain calibration of the instrument, however, to a lesser degree than in the case of HNO<sub>4</sub>. The single measurement precision ranges from 0.2 ppbv in the lower stratosphere to 0.7 ppbv around 2 hPa, being thus higher than 100% at the ClO peak height (see Figure 3). In consequence,  
 425 averaging is required for its analysis. Vertical resolution is 6–10 km below 2 hPa and 15–20 km above. Meaningful data are obtained below approximately 0.5 hPa (40 km).  
 435

species	energy	pressure (hPa)	approx. altitude (km)
protons	154 eV–500 MeV	10 <sup>-7</sup> –100	18–240/440
electrons	154 eV–5 MeV	10 <sup>-7</sup> –1	48–240/440

**Table 2.** AIMOS particle energy ranges and the corresponding pressure and altitude levels. As the upper altitude border for protons and electrons lies in the thermosphere, it varies by solar activity. The first number indicates solar minimum conditions while the second number represents solar maximum.

## 2.13 HOCl

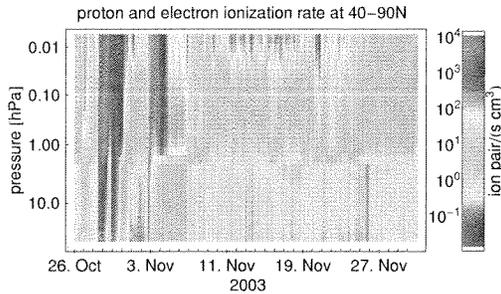
HOCl data versions used here are V3O.HOCL\_3 and V3O.HOCL\_4 (see Table 1), all based on the retrieval setup described in von Clarmann et al. (2006). Differences between both versions are of minor nature and do not affect noticeably the data characteristics. HOCl increases of around 0.3 ppbv show up in Figure 3 immediately after the main proton forcing at the beginning of November, consistent with previous findings (von Clarmann et al., 2005). The single measurement precision ranges from 0.05 to 0.1 ppbv around 2 hPa. Vertical resolution 8–12 km below 2 hPa and coarser then 15 km above. Meaningful data is obtained below approximately 0.5 hPa (40 km).  
 445

## 2.14 ClONO<sub>2</sub>

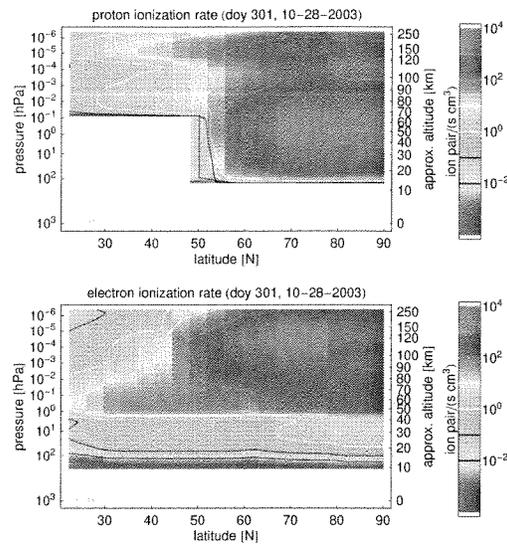
ClONO<sub>2</sub> data versions used here are V3O.CLONO2\_11 and V3O.CLONO2\_12 (see Table 1), all based on the retrieval setup described in Höpfner et al. (2007). Differences between both versions are of minor nature and do not affect noticeably the data characteristics. ClONO<sub>2</sub> increases of around 0.5 ppbv are visible in Figure 3 after the main proton forcing above 5 hPa and last until the end of November. This is consistent with previous findings based on data version V1.CLONO2\_1 (López-Puertas et al., 2005b) in qualitative terms, however, the peak height of the increases is slightly higher (~5 km) in the newer data versions included here. This difference is mainly related to a change of the height-dependent regularization strength in order to allow for more sensitivity at lower and higher altitudes. The single measurement precision ranges from 0.06 to 0.12 ppbv, increasing with altitude. Vertical resolution is 5–8 km below 2 hPa and 12–14 km above. Meaningful data is obtained below approximately 0.5 hPa (40 km).  
 460

## 3 Ionization rates

The model intercomparison is based on ionization rates calculated with Atmospheric Ionization Module OSnabrück (AIMOS). The reason is to avoid different model results due to different ionization rates as to better understand the differences in the dynamical and chemistry schemes of the models



**Fig. 4.** Temporal evolution of area-weighted averages (40–90°N) of AIMOS ion pair production rates for protons and electrons during the period of interest. Electron ionization rate below 1 hPa is induced by bremsstrahlung only.



**Fig. 5.** Altitude-latitude sections of AIMOS ion pair production rates for protons (top) and electrons (bottom) on 28 October 2003.

under assessment. AIMOS calculates ionization rates due to precipitating solar and magnetospheric particles. The altitude range of calculated ionization rates is defined by the energy range of the particles considered, which is specific to the satellite instruments used. The data used here and their altitude coverage are listed in Table 2. Given by the altitude range of this study, the focus lies on solar particles. As particle precipitation strongly depends on the geomagnetic field, the model accounts for different spatial precipitation zones. A detailed description on AIMOS can be found in Wissing and Kallenrode (2009).

AIMOS is composed of two parts. One describes the spatial particle flux on top of the atmosphere while the second calculates the resulting ionization rate. Both parts will be discussed in the following.

### 3.1 Spatial particle flux

The particle flux on top of the atmosphere is measured by the TED and MEPED instruments on POES 15/16 as well as the SEM instrument on GOES 10. As all particle measurements are in-situ, the main challenge is to derive a global coverage at any time. Inside an empirically determined polar cap where particle precipitation is homogeneous, the high energetic particle flux from GOES and the mean flux values from polar cap crossings of the POES satellites are used. Outside the polar cap, particle precipitation depends on geomagnetic latitude, geomagnetic activity and local time. Therefore, mean precipitation maps for the POES TED and MEPED channels, based on a 4 year data set, have been produced, sorted by the geomagnetic  $K_p$ -index and local time. These mean precipitation maps represent the spatial distribution, including, e.g., the movement of the auroral oval. According to the recent  $K_p$ -level, the mean precipitation maps are selected and scaled to recent POES particle flux.

In summary, the first part of the model describes the incoming particle flux at every grid point. The spatial resolution is 96 zonal cells, divided into 48 meridional sections. Regions of similar particle flux are combined as, e.g., the polar cap. Given by the scaling of the mean precipitation maps, the temporal resolution is limited by the POES orbit and has been set to 2 h.

### 3.2 Modeling ionization rates

The second part of AIMOS is the atmospheric particle detector model, which simulates particle interactions based on the GEANT4-Simulation Toolkit (Agostinelli et al., 2003). GEANT4 provides Monte-Carlo based algorithms to model energy deposition/ionization of protons and electrons. The atmospheric detector model is divided into 67 logarithmically equidistant pressure levels, ranging from sea-level to  $1.7 \times 10^{-5}$  Pa. Since the atmospheric parameters (density, altitude, composition and temperature) depend on latitude, season and solar activity, model versions for 80°N, 60°N, 60°S and 80°S, 3 different F10.7 flux values and 4 different months are used. These parameters are adopted from the HAMMONIA (Schmidt et al., 2006) and MSIS (Picone et al., 2002) models. The ionization rates for mono-energetic and isotropic particle ensembles are determined. As a final step, the mono-energetic ionization rates are combined with multiple power-law fits of the particle flux at various regions.

Figure 4 shows the temporal evolution of the resulting ion pair production rates averaged over 40–90°N during the pe-

riod of interest. The latitudinal distribution of the ionization rates of protons and electrons, respectively, is shown in Fig. 5 for the 28 October 2003.

The ionization rates should provide a similar forcing for all models, therefore the original data set has been adopted to every model grid. The data set and the adoption routine for a used specific grid is available at <http://aimos.physik.uos.de>.

## 4 Description of participating models

### 4.1 Bremen 2d model (B2dM)

The Bremen two-dimensional model is based on the two-dimensional transport, chemistry and radiation model formerly described in Sinnhuber et al. (2009) and Chipperfield and Feng (2003). It uses the dynamical core of the so-called two-and a half-dimensional model THIN AIR (Kinnersley, 1998), which calculates temperature, pressure, and horizontal transport on isentropic surfaces, interactive with the model chemistry. The model covers the altitude range from the surface to 100 km in 29 isentropic surfaces, providing a vertical spacing of about 3.5 km. The horizontal resolution is about 9.5 degree. Stratospheric dynamics are forced by the amplitudes of waves 1 to 3 of the Montgomery potential from meteorological analyses with a repeating annual cycle for the period of May 1980 to April 1981. There is no quasi biennial oscillation (QBO) in the model, i.e., the modeled tropical stratospheric wind is always in a weak easterly state. In this sense, the Bremen 2d model is a two-dimensional chemistry-climate model which is forced to repeat a very similar scenario by the repeating annual cycle of the Montgomery potential.

The chemistry is based on the SLIMCAT chemistry (Chipperfield and Jones, 1999), but adapted for the use in the mesosphere in several ways: (1) above 50km, no family approach is used; (2) H<sub>2</sub>O and CO<sub>2</sub> are treated as short-lived species explicitly, and H<sub>2</sub> is varied as well, to provide a realistic description of mesospheric HO<sub>x</sub> and CO. (3) NO<sub>x</sub> and HO<sub>x</sub> production by atmospheric ionization is parameterized based on Porter et al. (1976) and Solomon et al. (1981), i.e., 1.25 NO<sub>x</sub> are produced, of which 45% are produced as N, and 55% as NO, and up to 2 HO<sub>x</sub> are produced per ion pair depending on pressure and ionization rate, equally distributed to H and OH. Ionization due to Galactic Cosmic Rays in the stratosphere has been included based on Heaps (1978); the additional ionization due to solar and magnetospheric particles is considered by introducing atmospheric ionization rates of protons and electrons provided by the AIMOS model (see section 3).

All reaction and photolysis rates are taken from Sander et al. (2006). The Bremen 2d model has been used in the past to investigate the impact of large solar proton events on the composition of the middle atmosphere (Sinnhuber et al., 2003b; Rohen et al., 2005; Winkler et al., 2008). For

the HEPPA intercomparison, the two-dimensional model has been combined with a one-dimensional model sharing the same description of chemistry in the following way:

25 model runs with the two-dimensional model are carried out at different longitudes, to take into account the tilt of the geomagnetic poles. For every MIPAS measurement used in the intercomparison, a one-dimensional model run is started initialized with output of the 2-dimensional model runs interpolated to the geo-location of the measurement, at local noon of the day before the measurement took place. One-dimensional model runs are then carried out until the time of the measurement, providing model output at the exact time and geo-location of the measurement.

### 4.2 Bremen 3d Chemistry and Transport model (B3dCTM)

The Bremen three-dimensional Chemistry and Transport Model is a combination of the Bremen transport model (Sinnhuber et al., 2003a) and the chemistry code of the Bremen 2D model (Sinnhuber et al., 2003b; Winkler et al., 2008), which is based on the SLIMCAT model (Chipperfield and Jones, 1999).

The model has 28 isentropic levels ranging from 330 to 3402K (approx. 10-60km) and has a horizontal resolution of 3.75° × 2.5°. Output is provided hourly. The vertical transport across the isentropes is calculated through diabatic heating and cooling rates. These rates are calculated using the radiation scheme MIDRAD (Shine, 1987). The horizontal transport is driven by external wind-fields. Advection is calculated by using the second order moments scheme by Prather (1986). Meteorological data, such as horizontal wind speeds and temperatures, are taken from ECMWF ERA Interim (Simmons et al., 2006).

The model calculates the behavior of 58 chemical species, using a family approach for short-lived species (HO<sub>x</sub>, NO<sub>x</sub>, O<sub>x</sub>, ClO<sub>x</sub>, BrO<sub>x</sub> and CHO<sub>x</sub>). It includes about 180 gas phase, photochemical, and heterogeneous reactions and uses the recent set of recommendations for kinetic and photochemical data established by the Jet Propulsion Laboratory (Sander et al., 2006).

To account for ion chemistry reactions within the neutral code, the production of NO<sub>x</sub> and HO<sub>x</sub> is parameterized as suggested by Porter et al. (1976) and Solomon and Crutzen (1981). Hence 1.25 N atoms and about 2 HO<sub>x</sub> are produced per ion pair. Atmospheric ionization due to solar and magnetospheric particles is considered by introducing atmospheric ionization rates of protons and electrons provided by the AIMOS model (see section 3).

### 4.3 CAO

The Central Aerological Observatory (CAO) model consists of a CTM and a 3D dynamical core with a horizontal resolution of 10° × 10° and vertical resolution of 2 km. The

**Table 3.** Summarized description of the models involved in this study.

Model	type	vertical domain	vert. range (km)	horizontal resolution	vert. res. (km)	meteorological data nudging	kinetic data
B2dM	CTM/GCM (2D)	isentropic	~0–100	9.5°	~3.5	GCM	Sander et al. (2006)
B3dCTM	CTM	isentropic	~10–60	3.75° × 2.5°	~3.5	ECMWF ERA Interim	Sander et al. (2006)
CAO	CTM/GCM	altitude	0–90	10° × 10°	2	GCM	Sander et al. (2003)
FinROSE	CTM	hybrid	~0–65	10° × 5°	~2	ECMWF ERA Interim	Sander et al. (2006)
HAMMONIA	CCM	pressure	~0–200	4° × 4°	~3.5	ECMWF below 179 hPa	Sander et al. (2006)
KASIMA	CCM	pressure	~7–120	5.6° × 5.6°	0.75–3.8	ECMWF below 1 hPa	Sander et al. (2003)
EMAC	CCM	hybrid	~0–80	2.8° × 2.8°	~1	ECMWF below 200 hPa	Sander et al. (2006)
SOCOL(i)	CCM	hybrid	~0–80	3.75° × 3.75°	~2	-	Sander et al. (2000)
WACCM	CCM	pressure	~0–135	1.9° × 2.5°	~1.5	MERRA below 50 km	Sander et al. (2006)

CTM calculates the concentrations of 30 minor components, involved in 70 chemical and 35 photochemical reactions, in the range 0–90 km. Output is provided hourly. The reaction rate constants, absorption cross-sections, solar radiation intensity, and quantum outputs were assigned in the tabulated form according to Sander et al. (2003). The annual and daily variations of the solar zenith angle at a given point and its dependence on the height above the Earth's surface were taken into account. For zenith angle higher than 75°, Chapman functions have been used in accordance with Swinder and Gardner (1967). Photolysis rates have been recalculated every hour during the integration of the model. A family approach (Turco and Whitten, 1974) has been used for solving the chemical equations, including  $O_x$  ( $O_3+O+O(^1D)$ ),  $NO_y$  ( $N+NO+NO_2+NO_3+2N_2O_5+HNO_3+HNO_4+ClONO_2$ ),  $Cl_y$  ( $Cl+ClO+OCIO+ClOO+HOCl+HCl$ ), and  $HO_x$  ( $H+OH+HO_2+2H_2O_2$ ). Other long-lived species ( $N_2O$ ,  $CCl_4$ ,  $CFCl_3$ ,  $CF_2Cl_2$ ,  $CH_3Cl_3$ ,  $CH_4$ ,  $H_2O$ ,  $H_2$  and  $CO_2$ ) were included also in simulations. The CAO model applies additionally to electron and proton-induced ionization also ionization rates caused by alpha-particles provided by the AIMOS model (Wissing and Kallenrode, 2009).

The vertical profiles of molecular oxygen and air density were fixed during photochemical calculations. Heterogeneous removal for  $H_2O_2$ ,  $HNO_3$ ,  $HCl$ , and  $HNO_4$  was included in the troposphere. We assumed also fixed mixing ratios for long-lived and chemical families components at lower and upper boundaries during calculations in order to formulate the boundary conditions. Corresponding mixing ratio values were taken from Park et al. (1999). An accurate, non-diffuse method for three-dimensional advection of trace species suggested by Prather (1986) was used to solve the continuity equation for each transported species (families and long-lived species). The chemical constituents were initialized with profiles obtained from a one-dimensional model (Krivolutsky et al., 2001). Wind components used for transport by advection were obtained from the simulation with the 3D dynamical model for each day of the year. Daily averaged global zonal, meridional, vertical wind components,

and temperature have then be used in the CTM runs. More details concerning the chemical 3D model can be found in Krivolutsky and Vyushkova (2002). This model was used to study the response in composition and dynamics after the July 2000 SPE (Krivolutsky et al., 2006). The CAO simulation included in this study covers the period 26 October–4 November.

#### 4.4 FinROSE

FinROSE is a global 3-D chemistry transport model (Damski et al., 2007a). The model dynamics are from external sources except the vertical wind, which is calculated inside the model using the continuity equation. In this study FinROSE has 35 vertical levels (0–65 km), a horizontal resolution of 10° × 5° and uses ECMWF Interim analyses (Simmons et al., 2006) for dynamics. Output is provided every 3 hours. The model produces distributions of 40 species and includes about 120 homogeneous reactions and 30 photodissociation processes. Chemical kinetic data, reaction rate coefficients and absorption cross-sections are taken from look-up-tables based on the Jet Propulsion Laboratory compilation by Sander et al. (2006). Photodissociation frequencies are calculated using a radiative transfer model (Kylling et al., 1997). The model also includes formation and sedimentation of polar stratospheric clouds (PSCs) and reactions on PSCs. Tropospheric abundances are given as boundary conditions and long-lived trace gases are relaxed towards long time trends. The FinROSE model applies additionally to electron and proton-induced ionization also ionization rates caused by alpha-particles provided by the AIMOS model (Wissing and Kallenrode, 2009).

#### 4.5 HAMMONIA

The Hamburg Model of the Neutral and Ionized Atmosphere (HAMMONIA) is a 3-dimensional GCM and chemistry model covering an altitude range from the surface up to  $1.7 \times 10^{-7}$  hPa. A detailed description of the model is given by Schmidt et al. (2006). Simulations of particle pre-

715 precipitation effects use a modified version of HAMMONIA. It treats 54 photochemical, 139 bi- and termolecular, 5 ion-  
 720 electron recombination, and 12 ion-neutral reactions involving 50 neutral and 6 charged ( $O^+$ ,  $O_2^+$ ,  $N^+$ ,  $N_2^+$ ,  $NO^+$ ,  $e^-$ ) components. Neutral bi- and termolecular reactions and the corresponding rate coefficients are taken from Sander et al. (2006). Photochemistry involves 7 ionizing and dissociat-  
 725 ing reactions through solar irradiance of wavelengths shorter than Lyman-alpha using a parametrization of Solomon and Qian (2005) and observed solar spectral irradiance. Additionally, 6 ionizing, dissociating, and exciting reactions represent the direct influence of precipitating primary and sec-  
 730 ondary particles on thermospheric chemistry. Corresponding reaction rates are calculated using the particle induced ionization rates and branching ratios given by Roble and Ridley (1987) and Rusch et al. (1981). Below  $10^{-3}$  hPa, particle impact on chemistry is represented by the production of  $N(^2D)$ ,  $N(^4S)$  and  $HO_x$ . Here, HAMMONIA uses parametrizations of Jackman et al. (2005a) based on formulations of Porter et al. (1976) and Solomon et al. (1981). The simulations use 67 pressure levels and a horizontal resolution of T31 (96 longitudes  $\times$  48 latitudes). Output is provided every 2 hours.  
 735 Up to 179 hPa, the model is relaxed to ECMWF analyzed temperature, divergence, vorticity, and surface pressure.

#### 4.6 KASIMA

740 The KASIMA model is a 3D mechanistic model of the middle atmosphere including full middle atmosphere chemistry (Kouker et al., 1999). The model can be coupled to specific meteorological situations by using analyzed lower boundary conditions and nudging terms for vorticity, divergence and temperature. Here we use the version as described by Redmann et al. (2010). It has a horizontal resolution of about  
 745  $5.6^\circ \times 5.6^\circ$  with 63 pressure levels between 7 and 120 km and a vertical resolution in the lower stratosphere of 750 m, gradually increasing to 3.8 km at the upper boundary. The frequency of output is every 6 hours. The model is nudged to ECMWF analyses below 1 hPa. A numerical time step of  
 750 12 min was used in the experiments. The chemistry is calculated up to 90 km, above which only transport is applied. The chemistry uses JPL 2002 data (Sander et al., 2003) and is calculated up to 90 km, above which only transport is applied. The chemical fields of long-lived tracers have been initial-  
 755 ized from a multi-annual run starting in the year 1960. For the HEPPA experiments, the transport scheme has been revised to allow transport of the members of chemical families  $NO_x$  and  $HO_x$  individually in the mesosphere. In addition, the ozone heating rate is calculated interactively. The rate  
 760 constants of the gas phase and heterogeneous reactions are taken from Sander et al. (2003). For the production of  $HO_x$  the parameterization of Solomon et al. (1981) is used, for the production of  $NO_x$ , 0.7 NO molecules are produced per ion pair and 0.55 N atoms in ground state, including reactions  
 765 of  $N + O_2$ ,  $N + NO$ ,  $N + NO_2$ . The  $HNO_3$  production from

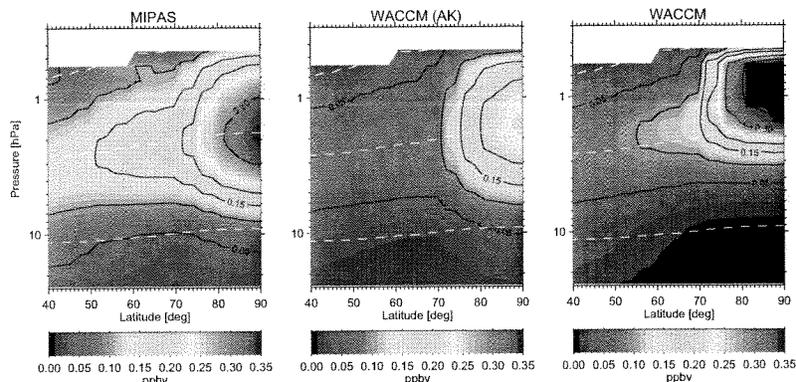
proton hydrates (de Zafra and Smyshlyayev, 2001) has been modified to be dependent on actual ionization rates.

#### 4.7 EMAC

The ECHAM5/MESSy Atmospheric Chemistry (EMAC) model is a numerical chemistry and climate simulation system that includes sub-models describing tropospheric and middle atmosphere processes and their interaction with oceans, land and human influences (Jöckel et al., 2006). It uses the Modular Earth Submodel System (MESSy, see Jöckel et al., 2005) to link multi-institutional computer codes. The core atmospheric model is the 5th generation European Centre Hamburg general circulation model (ECHAM5, Roeckner et al., 2006). Here, EMAC (ECHAM5 version 5.3.02, MESSy version 1.8+) was applied in the T42L90MA-resolution, i.e. with a spherical truncation of T42 (corresponding to a quadratic Gaussian grid of approximately  $2.8$  by  $2.8^\circ$  in latitude and longitude) with 90 vertical hybrid pressure levels up to 0.01 hPa. The frequency of output is every 2 hours. The model is weakly nudged at 200 – 700 hPa to ECMWF reanalysis data. The chemistry sub-model includes 104 chemical species and 250 homogeneous and heterogeneous reactions based on Sander et al. (2006). For more details on the setup used here refer to Baumgaertner et al. (2010).

#### 4.8 SOCOL and SOCOLi

SOCOL (modeling tool for Solar Climate Ozone Links studies) is a combination of the GCM MA-ECHAM4 and the chemistry-transport model (CTM) MEZON. It is a spectral model with T30 horizontal truncation resulting in a grid spacing of about 3.75; in the vertical direction the model has 39 levels in a hybrid sigma-pressure coordinate system spanning the model atmosphere from the surface to 0.01 hPa. Time step for dynamical and physical processes is 15 min and 2 hours for radiative transfer calculations and chemical reactions. The original version of the chemistry-climate model SOCOL was described by Egorova et al. (2005), and updated version in Schraner et al. (2008). For the HEPPA comparison, two versions of SOCOL have been used. One is with parameterized production of odd nitrogen, where for the  $NO_x$  sources, the fact that 1.25 NO molecules were produced were taken into account (Porter et al., 1976), for the  $HO_x$  sources, the table given by Solomon et al. (1981) has been used. The other version (SOCOLi) includes the chemistry of ionized species. SOCOLi is described in Egorova et al. (2010). As sources for ionization the model uses galactic cosmic rays (Heaps, 1978), energetic electron precipitation, solar proton events and observed solar irradiance. SOCOLi takes into account 580 reactions involving 43 neutral of the oxygen, hydrogen, nitrogen, carbon, chlorine and bromine groups, electrons, 31 positive and 17 negative charge species including clusters of  $O_2^+$ ,  $H^+$  and  $NO^+$ . The rate constants



**Fig. 6.** Effect of application of averaging kernels (AKs) to the model data on the example of MIPAS and WACCM4 HOCl zonal mean distribution (40–90°N) averaged over the period 29 October to 4 November 2003.

of the gas phase and heterogeneous reactions are taken from Sander et al. (2000). SOCOL and SOCOLi models apply additionally to electron and proton-induced ionization also ionization rates caused by alpha-particles provided by AIMOS model (Wissing and Kallenrode, 2009). This choice is based on the assumption that AIMOS model describe all physical processes relevant to particle precipitation during the event. Output is provided at the local time and location of the MIPAS overpass.

#### 4.9 WACCM

The fourth version of the Whole Atmosphere Community Climate Model (WACCM4) is part of the Community Earth System Model (<http://www.cesm.ucar.edu>). It is a coupled chemistry climate model with horizontal resolution of 1.9° latitude by 2.5° longitude. For this study WACCM4 has 88 vertical levels and is forced with meteorological fields from the Modern Era Retrospective-analysis for Research and Applications (MERRA, <http://gmao.gsfc.nasa.gov/research/merra/>). MERRA is a NASA reanalysis for the satellite era using the Goddard Earth Observing System Data Assimilation System Version 5 (Rienecker et al., 2008). The forcing is achieved by relaxing horizontal winds and temperatures with a time constant of approximately 50 hours from the surface to 40 km. Above that level the forcing is reduced linearly, so that the model is free-running between 50 km and the model top at approximately 135 km ( $4.5 \times 10^{-6}$  hPa). Heating rates and photolysis are calculated using observed daily solar spectral irradiance and geomagnetic activity effects in the auroral region are parameterized in terms of the Kp index (Marsh et al., 2007). A description of simulations of the effects of solar proton events using an earlier free-running version of WACCM and comparison with measurements is given in

Jackman et al. (2008, 2009). The standard WACCM chemistry is described and evaluated extensively in WMO (2010). Reaction rates are from Sander et al. (2006). For these simulations we have modified the N+NO<sub>2</sub> reaction to include two additional pathways as described in Funke et al. (2008). It should be noted that both WACCM and HAMMONIA use the same chemical solver based on the MOZART3 chemistry Kinnison et al. (2007), include the same set of ionized species, and use the parameterized EUV ionization rates from Solomon and Qian (2005). For these simulations the latter parameterization has been extended to include the photoionization of CO<sub>2</sub> in the EUV. Proton and electron ionization rates, used in the nominal simulation, are taken from AIMOS, however above  $5 \times 10^{-4}$  hPa (~100 km) ionization from electrons is instead calculated by the WACCM parameterized aurora. An additional simulation using proton ionization, only, has also been performed (in the following denoted as WACCMp). The HO<sub>x</sub> production per ion pair is included in WACCM using a lookup table from Jackman et al. (2005b, Table 1), which is based on the work of Solomon et al. (1981). It is assumed that 1.25 N atoms are produced per ion pair and divide the N atom production between ground state, N(<sup>4</sup>S), at 0.55 per ion pair and excited state, N(<sup>2</sup>D), at 0.7 per ion pair (Jackman et al., 2005b; Porter et al., 1976). In this study, WACCM constituent and temperature profiles were saved at the model grid point and time-step (model time-step is 30 minutes) closest to each of the MIPAS observation locations.

#### 5 Intercomparison method

In order to reduce errors related to the different sampling of the MIPAS observations and gridded model data (i.e., B3dCTM, CAO, FinROSE, HAMMONIA, KASIMA, and EMAC), we have linearly interpolated the model results to

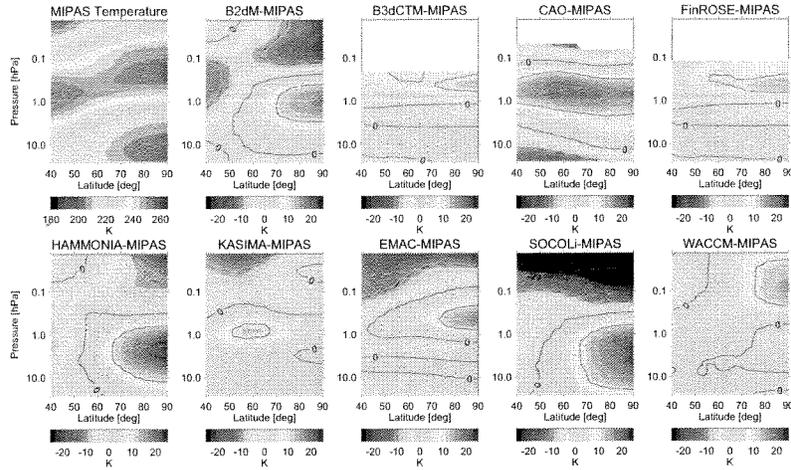


Fig. 7. Observed and modeled temperature zonal mean distributions at 40–90°N averaged over the period 29 October to 4 November 2003.

the MIPAS measurement locations and times, as well as to the corresponding pressure levels of the vertical retrieval grid of the species under consideration. This approach has the further advantage that diurnal variations of particular species are implicitly taken into account. Comparison of MIPAS measurements and model results requires the transformation of modeled profiles to MIPAS altitude resolution. Based on the formalism by Rodgers (2000), we calculate the model profiles adjusted to MIPAS resolution  $x_{adj}$  as

$$x_{adj} = Ax_{mod} + (I - A)x_a, \quad (1)$$

where  $A$  is the MIPAS averaging kernel matrix,  $x_{mod}$  is the original model profile,  $I$  is unity, and  $x_a$  is the a priori information used in the MIPAS retrievals. Assuming that the altitude resolution of the models is much finer than that of the MIPAS retrievals, the comparison of  $x_{adj}$  and MIPAS measurements is not affected by any smoothing error.

This procedure has been applied to each model result resampled at the corresponding measurement location. As an example, Figure 6 compares HOCl zonal mean distributions at 40–90°N, averaged over the period 29 October to 4 November 2003, as observed by MIPAS and as modeled by WACCM with and without application of averaging kernels. In the latter case, the vertical distribution is broader and slightly shifted towards lower altitudes, similar to the retrieved MIPAS profiles. Also, the absolute vmr peak values are smaller than without application of the averaging kernel. It should be noted that the apparent better agreement of the maximum vmr values between MIPAS and the unconvolved WACCM simulations are related to the fact that background HOCl vmrs are underestimated in the model. The relative vmr increase related to the SPE is in better agreement when

comparing observed and convolved model data (see also Section 6).

## 6 Results and discussion

### 6.1 Meteorological background conditions

Meteorological background conditions, particularly the thermal structure and the prevailing dynamics, can have an important impact on the magnitude and spatial distribution of SPE-induced composition changes. Temperature differences between models and observed data have, on the one hand, a significant impact on SPE-related chemistry due to involvement of highly temperature-dependent reactions (i.e.,  $N+O_2$  or  $NO_2+O_3$ ). On the other hand, meridional transport and mixing, depending largely on the development stage of the early winter polar vortex, control the redistribution of air masses between polar night and illuminated regions and hence, the efficiency of photochemical losses. Also, the strength of polar winter descent plays an important role in the vertical redistribution of some species on the time scale of the intercomparison period.

Figure 7 shows the MIPAS temperature zonal mean distribution at 40–90°N averaged over the period of the main proton forcing, 29 October to 4 November 2003, and the corresponding differences between the models and the observations. It is evident that models which are driven or strongly forced by assimilated meteorological data up to the upper stratosphere (i.e., B3dCTM, FinROSE, KASIMA, and WACCM) reproduce reasonably well the observed temperatures below approximately 1 hPa. On the other hand, free-running models (B2dM, CAO and SOCOLi) and those which are nudged to meteorological in the troposphere,

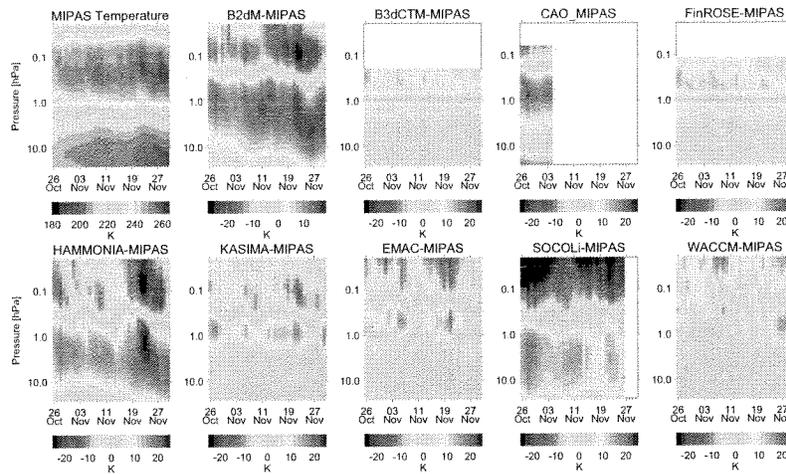


Fig. 8. Temporal evolution of MIPAS temperature and model - MIPAS differences averaged over 70–90°N.

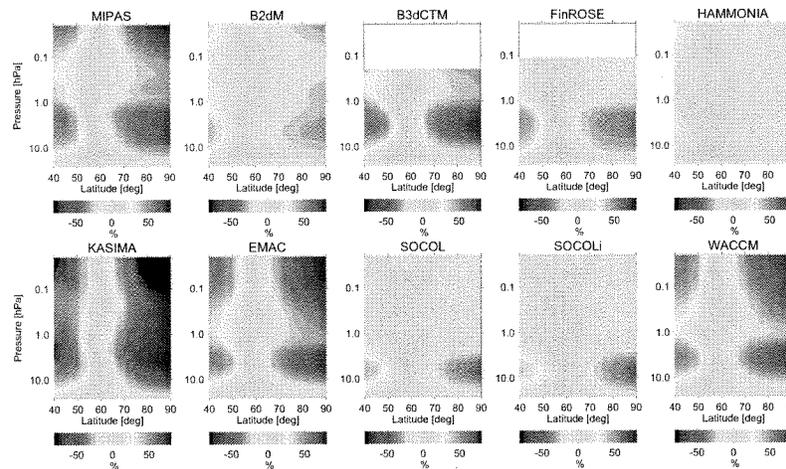
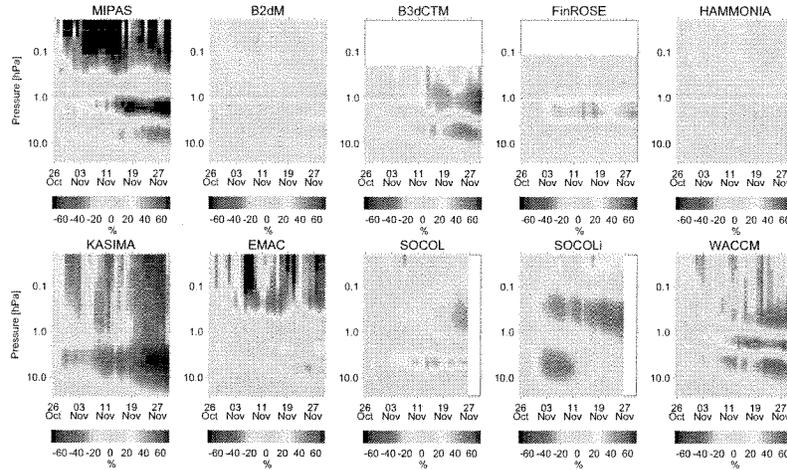


Fig. 9. Relative meridional CH<sub>4</sub> anomaly in MIPAS observations and model simulations at 40–90°N averaged over the whole time period.

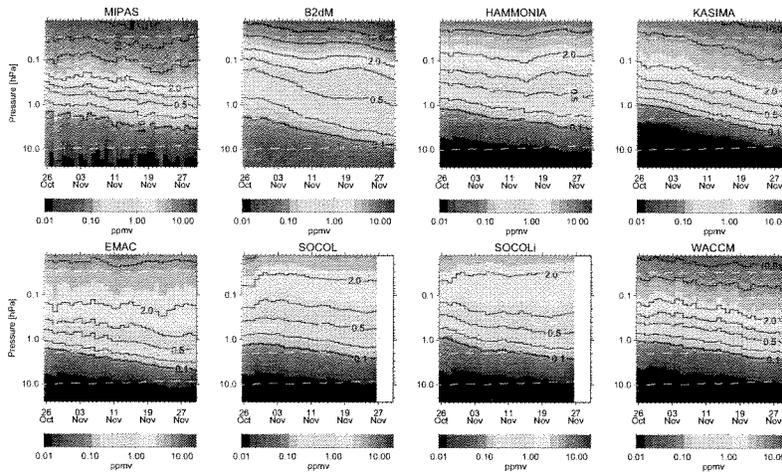
only (EMAC and HAMMONIA) tend to overestimate the observations inside the polar vortex by more than 15 K around approximately 1 hPa or slightly below. Slightly too high stratopause temperatures are found in EMAC, CAO, B3dCTM, and FinROSE simulations. In the polar mesosphere, temperatures are underestimated by HAMMONIA (up to 15 K) and SOCOLi (more than 25K). The temporal evolution of observed polar temperatures (70–90°N) and the corresponding differences between model and observations are shown in Figure 8. No significant trend in both, observations and model data, can be observed during the period of interested, while short-term temperature fluctuations of more

than 10 K compared to the observations, most likely related to differences in the planetary wave activity, show up particularly in the case of the free-running or weakly nudged models (B2dM, CAO, HAMMONIA, and SOCOLi).

Differences in the magnitude of meridional redistribution between models and observations have been assessed by comparing CH<sub>4</sub> zonal mean distributions provided by all models except CAO. Since the global stratospheric CH<sub>4</sub> abundances differ noticeably among the models, we used the relative meridional CH<sub>4</sub> anomaly as indicator for meridional redistribution rather than absolute vmrs. Figure 9 shows the observed and modeled meridional CH<sub>4</sub> anomalies at 40–



**Fig. 10.** Temporal evolution of  $\text{CH}_4$  changes with respect to 26 October 2003 in MIPAS observations and model simulations averaged over  $70\text{--}90^\circ\text{N}$ .



**Fig. 11.** Temporal evolution of CO abundances in MIPAS observations and model simulations averaged over  $70\text{--}90^\circ\text{N}$ . The 0.1, 0.2, 0.5, 1, 2, 5, 10, and 20 ppmv contours are shown by solid lines.

970  $90^\circ\text{N}$  averaged over the whole period. A pronounced gra-  
 975 dient in the observed anomalies around  $60^\circ\text{N}$  indicates the  
 early winter vortex boundary. In general, the vortex bound-  
 ary position is well reproduced by all models, although there  
 are significant differences in the overall  $\text{CH}_4$  change from  
 mid-latitudes to the pole between the models. Strongest lat-  
 itudinal gradients (i.e., weakest redistribution) were found  
 in the KASIMA simulations, while smallest gradients (i.e.,  
 strongest redistribution) are visible in HAMMONIA. The  
 reason for the underestimation of meridional redistribution

in KASIMA is not fully understood, particularly because  
 other ECMWF-driven models have simulated considerably  
 stronger mixing. The too strong mixing in HAMMONIA  
 is most probably related to wave-1 activity, being present in  
 the whole time period. The vertical distribution of the ob-  
 served  $\text{CH}_4$  meridional anomaly shows a broadening in the  
 stratopause region ( $1\text{--}0.1\text{ hPa}$ ), indicating a weakened trans-  
 port barrier at the vortex top. This behavior is reproduced by  
 the models in general although there are differences with re-  
 spect to the altitude and magnitude of the broadening region.

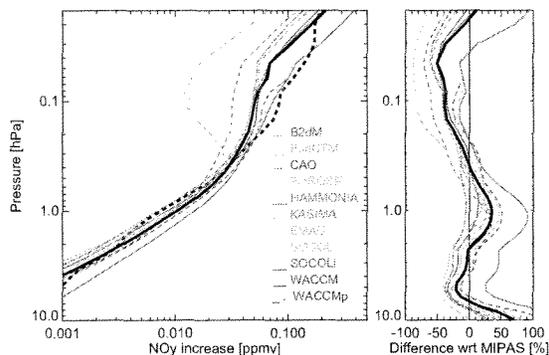
In B2dM, it is shifted slightly upwards while the opposite is observed in EMAC, SOCOL, and SOCOLi simulations. In these latter models, meridional redistribution seems also to be slightly overestimated around the stratopause. It should be noted that our analysis of  $\text{CH}_4$  meridional anomalies does not allow to distinguish between meridional redistribution by eddy diffusion and large-scale transport by planetary waves, the latter being of higher importance for the redistribution of air masses between polar night and illuminated regions.

The variability of the polar vortex strength has been assessed by comparing the temporal evolution of the relative change of  $\text{CH}_4$  abundances with respect to 26 October averaged over  $70\text{--}90^\circ\text{N}$  (see Fig. 10). The observed evolution indicates a vortex intensification and descent in the lower and middle stratosphere while a  $\text{CH}_4$  increase above 0.3 hPa, particularly during the proton forcing at the beginning of November, hints at an increase of meridional mixing in the mesosphere. This general behavior is qualitatively reproduced by the models, although important differences with respect to the vertical structure and magnitude exist. These differences have to be taken into account when analyzing the temporal evolution of SPE-induced composition changes (see next sections).

Carbon monoxide is an ideal tracer for upper stratospheric and mesospheric dynamics. Particularly, it allows to identify air masses which have descended from the upper mesosphere and contain enhanced  $\text{NO}_x$  related to energetic electron precipitation (EEP). Since polar winter descent of  $\text{NO}_x$  generated by EEP prior to the SPE event, is not resolved by all models and since we focus here on SPE-related effects, observed  $\text{NO}_x$  enhancements due to descending upper mesospheric air masses perturb our analysis and should hence be excluded. MIPAS CO observations provide an excellent criterion for identification of EEP-related enhancements (see Section 6.2).

CO distributions also allows for the characterization of descent and vortex perturbations by large-scale wave activity and isentropic mixing across the vortex boundary in the upper stratosphere and mesosphere. Figure 11 shows the observed and modeled temporal evolution of CO abundances average over  $70\text{--}90^\circ\text{N}$ . In general, the continuous decrease in altitude of CO vmr isolines in the upper stratosphere related to polar winter descent, agrees well in models and data. Around 1 hPa, polar air masses descended approximately 5 km in both models and observations during the time period under investigation.

A higher variability is found in the mesosphere. Observed CO abundances decreases around the beginning of November, at the same time when  $\text{CH}_4$  increased significantly (see Fig. 10). A pronounced CO increase occurred around 20 November, hinting at enhanced descent and vortex intensification. Modeled CO distributions show a different temporal evolution in the mesosphere, although some similarities can be found. For instance, EMAC, KASIMA and WACCM reproduce the CO increase in late November, how-



**Fig. 12.** Area-weighted averages ( $40\text{--}90^\circ\text{N}$ ) of observed and modeled  $\text{NO}_y$  enhancements during 30 October–1 November with respect to 26 October (left) and relative deviations of modeled averages from the MIPAS observations (right). Thick solid and dashed lines represent model multi-model mean average and MIPAS observations, respectively. WACCMp denotes the WACCM simulation including proton ionization, only (excluded from the multi-model mean).

ever, with a smaller magnitude and slightly shifted in time. A CO decrease around 0.1 hPa at the beginning of November, as observed by MIPAS, is also visible in SOCOL, SOCOLi, and - to a lesser extent - in WACCM simulations.

In contrast to the observations, these modeled decreases occur nearly instantaneously on 31 October, suggesting that the simulated CO changes might be related to the proton event rather than dynamical modulations. Indeed, CO is removed by the reaction with OH, which is strongly enhanced during the SPE at nighttime. The isolation of a possible SPE-induced chemical CO loss from dynamical effects is difficult in both, observations and simulations. Nevertheless, we have analyzed the observed CO abundances at fixed  $\text{CH}_4$  levels in the vertical range of 0.2–0.05 hPa in order to exclude CO variations related to isentropic mixing or meridional redistribution. CO abundances observed simultaneously with  $\text{CH}_4$  vmr of less than 40 ppbv decreased by approximately 1 ppmv from 29 October to 1 November, thus suggesting a chemical removal of the order of 10% which could be related to enhanced OH. The CO decreases found in the WACCM simulations have a similar magnitude, while SOCOL and SOCOLi simulations show a CO decrease around 30%.

## 6.2 Enhancements of $\text{NO}_y$ and $\text{N}_2\text{O}$

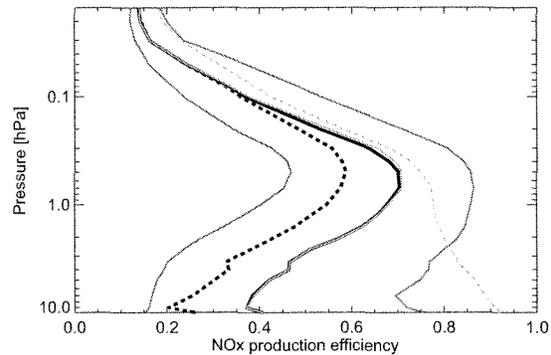
The most important impact of proton precipitation on the middle atmosphere is the immediate formation of  $\text{NO}_x$  ( $= \text{NO} + \text{NO}_2$ ) via dissociation of molecular nitrogen by ionization and subsequent recombination with oxygen. Due to its relatively long chemical lifetime in the stratosphere, SPE-induced  $\text{NO}_x$  enhancements have a strong potential to de-

plete ozone on a mid- to long-term scale via catalytic cycles. A fraction of excess  $\text{NO}_x$  produced by proton forcing is subsequently buffered into  $\text{NO}_y$  reservoir species (i.e.,  $\text{N}_2\text{O}_5$ ,  $\text{HNO}_3$ , and  $\text{ClONO}_2$ ) by a series of chemical processes (see next section) at different time scales. In general, the  $\text{NO}_x$  deactivation is very slow in the upper stratosphere. At lower altitudes, however, observed  $\text{HNO}_3$  and  $\text{ClONO}_2$  increases immediately after the onset of the proton forcing during the Halloween event indicate a much faster conversion. In order to assess the agreement of observed and modeled SPE-related odd nitrogen enhancements, we have thus compared, at first instance, total  $\text{NO}_y$  ( $= \text{NO} + \text{NO}_2 + \text{HNO}_3 + 2\text{N}_2\text{O}_5 + \text{ClONO}_2 + \text{HNO}_4$ ) rather than  $\text{NO}_x$ . Since meridional redistribution is an issue (see discussion in the previous subsection), we have analyzed area-weighted averages of  $\text{NO}_y$  enhancements with respect to 26 October within  $40\text{--}90^\circ\text{N}$ , i.e., in an area that entirely covers the source region.

As a first step, we analyze the instantaneous  $\text{NO}_y$  enhancements during the main proton forcing around 29 October–1 November. Figure 12 shows the observed and modeled  $\text{NO}_y$  enhancements during this period, ranging from a few ppbv in the middle stratosphere to several 100 ppbv in the mesosphere. The agreement between the observations and the multi-model average, the latter providing a measure of the overall ability of current atmospheric models to reproduce SPE-related  $\text{NO}_y$  increases, is reasonable, exhibiting differences below 30% in the whole altitude range. There is, however, a systematic overestimation (underestimation) of the models around 1 hPa (above 0.3 hPa).

The  $\text{NO}_y$  underestimation of the models above 0.3 hPa could be related to an overestimation of NO photolysis, the principal  $\text{NO}_y$  loss mechanism in the sunlit mesosphere. It has been pointed out by Minschwaner and Siskind (1993) that absorption of solar irradiance by thermospheric NO, being significantly enhanced during SPEs, has an important impact on the photolysis rates of nitric oxide in the middle atmosphere.

The systematic behavior of the  $\text{NO}_y$  overestimation around 1 hPa suggests that these differences are related - at least partly - to the simulated ionization rate profile. In this pressure range, there are uncertainties in the modeling of electron precipitation at 300 keV to 5 MeV. Electrons contribute there to the total ionization within  $40\text{--}90^\circ\text{N}$  by approximately 15%. As the highest electron channel on POES does not provide data up to 5 MeV, the energy spectra was extended according to Klassen et al. (2005). However, the overestimated  $\text{NO}_y$  at 1 hPa questions the extended spectra. In addition, the energy range of the highest electron channel *mep0e3* is not known for sure (private communication, Janet Green, NOAA) and it might be smaller than the published 300 keV–2.5 MeV (Evans and Greer, 2000). A smaller energy range would give an increase to  $\text{NO}_y$  production at 0.1 hPa. A possible overestimation of electron ionization is also supported by the better agreement of the WACCM simulation without electrons (WACCMp) with the

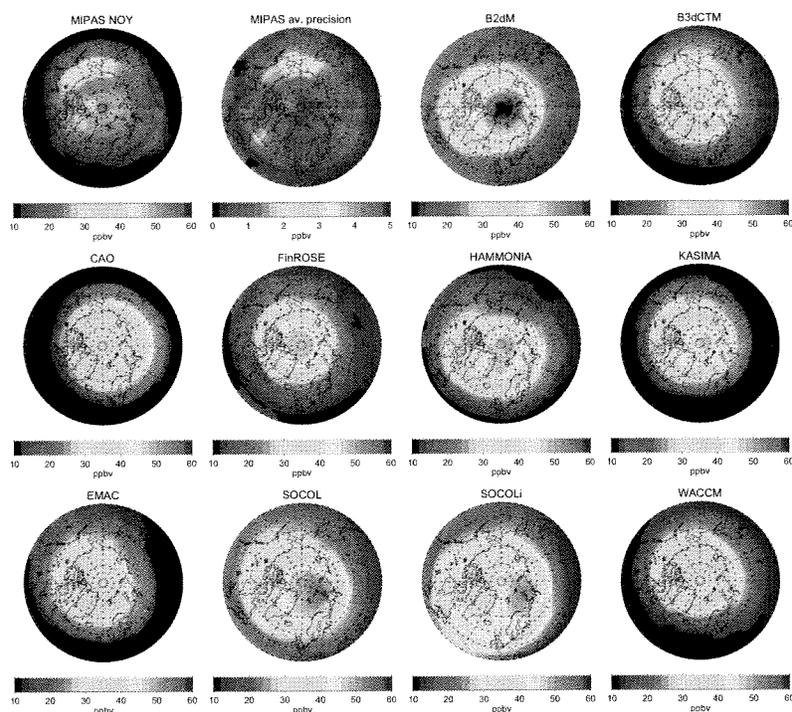


**Fig. 13.**  $\text{NO}_x$  production efficiency (ratio of the net  $\text{NO}_x$  increase and the integrated initial N production) during the period of the main proton forcing (28 October–1 November) from box model calculations for night- and daytime conditions (solid and dashed black lines, respectively), assuming initial atmospheric conditions as observed by MIPAS in the polar cusp region. The following variations for dark conditions are also shown: a 20 K temperature increase (red) and decrease (blue), a factor of 2 increase of  $\text{O}_3$  (solid green), and initial  $\text{NO}_x$  abundances set to zero (dashed green).

observations. Above 2 hPa, this simulation shows approximately 20% less enhanced  $\text{NO}_y$  than the nominal simulation, including protons and electrons. Additional ionization by alpha particles, included in CAO, FinROSE, SOCOL, and SOCOLi contributes only by approximately 5% to the total ionization within  $40\text{--}90^\circ\text{N}$ , hence increasing the SPE-related  $\text{NO}_y$  enhancements only marginally.

On the other hand, there is an important spread of up to 100% among the modeled  $\text{NO}_y$  enhancements. This is surprising, given that all models use the same AIMOS ionization rates and, thus, rather similar modeled  $\text{NO}_y$  enhancements are expected at least during the first days of the main proton forcing.  $\text{NO}_y$  enhancements are most strongly overestimated (up to 100%) by SOCOLi, SOCOL, and CAO in the stratosphere around 1 hPa. In the mesosphere, smallest  $\text{NO}_y$  increases are obtained by B2dM and EMAC (up to 80% less than observed), while SOCOL and SOCOLi simulations overestimate the MIPAS enhancements by 50%.

In order to investigate possible reasons for the spread among the model results, a more detailed look into the  $\text{NO}_x$  production mechanism is required. Generally, it is assumed that each ion pair produces 1.25 atomic nitrogen atoms, distributed between the electronic ground state  $\text{N}(^4\text{S})$  and the excited  $\text{N}(^2\text{D})$  state with a branching ratio of 0.45 and 0.55, respectively (Jackman et al., 2005b). The value of 1.25 atomic nitrogen atoms per ion pair has been adapted by all models involved in this study, except for EMAC and SOCOLi. In the latter model, N production is implicitly modeled by means of the involved ion chemistry scheme. In EMAC, an altitude-dependent N production has been as-



**Fig. 14.** Spatial distributions of observed and modeled  $\text{NO}_y$  at 1 hPa averaged of the period of the main proton forcing during 30 October–1 November. The average precision of MIPAS observations is also shown (upper second panel from the left).

sumed which has been determined empirically by the adjustment of the simulations to observed  $\text{NO}_2$  and  $\text{N}_2\text{O}$  abundances (Baumgaertner et al., 2010). The resulting N production profile is slightly higher than that used by the other models in the upper stratosphere (around 1.5 N per ion pair) and considerably lower in the mesosphere (less than 0.3 N per ion pair) which explains to a major extent the behavior of the EMAC  $\text{NO}_y$  enhancements compared to other models.

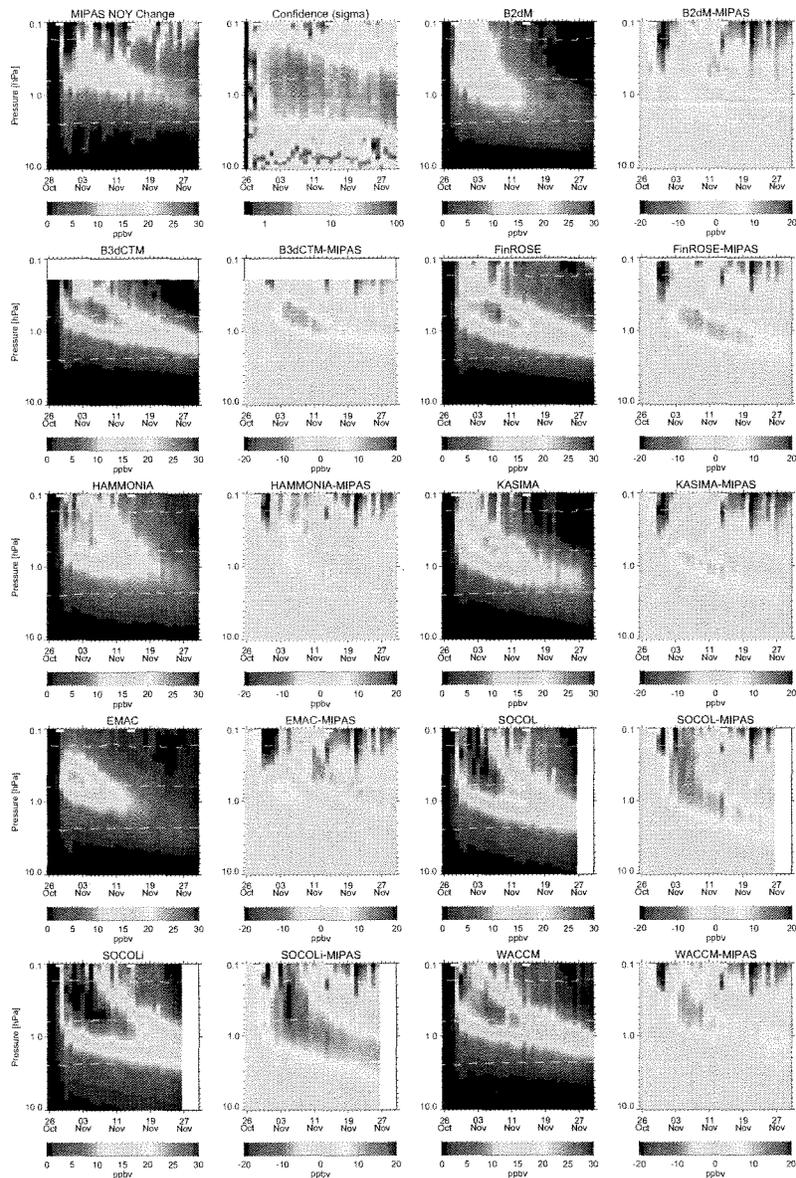
An important source of variability in the  $\text{NO}_y$  production is related to the reaction paths of the produced atomic nitrogen in its ground and excited states. While the reaction of  $\text{N}(^2\text{D})$  with oxygen to form NO is very fast such that practically all  $\text{N}(^2\text{D})$  is immediately converted to NO below the thermosphere, the corresponding reaction of the nitrogen ground state



is slower and highly temperature-dependent. Hence, it competes with other reactions, namely:



both destroying  $\text{NO}_x$ . As a consequence, only a fraction of the initially produced  $\text{NO}_x$  remains available after the proton forcing. This fraction depends strongly on temperature due to reaction R1 and to a lesser extent on the repartitioning between NO and  $\text{NO}_2$ , driven by illumination and odd oxygen availability. In order to assess the sensitivity of the SPE-related  $\text{NO}_x$  production to these parameters, we have integrated the relevant chemical equations for the period 28 October–1 November with a simple box model including AIMOS ionization rates and assuming initial atmospheric conditions as observed by MIPAS at 70–90°N before the SPE, as well as the  $\text{N}(^4\text{S})/\text{N}(^2\text{D})$  branching ratio recommended by Jackman et al. (2005b). The modeled  $\text{NO}_x$  enhancements have then been compared to a similar simulation, but setting the rate coefficient for reactions R2 and R3 to zero (i.e., assuming that all initially produced NO survives). The ratio of both simulations reflects the  $\text{NO}_x$  production efficiency. It is shown in Fig. 13 for nighttime and daytime conditions (solid and dotted black lines, respectively), showing maximum value of 0.55–0.7 around the stratopause and smaller values (0.15–0.4) above and below. Reduced values below the stratopause are related to the background  $\text{NO}_x$ : if initial  $\text{NO}_x$  abundances are set to zero, the production effi-

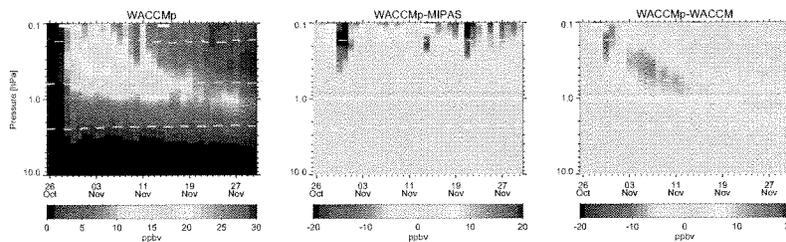


**Fig. 15.** Temporal evolution of area-weighted averages of  $\text{NO}_y$  changes with respect to 26 October 2003 in MIPAS observations and model simulations at  $40\text{--}90^\circ\text{N}$ , as well as differences between modeled and observed averages. The confidence of observed  $\text{NO}_y$  changes (in units of  $\sigma$ ) is shown in the upper second panel (from the left). Note that observations exhibiting CO abundances higher than 1 ppmv have been omitted in the averaging in order to exclude EEP-induced contributions to the  $\text{NO}_y$  enhancements. See text for further details.

ciency increases with pressure to values close to unity in the lower stratosphere (see Fig. 13, dotted green line). A temperature increase (decrease) of 20 K results in an enhancement (reduction) of this quantity by approximately 30–50% (see

red and blue lines in Fig. 13). On the other hand, assuming a two times higher ozone abundance results in an increase of the  $\text{NO}_x$  production efficiency by only a few percent.

The chemical scheme described above (including a  $\text{N}(^4\text{S})$



**Fig. 16.** As Fig. 15, but showing area-weighted averages for WACCMp (proton ionization, only, left), differences between WACCMp and MIPAS (middle), and differences between WACCMp and WACCM (right).

and  $N(^2D)$  branching ratio of 0.45 and 0.55) has been employed in most of the atmospheric models included in the intercomparison, with some exceptions: B3dCTM and CAO<sub>1250</sub> use a family approach which implies the immediate conversion of all atomic nitrogen to NO (equivalent to a ratio of 1 in Fig. 13), explaining - at least partly - the relatively high  $NO_y$  increases above 2 hPa in these models. Also FinROSE applies a family approach, however, in this model it implicitly assumed that all  $N(^4S)$  produced by ionization destroys NO via reaction R2, resulting in a net  $NO_x$  production of 0.25 per ion pair (i.e., an altitude-independent production efficiency of 0.2 in Fig. 13). However, although a considerably smaller  $NO_y$  production is hence expected, FinROSE model results show more excess  $NO_y$  than found in the observations. EMAC uses a  $N(^4S)$  and  $N(^2D)$  branching ratio of approximately 0.2 and 0.8, respectively. Box model calculations using this atomic nitrogen branching yield weakly altitude-dependent  $NO_x$  production efficiencies of 0.6–0.8, considerably higher than the nominal efficiency of  $\sim 0.2$  in the mesosphere. Therefore, the smaller atomic nitrogen production in the mesosphere applied in EMAC is partly compensated by the modified  $N(^4S)$  and  $N(^2D)$  branching ratio.

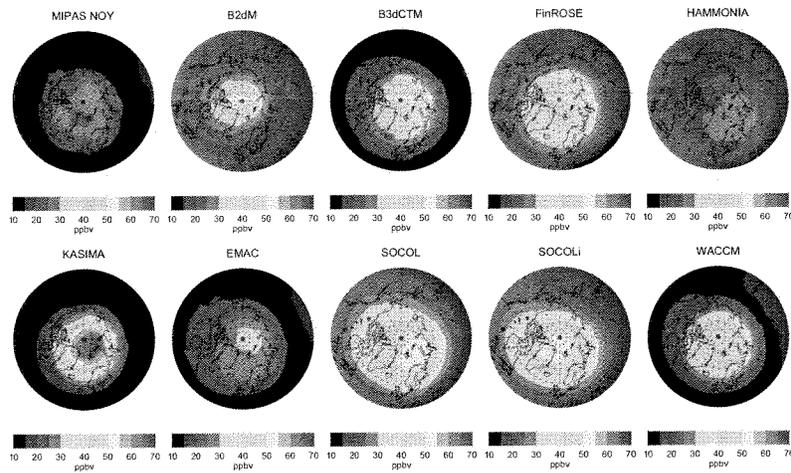
As shown above, temperature differences might explain the differences of the  $NO_y$  enhancements simulated by the remaining models. B2dM underestimates the observed temperatures in the mesosphere by about 15 K, consistent with the relatively low  $NO_y$  enhancements compared to the other models and observations, there. In contrast, HAMMONIA and SOCOLi simulations, exhibiting relatively low mesospheric temperatures, show much larger  $NO_y$  enhancements. Stratospheric temperatures are significantly overestimated by B2dM, CAO, HAMMONA, and SOCOLi. However, only the latter model shows stratospheric  $NO_y$  enhancements well above the model average. Thus, temperature differences among the models cannot be the only reason for the spread encountered in the modeled  $NO_y$  enhancements.

Therefore, we have looked at the spatial  $NO_y$  distribution in order to investigate if the spread in the modeled  $NO_y$  could also be related to dynamical effects. Figure 14 shows the observed and modeled  $NO_y$  distributions in the upper

stratosphere (1 hPa) averaged over the period 30 October–1 November. The spatial extension of the modeled  $NO_y$  enhancements exhibits pronounced differences. In some cases,  $NO_y$  enhancements are confined to the polar region northward of  $70^\circ N$  (i.e., B2dM, KASIMA, FinROSE) while in other cases they extend even to regions equatorwards of  $50^\circ N$  (i.e., SOCOL and SOCOLi). Taking into account that the spatial extension of the source region is the same in all models, these differences must be related to transport acting on a very short time scale. As discussed above, SOCOLi shows higher  $NO_y$  averages than other models with similar stratospheric temperatures (i.e., HAMMONIA, B2dM). The spatial  $NO_y$  distribution of SOCOLi at 1 hPa indicates strong wave activity resulting in a deformation of the pole-centered shape of the  $NO_y$  distribution. Thus, it cannot be excluded that tropical  $NO_y$ , transported into the  $40$ – $90^\circ N$  region, contributed to the large  $NO_y$  enhancements identified in this simulation. Further, the fast transport of SPE-generated  $NO_y$  out of the source region in the SOCOLi simulations might result in a higher net  $NO_y$  production since  $NO_x$  destruction by reactions with atomic nitrogen (R2 and R3) is then less efficient.

During the following month, the SPE-induced  $NO_y$  enhancements were transported downwards with the meridional circulation, forming a  $NO_y$  layer around 45 km at the end of November (López-Puertas et al., 2005a). At the same time,  $NO_x$ , generated by continuous EEP in the lower stratosphere, reached the upper stratosphere and began to merge with the upper part of the SPE-induced layer (see also Fig. 1). This behavior is not reproduced by the models since low and mid-energy EEP is not included in the majority of the models. In order to facilitate the comparison of observed and modeled SPE-induced  $NO_y$  enhancements in the following month after the proton forcing, we have excluded those parts of all observed and modeled  $NO_y$  profiles where MIPAS CO abundances were higher than 1 ppmv. This value has been chosen such that the major fraction of EEP-induced  $NO_y$  enhancements has been filtered out without removing too many MIPAS locations, particularly at higher altitudes.

Figure 15 shows the temporal evolution of the observed



**Fig. 17.** Spatial distributions of observed and modeled  $\text{NO}_y$  at 2 hPa averaged of the period 20–27 November.

and modeled  $\text{NO}_y$  enhancements (related to the SPE, only) with respect to 26 October within 40–90°N for the following month. While the magnitude of the enhancements is generally larger than in the observations and further shows a significant spread related to the differences in the  $\text{NO}_y$  production during the proton forcing (see discussion above), the observed evolution of the SPE-induced  $\text{NO}_x$  layer is well reproduced by all models in terms of vertical distribution and relative vmr decrease. A more detailed look into the temporal  $\text{NO}_y$  evolution of individual models shows that smaller fluctuations can be attributed to dynamical variability.

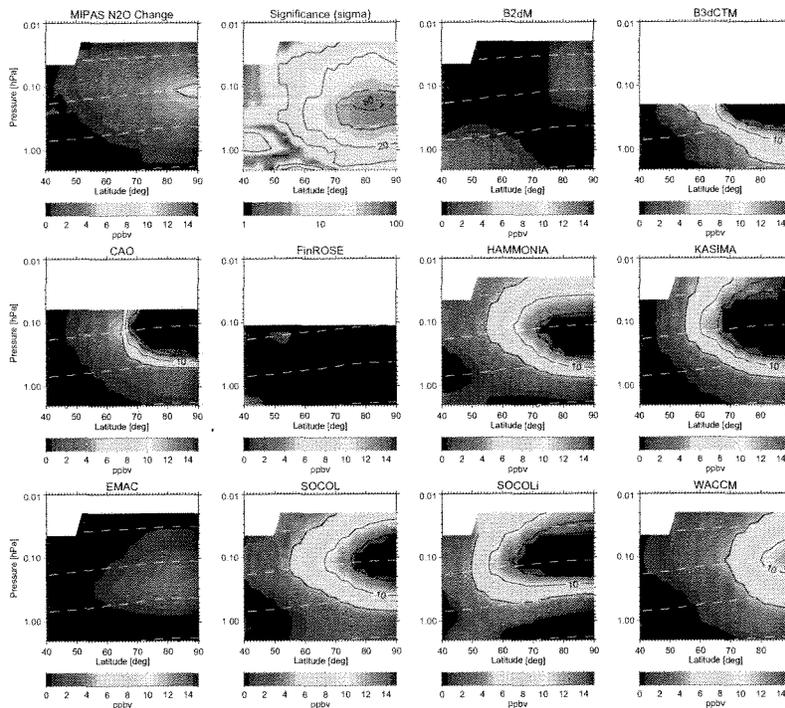
It is interesting to notice that the WACCM simulation without electron-induced ionization yields a much better agreement with the observations than the nominal simulation throughout the period under investigation (see Figure 16). Additional  $\text{NO}_y$  buildup related to electron-induced ionization is even more pronounced during the second event (4–5 November) below 0.4 hPa compared to the main proton forcing (see right panel of this Figure). This excess production during the second event dominates the  $\text{NO}_y$  overestimation of 5–10 ppbv encountered in the nominal WACCM simulation during the following weeks.

The meridional distributions of the observed and modeled  $\text{NO}_y$  enhancements exhibit important differences towards the end of November (see Figure 17, showing  $\text{NO}_y$  distributions at 2 hPa averaged over 20–27 November). The observed and modeled latitudinal gradients correlate well with the meridional  $\text{CH}_4$  anomalies (see Fig. 9), highlighting the important role of mixing and large-scale transport. The meridional redistribution of the SPE-induced  $\text{NO}_y$  enhancements, particularly the transport out of the polar night region, has important implications on the  $\text{NO}_y$  repartitioning which is to a major part driven by photochemistry (see next

subsection).

An interesting detail of the observed evolution of SPE-induced  $\text{NO}_y$  enhancements (Fig. 15, upper left panel) is the appearance of several “spikes” at mesospheric altitudes, which are temporally correlated with peaks in the ionization related to high energy (>300 keV) electron precipitation, the most pronounced event occurring on 21 November. Ionization by high-energetic electrons is included in the models which, however, do not reproduce such sudden  $\text{NO}_y$  increases. It is therefore unlikely the observed mesospheric  $\text{NO}_y$  peaks are related to in situ production by EEP associated to the Halloween event. Instead, they could be related to residual contributions of descending  $\text{NO}_x$  from the upper mesosphere which have not completely been filtered out. It should be noted that the observed CO temporal evolution (see Figure 11) indicates particularly strong descent around 20 November.

A fraction of the  $\text{NO}_x$  deactivation by reaction with atomic nitrogen during the proton forcing discussed above occurred via reaction R3, giving rise for the buildup of  $\text{N}_2\text{O}$ . Upper stratospheric and mesospheric nitrous oxide increases up to 7 ppbv have been observed by MIPAS during the Halloween SPE and have been attributed to this reaction channel (Funke et al., 2008). Reasonable agreement with CMAM model calculations has been obtained by assuming that only half of the products of reaction R3 is  $\text{N}_2\text{O}$  and O, while the other half is  $\text{N}_2$  and  $\text{O}_2$ . Figure 18 shows the observed and modeled  $\text{N}_2\text{O}$  zonal mean enhancements averaged over the period of the main proton forcing (29–31 October). Except for FinROSE and B2dM, which do not include the reaction channel R3,  $\text{N}_2\text{O}$  increases are simulated by all models. The observed enhancements, however, are generally overestimated by a factor 2 to 10, except for EMAC which shows smaller  $\text{N}_2\text{O}$  in-



**Fig. 18.** Zonal mean N<sub>2</sub>O changes with respect to 26 October 2003 in MIPAS observations and model simulations averaged over the period 29-31 October. The significance of observed N<sub>2</sub>O changes (in units of  $\sigma$ ) is shown in the upper second panel (from the left).

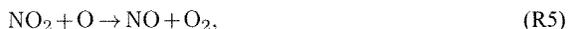
1355 creases than observed by MIPAS. In the latter model, this  
 1360 can be clearly attributed to the modified N(<sup>4</sup>S) and N(<sup>2</sup>D)  
 branching ratio (see discussion above). Except for WACCM,  
 the remaining models do not include the additional reaction  
 channel of R3, responsible for the formation of N<sub>2</sub> and O<sub>2</sub>,  
 1365 which has been included in the CMAM simulations (Funke  
 et al., 2008). But even when taking into account a reduction  
 by a factor of 2 of the simulated enhancements, these mod-  
 els tend to overestimate the observations and further show  
 a significant spread among the individual results. As in the  
 case of NO<sub>y</sub>, also the total SPE-induced N<sub>2</sub>O production  
 depends on temperature, NO<sub>x</sub> partitioning, and dynamical  
 redistribution. However, a dominant relationship of none of  
 these quantities with the differences of the magnitudes of the  
 modeled N<sub>2</sub>O increases can be established.

### 6.3 Repartitioning of nitrogen species

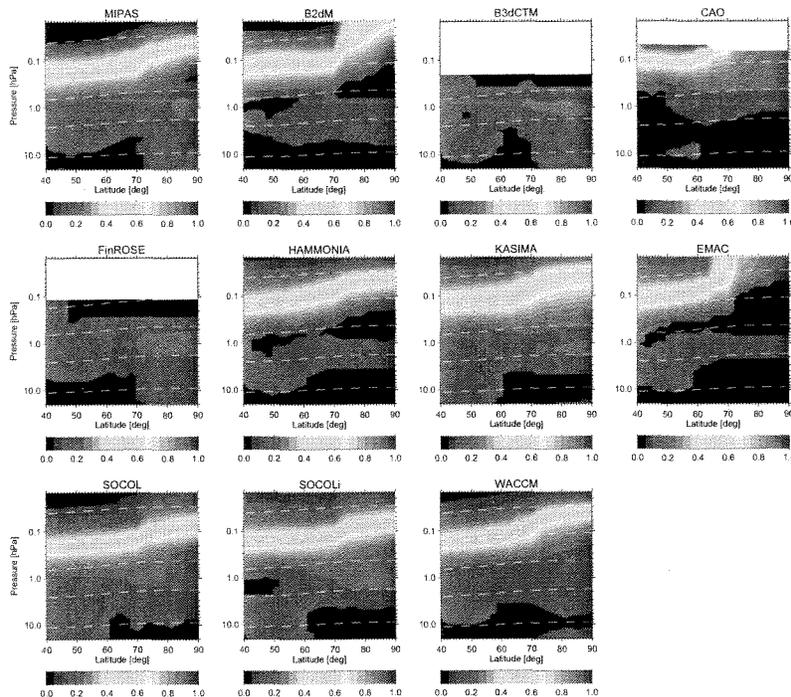
1370 After having assessed the observed and modeled total NO<sub>y</sub>  
 and N<sub>2</sub>O enhancements generated by the Halloween event,  
 we analyze in this subsection the repartitioning of initially  
 produced nitric oxide into other NO<sub>y</sub> species in the aftermath  
 of the SPE.

#### 6.3.1 NO<sub>x</sub>

The conversion of the excess NO generated by the proton forcing into NO<sub>2</sub> acts on a very short timescale (seconds to minutes) and is controlled at dark conditions by the reactions



giving rise to a NO<sub>2</sub>/NO<sub>x</sub> ratio close to one in the stratosphere, but decreasing in the mesosphere due to the availability of atomic oxygen. This decrease occurs at higher altitudes in the polar night region compared to midlatitudes. Figure 19 shows the observed and modeled nighttime NO<sub>2</sub>/NO<sub>x</sub> ratios averaged over the initial SPE period. The observed decrease of this ratio above 0.3 hPa at midlatitudes and 0.1 hPa in the polar region is generally well reproduced by the models which resolve the mesosphere, except for B2dM and EMAC, which both overestimate the polar NO<sub>2</sub> fraction at these altitudes. The higher mesospheric NO<sub>2</sub> abundances in these two models might be related to lower atomic oxygen concentrations at high altitudes and/or less efficient mixing between polar night and illuminated regions. At sunlit conditions, photolysis of NO<sub>2</sub> and higher atomic oxygen abun-



**Fig. 19.** Zonal mean nighttime  $\text{NO}_2/\text{NO}_x$  ratios averaged over the period 28 October–15 November in MIPAS observations and model simulations.

dances shift the  $\text{NO}_2/\text{NO}_x$  ratio to lower values compared to dark conditions. Figure 20 shows the observed and modeled daytime ratios. The observed values are well reproduced by B2dM, SOCOL, and SOCOLi, while other models tend to overestimate the polar upper stratospheric and meso-1420 spheric  $\text{NO}_2$  fraction close to the terminator. These differences in the  $\text{NO}_x$  partitioning among the models and observations highlight the difficulties in drawing conclusions on the SPE-induced total  $\text{NO}_x$  enhancements from the compar- 1405 ison if only one of its components is considered.

### 6.3.2 $\text{N}_2\text{O}_5$ and $\text{HNO}_3$

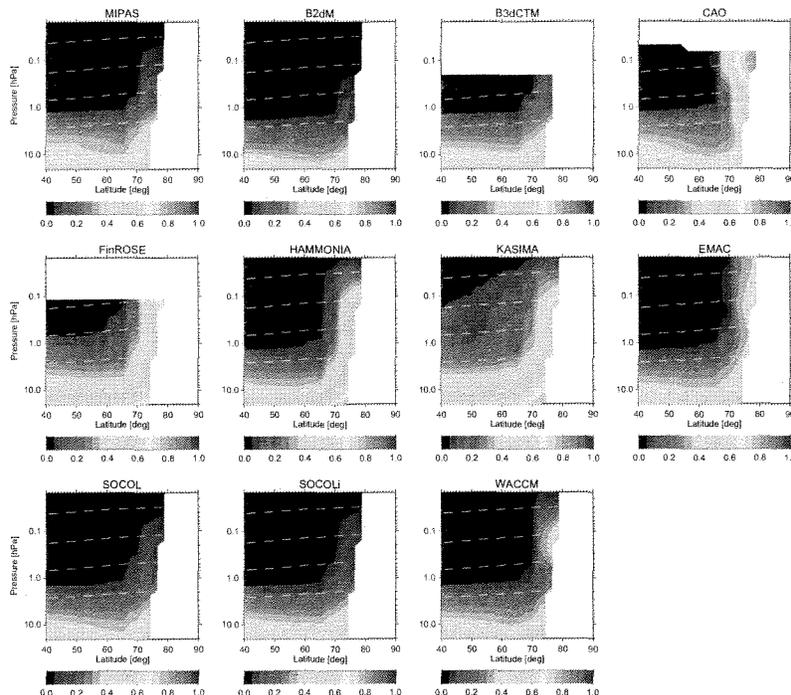
In the stratosphere, excess  $\text{NO}_x$  produced by the proton forcing, is slowly converted into  $\text{N}_2\text{O}_5$  in the following weeks after the SPE by the reactions



The rate-limiting reaction of this conversion is R6 which exhibits a strong temperature dependence.  $\text{N}_2\text{O}_5$  enhancements around 1–2 ppbv, appearing 10–15 days after the Hal- 1415 loween event, have been observed by MIPAS around 70–

90°N and have been attributed to the repartitioning of SPE-induced excess  $\text{NO}_x$  (López-Puertas et al., 2005b). This conversion is further accelerated in the course of November by the growth of the polar night region, reducing the efficiency of  $\text{N}_2\text{O}_5$  losses by photolysis.

Figure 21 shows the observed and modeled temporal evolutions of the  $\text{N}_2\text{O}_5$  enhancements with respect to 26 October averaged over 70–90°N. A stratospheric  $\text{N}_2\text{O}_5$  buildup, being most pronounced in the second half of November, is simulated by all models, qualitatively reproducing the observed behavior. The modeled  $\text{N}_2\text{O}_5$  increases are, however, generally overestimated (except for KASIMA) and exhibit a wide spread among the models. Taking into account that the magnitude of the  $\text{N}_2\text{O}_5$  increase depends on various factors such as  $\text{NO}_x$  availability, temperature, ozone abundances, and the efficiency of  $\text{N}_2\text{O}_5 \rightarrow \text{HNO}_3$  conversion (see below), a large spread of the model results is expected. B2dM and EMAC, however, overestimate the observed  $\text{N}_2\text{O}_5$  increases by factors of 4 and 6, respectively. While in the case of B2dM the extraordinarily high  $\text{N}_2\text{O}_5$  amounts can be explained by the very pole-centered distribution of the precursor  $\text{NO}_x$ , implying insignificant photochemical losses in the source region (see also discussion below), the reason for the



**Fig. 20.** Zonal mean daytime  $\text{NO}_2/\text{NO}_x$  ratios averaged over the period 28 October–15 November in MIPAS observations and model simulations.

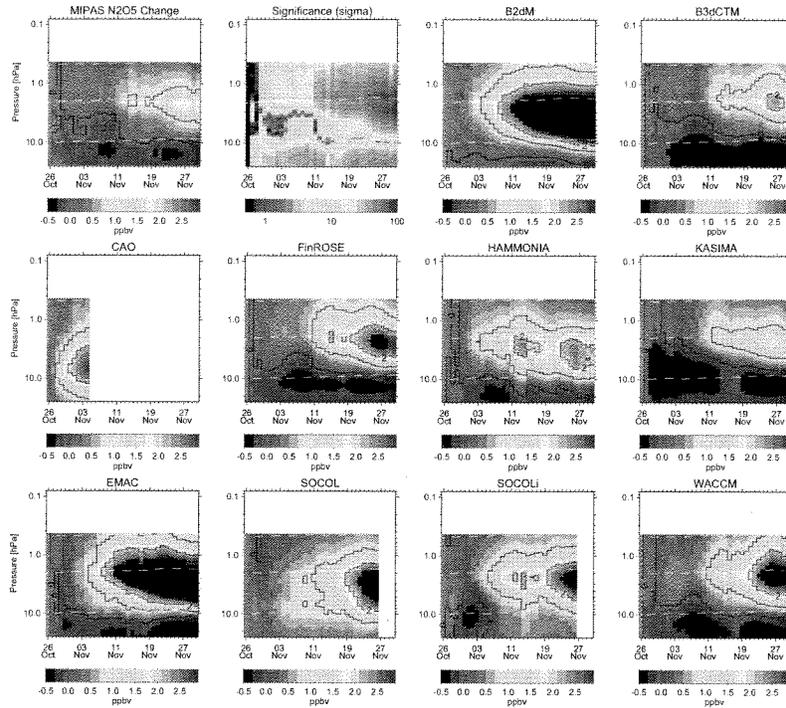
1440 unreasonably high  $\text{N}_2\text{O}_5$  abundances of up to 12 ppbv in the case of EMAC is still under investigation.  $\text{N}_2\text{O}_5$  enhancements simulated by CAO until 4 November are likely to be caused by seasonal variations rather than by the SPE. 1445

Two distinct  $\text{HNO}_3$  enhancements were observed by MIPAS in the aftermath of the Halloween SPE (López-Puertas et al., 2005b). The first one, reaching vmrs around 2 ppbv, occurred immediately after the SPEs at altitudes above 40 km and has been initially attributed to the gas-phase reaction  $\text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3 + \text{M}$ . Verronen et al. (2008), however, have shown that the instantaneous  $\text{HNO}_3$  increase after the proton forcing can only be reproduced by model calculations including ion-ion recombination between  $\text{NO}_3^-$  and  $\text{H}^+$  cluster ions. The second enhancement of 1–5 ppbv started around 10 November and lasted until the end of December. Also in this case, attempts to reproduce the magnitude of the observed increases by model calculations including gas phase chemistry only, have failed (Jackman et al., 2008). 1450 1475 1480

1460 Figure 22 shows the observed and modeled temporal evolutions of the  $\text{HNO}_3$  enhancements with respect to 26 October averaged over  $70\text{--}90^\circ\text{N}$ . Consistent with previous findings, the first instantaneous enhancement is considerably un-

derestimated by all models, except FinROSE, which includes the ion chemistry proposed by Verronen et al. (2008). This model, however, overestimates the observed increases by up to a factor of 3. The overestimation below 50 km is surprising, given that 1-D simulations with the Sodankylä Ion and Neutral Chemistry (SIC) model which includes the ion-ion recombination were found to be in good agreement with the same MIPAS dataset at these altitudes. It should be noted, however, that different ionization rates have been used in the SIC calculations of Verronen et al. (2008), and -probably even more important - that FinROSE uses a parameterization of the ion-ion recombination included in the full ion chemistry scheme of the SIC model.

The second enhancement, occurring around 15 November at 1–2 hPa, is only reproduced by KASIMA, however, overestimating the observed increases by a factor of 3. Contrary to other models, KASIMA simulations account for  $\text{HNO}_3$  formation via water cluster ions (Böhringer et al., 1983) combined with heterogeneous reactions on sulfate aerosols by means of a parameterization provided by de Zafra and Smyshlyaev (2001). At lower altitudes (i.e., below 10 hPa), midterm  $\text{HNO}_3$  increases are visible in the observations, as well as in the B2dM, B3dCTM, EMAC, FinROSE, and



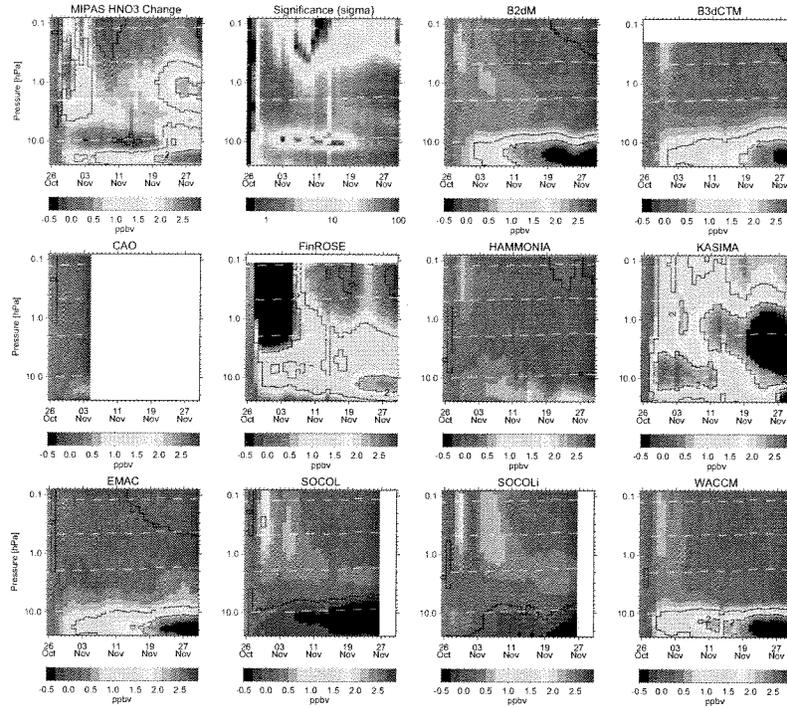
**Fig. 21.** Temporal evolution of area-weighted averages of  $\text{N}_2\text{O}_5$  changes with respect to 26 October 2003 in MIPAS observations and model simulations at  $70\text{--}90^\circ\text{N}$ , as well as differences between modeled and observed averages. Solid contour lines reflect 1 ppbv steps. The confidence of observed  $\text{N}_2\text{O}_5$  changes (in units of  $\sigma$ ) is shown in the upper second panel (from the left).

1485 WACCM model results. These increases are not related to  
1490 the SPE and can be explained by seasonal variations.

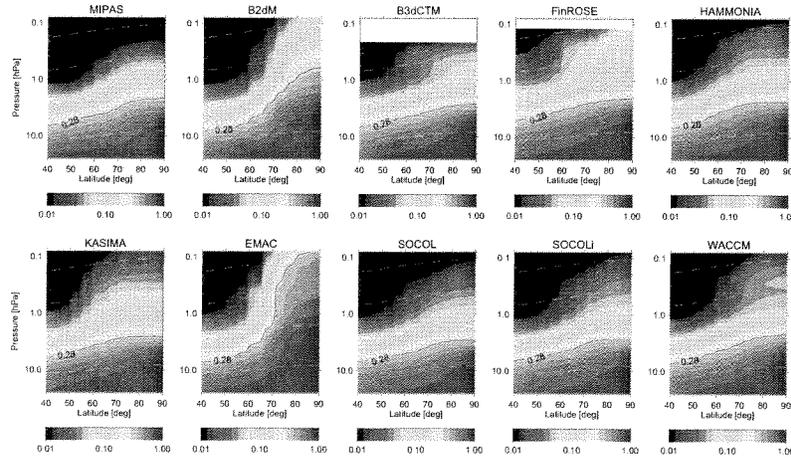
In order to assess the repartitioning of the main  $\text{NO}_y$  species towards the end of November in a more quantitatively way, we have analyzed their relative contributions to the total  $\text{NO}_y$ . This is necessary because of the encountered differences in the total amount of SPE-induced excess  $\text{NO}_y$  among the different models and the observations. Due to the observed conversion of  $\text{N}_2\text{O}_5$  into  $\text{HNO}_3$ , we have looked, as a first step, at the relative contribution of the sum of both reservoir species to  $\text{NO}_y$ . Observed and simulated zonal mean  $(2\text{N}_2\text{O}_5 + \text{HNO}_3)/\text{NO}_y$  ratios, averaged over the period 15–30 November, are shown in Fig. 23. The observed ratio of 0.28 at the peak height ( $\sim 0.2$  hPa, see Fig. 15) of the  $\text{NO}_y$  enhancements in late November (indicated by a black line in Fig. 23) is very well reproduced by all models, except B2dM and EMAC. As discussed above, the disagreement found in these models is produced by too efficient buildup of  $\text{N}_2\text{O}_5$  (see Fig. 21). The differences of the  $(2\text{N}_2\text{O}_5 + \text{HNO}_3)/\text{NO}_y$  ratio in the observations and the B2dM simulations are, however, much less pronounced than those encountered in the absolute  $\text{N}_2\text{O}_5$  abundances: while

B2dM  $\text{N}_2\text{O}_5$  exceeds the observed amounts by a factor of 4, the modeled  $2\text{N}_2\text{O}_5 + \text{HNO}_3$  contribution to  $\text{NO}_y$  at its peak height is around 40%, exceeding the observed contribution by only a factor of 0.5. The  $\text{N}_2\text{O}_5$  overestimation in this model is hence mainly related to the higher amounts and more pole-centered distribution of the precursor  $\text{NO}_2$ . In contrast to B2dM, EMAC simulations obtain more than 90% of the available  $\text{NO}_y$  at its peak altitude in the form of  $\text{N}_2\text{O}_5$ . This contribution decreases with altitude, but still exceeds 30% in the mesosphere. Other models show, in some cases, a minor overestimation of the reservoir species fraction which can be partly explained by differences in the modeled temperatures and ozone abundances, controlling the efficiency of reaction R6.

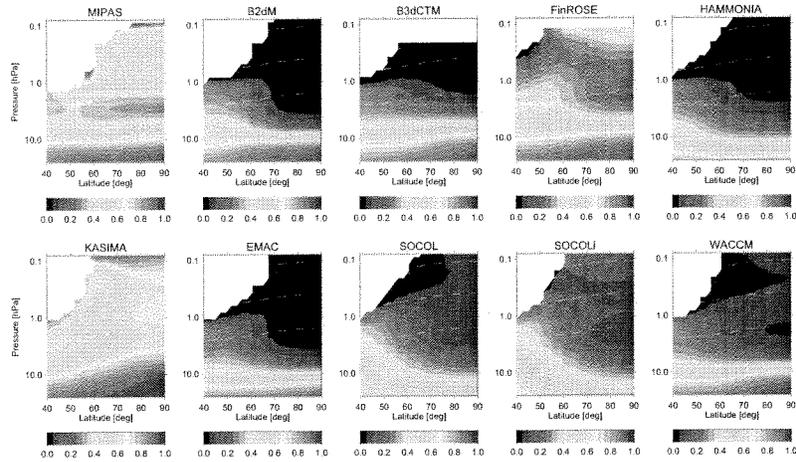
The repartitioning between  $\text{HNO}_3$  and  $\text{N}_2\text{O}_5$  has been assessed by comparing the observed and modeled zonal mean  $\text{HNO}_3/(2\text{N}_2\text{O}_5 + \text{HNO}_3)$  ratios averaged over the period 15–30 November (Fig. 24). As expected, the observed ratio is strongly underestimated above approximately 10 hPa by all models, except KASIMA. The qualitative agreement of KASIMA simulations and MIPAS observations is very good, particularly regarding the vertical shape of this ratio. The



**Fig. 22.** Temporal evolution of area-weighted averages of  $\text{HNO}_3$  changes with respect to 26 October 2003 in MIPAS observations and model simulations at  $70\text{--}90^\circ\text{N}$ , as well as differences between modeled and observed averages. Solid contour lines reflect 1 ppbv steps. The significance of observed  $\text{HNO}_3$  changes (in units of  $\sigma$ ) is shown in the upper second panel (from the left).



**Fig. 23.** Zonal mean  $(2\text{N}_2\text{O}_5 + \text{HNO}_3)/\text{NO}_y$  ratios averaged over the period 15–30 November in MIPAS observations and model simulations. The MIPAS ratio of 0.28, encountered at altitude of the maximum of the SPE-induced  $\text{NO}_y$  layer, is indicated by a black line.



**Fig. 24.** Zonal mean  $\text{HNO}_3/(2\text{N}_2\text{O}_5+\text{HNO}_3)$  ratios averaged over the period 15–30 November in MIPAS observations and model simulations. Regions with observed vmrs of  $2\text{N}_2\text{O}_5+\text{HNO}_3$  smaller than 0.1 ppbv have been omitted.

modeled ratio, however, exhibits a positive bias of 0.2 with respect to the observations, most pronounced in the polar region. We conclude that the  $\text{HNO}_3$  formation via water cluster ions and/or heterogeneous reactions on sulfate aerosols, both included in KASIMA by means of the parameterization of de Zafra and Smyshlyayev (2001), is the responsible mechanism for the observed  $\text{HNO}_3$  enhancements in late November. However, some further work is required to adjust the parameterization quantitatively to the measurements.

### 6.3.3 Minor $\text{NO}_y$ species

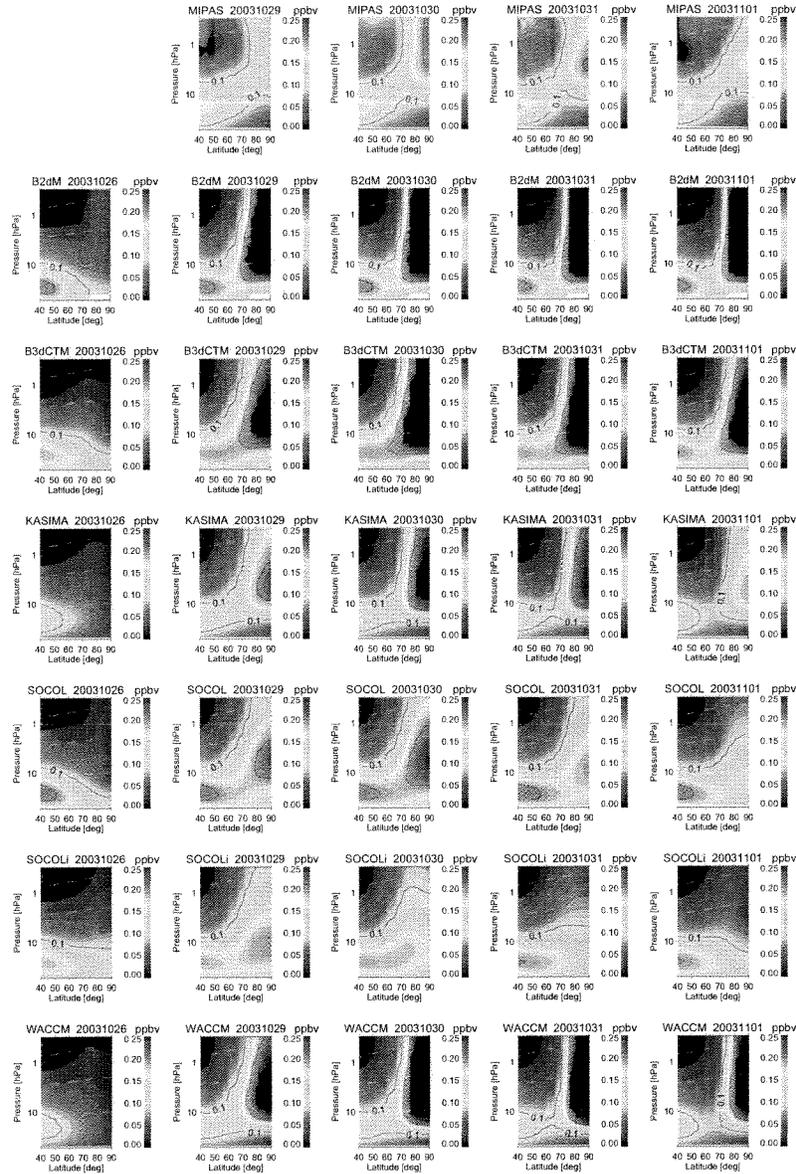
Also minor  $\text{NO}_y$  species were found to be enhanced in the aftermath of the Halloween SPE due to the repartitioning of initially produced  $\text{NO}_x$ . López-Puertas et al. (2005b) reported  $\text{ClONO}_2$  enhancements up to 0.4 ppbv a few days after the proton forcing from MIPAS observations. These observations are compared to the model simulations in Section 6.6, together with observations of other chlorine species. MIPAS has also observed enhanced  $\text{HNO}_4$  during the first days of the Halloween SPE which have not been reported so far. These increases can be attributed to the termolecular reaction  $\text{HO}_2 + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_4 + \text{M}$ . (R8)

Since at the altitude of the  $\text{HNO}_4$  enhancements (around 2–3 hPa) SPE-related increases of the precursor  $\text{NO}_2$  are relatively small ( $\sim 2$  ppbv) compared to the background  $\text{NO}_2$  abundance, the observed  $\text{HNO}_4$  changes are mainly driven by enhanced  $\text{HO}_2$  abundances, and hence, represent an indicator of SPE-generated  $\text{HO}_x$  in the middle stratosphere. At dark conditions,  $\text{HO}_x$  is in steady state even during a SPE, and its abundance is hence directly proportional to atmospheric ionization. Stratospheric  $\text{HNO}_4$  is destroyed during

the day by photolysis and by reaction with OH. Nighttime losses are negligible under quiescent conditions, and even during SPEs, OH-related  $\text{HNO}_4$  destruction is small compared to its production via reaction R8.

Due to problems with the gain calibration, particularly affecting this species (see discussion in Section 2), we restrict our analysis to data from the gain calibration period 28 October – 5 November. Figure 25 shows the observed and modeled zonal mean distributions of  $\text{HNO}_4$  vmrs during the first four days of the proton forcing (29 October–1 November). Model results for pre-SPE conditions (26 October) are also shown.  $\text{HNO}_4$  model output is not available from CAO, EMAC, HAMMONIA and FinROSE. Polar upper stratospheric enhancements of up to 0.18 ppbv are visible in the observations on 29 October, decreasing until 1 November by about 20%. The  $\text{HNO}_4$  enhancements are also simulated by the models in the first days of the SPE, however, generally overestimating the measurements. The overestimation is most pronounced in the B2dM, B3dCTM, and WACCM simulations (a factor 2–3), while SOCOLi shows smaller  $\text{HNO}_4$  increases. The  $\text{HNO}_4$  peak height is located at somewhat lower altitudes in SOCOLi which might be related to the relatively high abundances inside the ambient  $\text{HNO}_4$  layer around 5 hPa. Both, the SPE-related and ambient peaks can not be vertically resolved and merge together after the application of MIPAS averaging kernels. The moderate decrease of  $\text{HNO}_4$  in the following days is qualitatively reproduced by all models except B2dM. In this particular model, the  $\text{HNO}_4$  enhancements are confined to the polar night region, hence experiencing less photochemical losses.

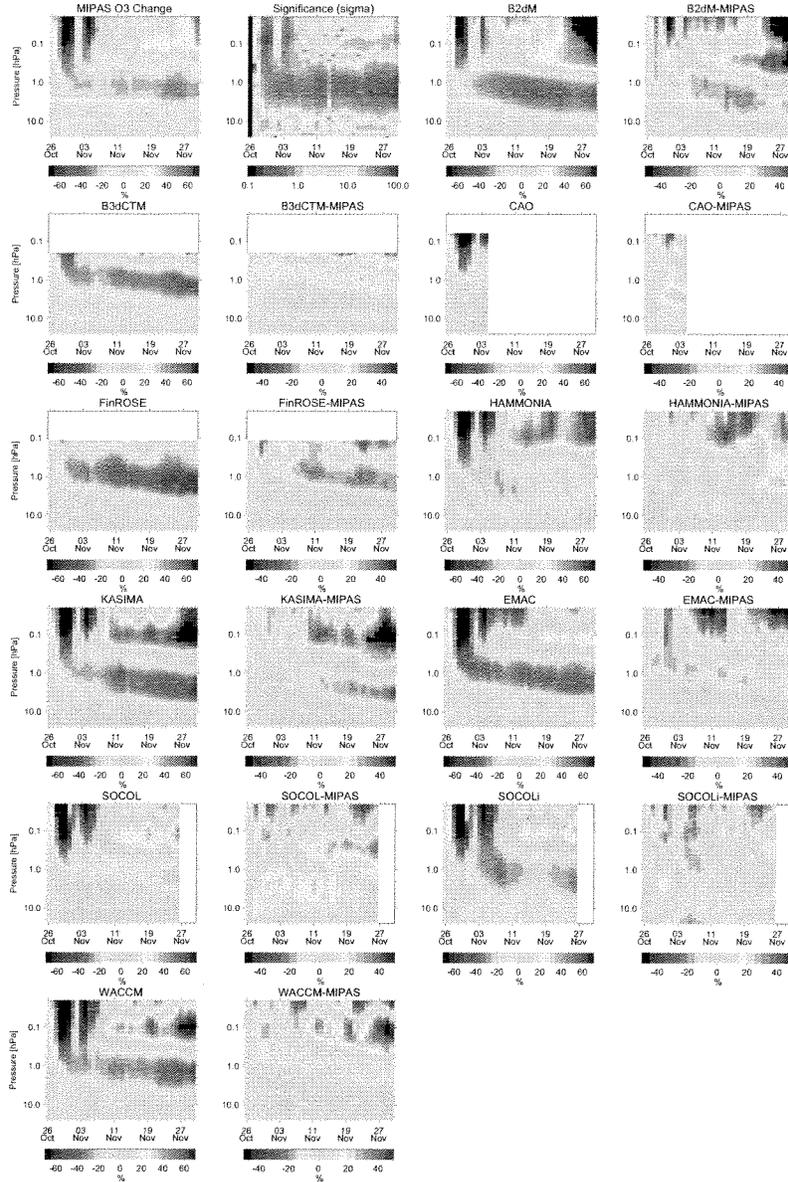
The differences in the magnitude of the  $\text{HNO}_4$  enhancements in the simulations and the observations can partially



**Fig. 25.** Observed and modeled zonal mean  $\text{HNO}_4$  vmrs for pre-SPE conditions (26 October) and during the main proton forcing (29 October–1 November). Solid contour lines reflect 0.1 ppbv steps. Note that MIPAS observations from 26 October have been omitted due to gain calibration problems.

be explained by differences in the abundances of the precursor  $\text{NO}_2$ . During the main proton forcing, modeled  $\text{NO}_2$  abundances at 70–90°N at the  $\text{HNO}_4$  peak height are on average 50–100% higher than the observed ones (not shown). The  $\text{NO}_2$  overestimation in the models is mainly related to

a weaker degree of denoxification compared to the observations already before the SPE event. Additionally, differences in the  $\text{HO}_2$  availability might also play an important role in explaining the behavior of modeled  $\text{HNO}_4$ . At the peak height of the  $\text{HNO}_4$  enhancements and in the absence of sun-



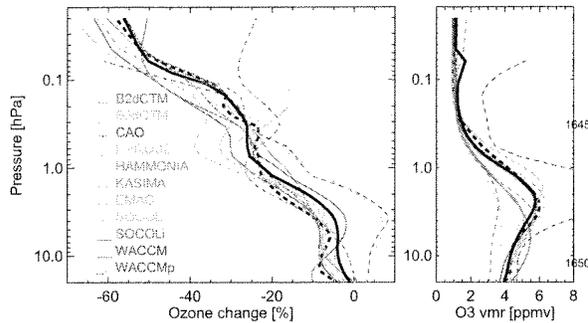
**Fig. 26.** Temporal evolution of area-weighted averages of relative O<sub>3</sub> changes with respect to 26 October 2003 in MIPAS observations and model simulations at 70–90°N, as well as differences between modeled and observed averages. The significance of observed O<sub>3</sub> changes (in units of  $\sigma$ ) is shown in the upper second panel (from the left).

light, HO<sub>2</sub> is the dominant HO<sub>x</sub> compound in the presence of proton forcing. Since HO<sub>x</sub> productions by SPE-induced ionization is not expected to differ significantly among the models, different HO<sub>2</sub> abundances are most likely related to differences in the HO<sub>x</sub> losses. These are dominated by the

cannibalistic reaction



In this sense, the HO<sub>x</sub> partitioning plays a crucial role in the HO<sub>2</sub> availability at these altitudes despite the approximately



**Fig. 27.** Area-weighted averages ( $70\text{--}90^\circ\text{N}$ ) of observed and modeled relative  $\text{O}_3$  changes during 29 October–4 November (left) with respect to the abundances on 26 October (right). Thick solid and dashed lines represent multi-model mean average and MIPAS observations, respectively. WACCMp denotes the WACCM simulation including proton ionization, only (excluded from the multi-model mean).

1610 20 times smaller OH concentrations compared to  $\text{HO}_2$ .

It might also be possible that the  $\text{HO}_x$  partitioning is affected by ion chemistry. Several ion chemistry reactions are known which transfer H into  $\text{OH}^-$ , and therefore might act as a sink of  $\text{HO}_2$ ; one reaction is known which transfers OH into  $\text{HO}_2$ . While it is beyond the scope of this investigation to determine whether these reactions really significantly affect the partitioning between odd hydrogen species, it might be worthwhile to investigate this point in the future.

#### 6.4 Ozone loss

1620 One of the most important aspects of the model-data inter-  
comparison of SPE-induced composition changes during the  
Halloween event is the evaluation of the ability of the mod-  
els to reproduce the observed ozone destruction caused by  
acceleration of catalytic  $\text{HO}_x$  and  $\text{NO}_x$  cycles. SPE-induced  
ozone losses have been observed by a variety of space-borne  
instruments during several of the stronger events of the past  
two solar cycles (see Jackman et al., 2000, for a review).  
Two different types of ozone destruction could be distin-  
guished:  $\text{HO}_x$ -related short-time losses, acting principally  
in the mesosphere during the event itself, and  $\text{NO}_x$ -related mid-  
term losses in the stratosphere which can last up to several  
months in the polar winter atmosphere. Such a behavior has  
also been observed by MIPAS in the aftermath of the Hal-  
loween event. López-Puertas et al. (2005a) reported  $\text{HO}_x$ -  
driven mesospheric ozone losses up to 70% and  $\text{NO}_x$ -driven  
stratospheric losses of around 30%, the latter lasting for more  
than 2 weeks in the Northern hemisphere.

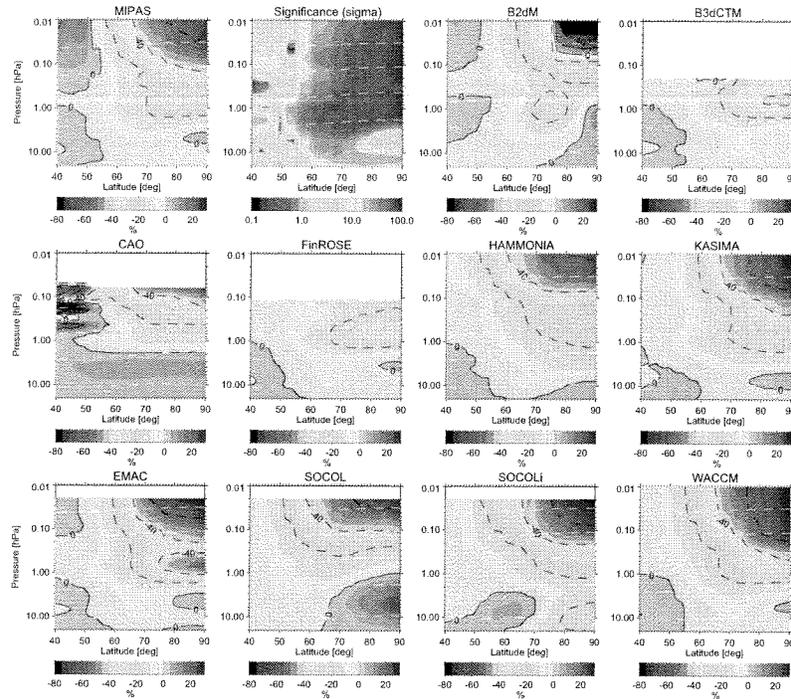
Figure 26 shows the observed and modeled temporal evolu-  
tions of the relative  $\text{O}_3$  changes with respect to 26 Octo-  
ber, averaged over  $70\text{--}90^\circ\text{N}$ . The mesospheric ozone losses

above 0.3 hPa, which exhibit two distinct peaks related to the main proton events on 29 October and 4 November, are well reproduced by most of the models. Also the stratospheric  $\text{O}_3$  losses during the following month, peaking around 1 hPa, are qualitatively reproduced by the simulations, however, with a more pronounced spread of the model results. This is not surprising since these losses are driven by  $\text{NO}_x$  which exhibits important differences between the models, particularly during the second half of November (see sections 6.2 and 6.3). Further,  $\text{NO}_x$ -induced ozone loss is driven by reaction R4 which is very sensitive to temperature differences. The midterm evolution in the mesosphere is characterized by ozone buildup which is related to seasonal variations (summer to winter transition), and which is generally more pronounced in the model simulations compared to the observations.

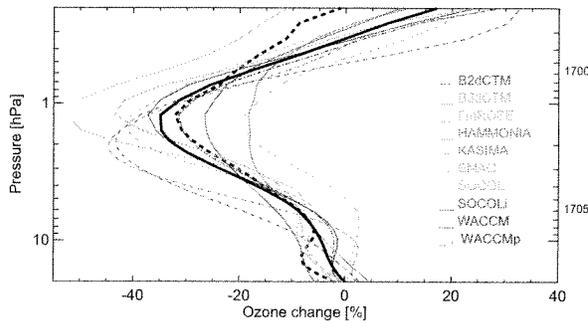
In order to assess observed and modeled short-term ozone depletion in a more quantitative way, we have compared profiles of relative ozone changes at  $70\text{--}90^\circ\text{N}$ , averaged over the period of the main proton forcing (28 October–4 November), in Figure 27. The agreement between observations and the multi-model average is excellent in the mesosphere, indicating a very good overall ability of the models to reproduce  $\text{HO}_x$ -related ozone losses under SPE conditions. Also, the models themselves agree reasonably well in this altitude range, except for B2dM. In the stratosphere, where  $\text{NO}_x$ -related losses are dominant, the agreement between the models is worse, though the model average is very close to the observations within 5%. Ozone depletion around 1 hPa is overestimated by EMAC and B3dCTM. CAO and SOCOL results indicate a somewhat smaller ozone loss throughout the stratosphere. WACCM simulations performed with and without electron-induced ionization (WACCM and WACCMp, respectively in Figure 27) indicate an additional ozone loss induced by electrons in the order of 5% above 2 hPa. It is interesting to notice that the agreement of the WACCM simulations with the observation is better when excluding the electron contribution.

Figure 28 shows the corresponding zonal mean distributions. Observed mesospheric losses extend to around  $60^\circ\text{N}$  in consonance with the expected cut-off latitude of proton precipitation. This latitudinal distribution is well reproduced by the models. B2dM shows a mesospheric ozone buildup poleward of  $80^\circ\text{N}$  related to seasonal changes, which overcompensates  $\text{HO}_x$ -related losses at these particular latitudes. This behavior, which can be attributed to deficient meridional mixing in the polar region, give rise for the apparent underestimation of mesospheric ozone losses of B2dM in Figure 27. Oscillations encountered in the CAO ozone changes above 1 hPa at  $40\text{--}50^\circ\text{N}$  are related to the background  $\text{O}_3$  and are not caused by the SPE.

The latitudinal extension of observed and modeled stratospheric ozone losses around 1 hPa correlates well with the area of  $\text{NO}_x$  increases shown in Fig. 14. In this altitude region, ozone depletion is restricted to latitudes poleward of



**Fig. 28.** Zonal mean relative  $O_3$  changes with respect to 26 October averaged over the period 28 October–4 November in MIPAS observations and model simulations. Solid contour lines reflect 20% steps. The significance of the observations is also shown (second top panel from the left, in units of  $\sigma$ ).



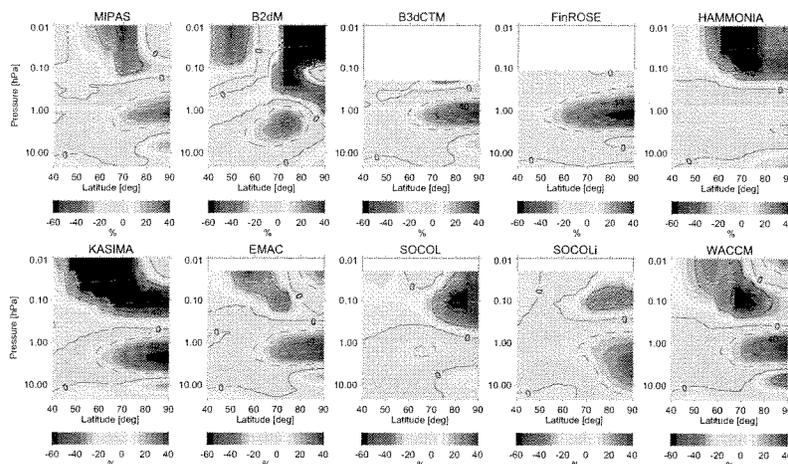
**Fig. 29.** Area-weighted averages ( $70\text{--}90^\circ\text{N}$ ) of observed and modeled relative  $O_3$  changes with respect to 26 October during 16–26 November. Thick solid and dashed lines represent model mean average and MIPAS observations, respectively. WACCMp denotes the WACCM simulation including proton ionization, only (excluded from the multi-model mean).

$70^\circ\text{N}$ . It is interesting to notice that B2dM simulations show no  $\text{NO}_x$ -induced ozone loss in the upper stratospheric polar

night region, in contrast to the observations and other models. Indeed, the  $\text{NO}_x$  catalytic cycle is expected to be inefficient at dark conditions since  $\text{NO}_2$  is not reconverted to  $\text{NO}$ . Strong mixing is hence required in order to obtain a homogeneous ozone distribution in the polar stratosphere as found in the observations. Ozone increases occur in the SOCOL simulation below 1 hPa which can be related to intrusions of mid-latitude air into the polar region, over-compensating the SPE-induced ozone losses.

Figure 29 shows profiles of stratospheric mid-term ozone changes at  $70\text{--}90^\circ\text{N}$ , averaged over the period 16–26 November. As expected, modeled ozone depletions have a larger spread than during the main proton forcing, ranging from 10 to 50% at the peak height. The model average, however, is in very good agreement with the observed depletion of 30% at 1–2 hPa. Only minor differences of 5% are found at its maximum. WACCM simulations with and without electron-induced ionization, however, suggest that these remaining differences could be significantly reduced when excluding the electron contribution to atmospheric ionization.

Figure 30 shows the corresponding zonal mean distributions. Generally, the magnitude of the stratospheric ozone



**Fig. 30.** Zonal mean relative  $O_3$  changes with respect to 26 October averaged over the period 16–26 November in MIPAS observations and model simulations. Solid contour lines reflect 20% steps.

loss at 70–90°N is anti-correlated to its latitudinal extension which, in turn, is linked to the spatial distribution of the SPE-related  $NO_x$  layer (see Fig. 17). Meridional redistribution is hence a key factor for explaining the differences in the modeled ozone depletions shown in Fig. 29. In particular, SOCOL simulations indicate strong meridional distribution around 1 hPa, resulting in polar higher ozone abundances than in the other models, despite of the relatively high  $NO_y$  availability shown in Fig. 17. There,  $NO_x$ -driven ozone loss is partly compensated by in-mixing of  $O_3$ -rich air-masses from lower latitudes.

Observed mesospheric ozone changes in late November are characterized by a pronounced increase around the polar night terminator which is related to the buildup of the third ozone maximum (Marsh et al., 2001). This rapid buildup is responsible for the short lifetime of  $HO_x$ -related ozone depletion at these altitudes. Only in the polar night region, reduced ozone abundances are found until the end of November. This behavior is well reproduced by EMAC, KASIMA, WACCM and, to a lesser extent, HAMMONIA. B2dM behaves in an opposite way.

In summary, SPE-related short- and midterm ozone changes are well reproduced by the atmospheric models on average, though individual model results can vary significantly due to differences in dynamical and meteorological background conditions. The good agreement between models and observations in the mesosphere can be interpreted as a verification of the parameterization of  $HO_x$  production by atmospheric ionization included in the models. On the other hand, WACCM simulations with and without electron-induced ionization suggest that the agreement between models and observations could be even improved when excluding

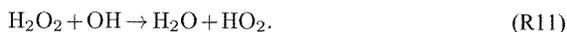
the electron contribution to atmospheric ionization.

### 6.5 Enhancements of $H_2O_2$

MIPAS observed  $H_2O_2$  increases of short duration immediately after the Halloween SPE in polar night stratosphere.  $H_2O_2$  is formed by the reaction

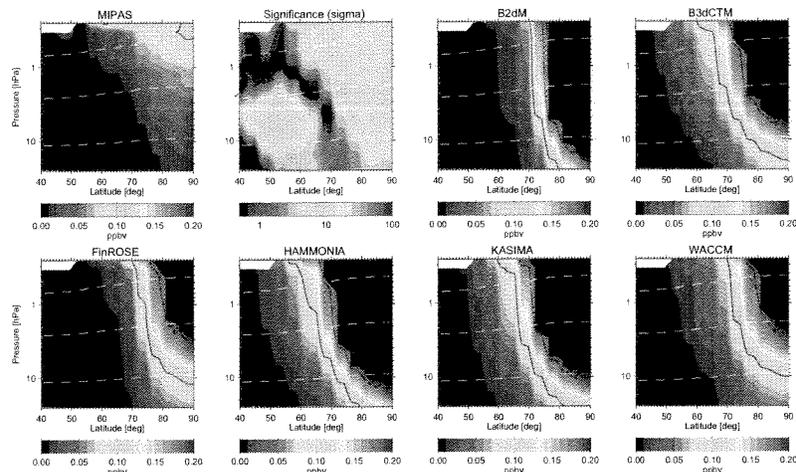


and is hence - together with  $HNO_4$  - an indicator for SPE-generated  $HO_x$  in the stratosphere. During daytime, it is photolyzed within several hours to a day, or destroyed by the reaction



Chemical nighttime losses are negligible at quiescent conditions. The availability of OH during periods of proton forcing allows for  $H_2O_2$  destruction also at night. These losses, however, are most important above the stratopause. In the dark stratosphere, reaction R11 is expected to deplete  $H_2O_2$  by less than 10%. Therefore, observed  $H_2O_2$  increases are primarily driven by the production mechanism R10.

Model output of  $H_2O_2$  is available from B2dM, B3dCTM, FinROSE, HAMMONIA, KASIMA, and WACCM. Figure 31 shows observed and modeled zonal mean  $H_2O_2$  changes during the period of the main SPEs (28 October–4 November). The observed increases of up to 0.1 ppbv are considerably overestimated by the simulations by a factor of 4–7. This huge difference between observed and modeled  $H_2O_2$  increases can hardly be explained by a possible overestimation of the ionization rates by a factor of 1.2–2, as suggested from the comparison of  $NO_y$  increases. Although



**Fig. 31.** Zonal mean  $\text{H}_2\text{O}_2$  changes with respect to 26 October averaged over the period 28 October–4 November in MIPAS observations and model simulations. Solid contour lines reflect 0.1 ppbv steps. The significance of observed  $\text{H}_2\text{O}_2$  changes (in units of  $\sigma$ ) is shown in the upper second panel (from the left).

$\text{H}_2\text{O}_2$  production depends quadratically on  $\text{HO}_2$ , total  $\text{HO}_x$  scales with the square root of the ionization rate due to reaction R9, being the principal chemical loss mechanism at nighttime. Thus, 4–7 times lower ionization rates would be required in order to reduce modeled  $\text{H}_2\text{O}_2$  increases to the observed values. As already mentioned in the discussion of  $\text{HNO}_4$  enhancements, the availability of  $\text{HO}_2$  during nighttime SPE conditions is largely controlled by the  $\text{HO}_x$  partitioning. At the peak height of the  $\text{H}_2\text{O}_2$  increases (0.5–1 hPa), this dependence is even more pronounced than at the pressure levels of the  $\text{HNO}_4$  enhancements (2–3 hPa) due to the increasing OH contribution to  $\text{HO}_x$  with altitude. Thus, the disagreement of observed and simulated  $\text{H}_2\text{O}_2$  hints at an underestimation of the OH/ $\text{HO}_2$  ratio in the upper polar stratosphere during the proton forcing. Alternatively,  $\text{H}_2\text{O}_2$  formation by reaction R10 might be significantly overestimated in the models.

Meridional transport to illuminated latitudes, where  $\text{H}_2\text{O}_2$  is photochemically destroyed, could also affect the magnitude of the SPE-related enhancements.  $\text{H}_2\text{O}_2$  distributions simulated by B2dM, which has a very strong mixing barrier, might hence experience less photochemical losses than in other models. In fact, B2dM enhancements are more confined to the polar night region. Other models, however, show a similar meridional distribution as observed by MIPAS. It is thus unlikely, that differences in the efficiency of photochemical losses related to transport can explain the pronounced differences between observed and modeled  $\text{H}_2\text{O}_2$  enhancements.

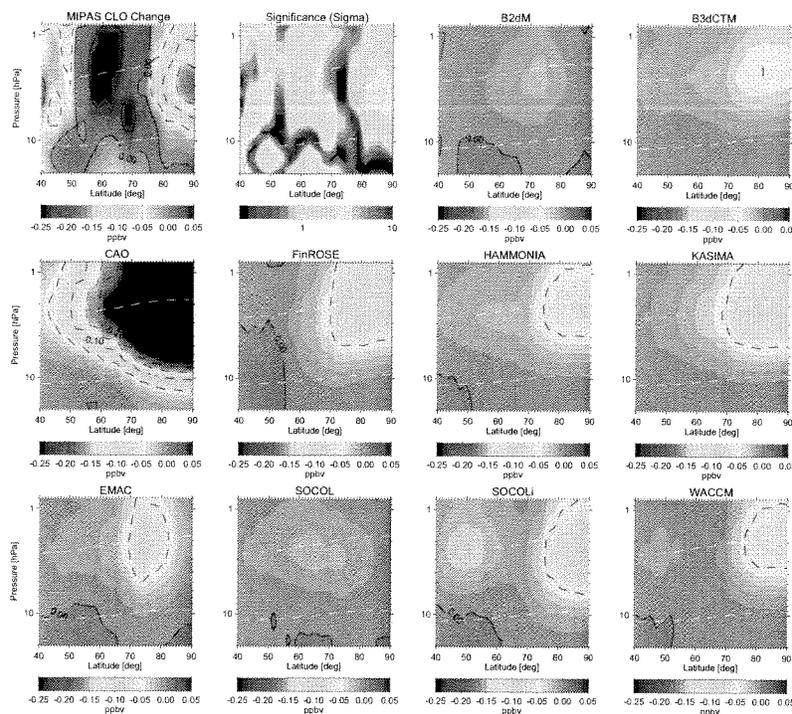
## 6.6 Enhancements and repartitioning of chlorine species

Enhancements of the chlorine species ClO, HOCl, and ClONO<sub>2</sub> have been detected by MIPAS in the aftermath of the Halloween SPE in the NH polar stratosphere (von Clarmann et al., 2005; López-Puertas et al., 2005b). Short-term ClO and HOCl increases of the order of 0.2 ppbv occurred immediately after the onset of the proton forcing on 29 October. ClONO<sub>2</sub> increases up to 0.4 ppbv appeared approximately 2 days later, remaining in the stratosphere for several weeks. SPE-related HOCl increases have also been observed by MLS on Aura during the January 2005 proton event (Damiani et al., 2008). These enhancements were accompanied by a HCl decrease of similar magnitude, thus clearly demonstrating SPE-induced chlorine activation. The conversion of HCl to active species occurred in presence of enhanced OH via the reaction



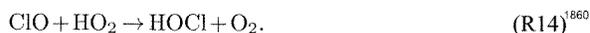
HCl can also be incorporated into negative ions, from which chlorine is released mainly in the form of atomic chlorine or chlorine monoxide. There are also reverse reactions releasing HCl, however, it has been shown in a recent publication (Winkler et al., 2009) that during large solar proton events, chlorine activation dominates, and negative ion reactions can act as a significant sink of HCl, and a source of active chlorine. Atomic chlorine is rapidly converted to ClO by





**Fig. 32.** Zonal mean ClO changes during the main proton forcing (29–31 October) with respect to 26–27 October in MIPAS observations and model simulations. Solid contour lines reflect 0.05 ppbv steps. The significance of observed ClO changes (in units of  $\sigma$ ) is shown in the upper second panel (from the left).

In the polar night stratosphere, where SPE-generated  $\text{HO}_x$  is dominated by  $\text{HO}_2$ , ClO is further converted to HOCl:

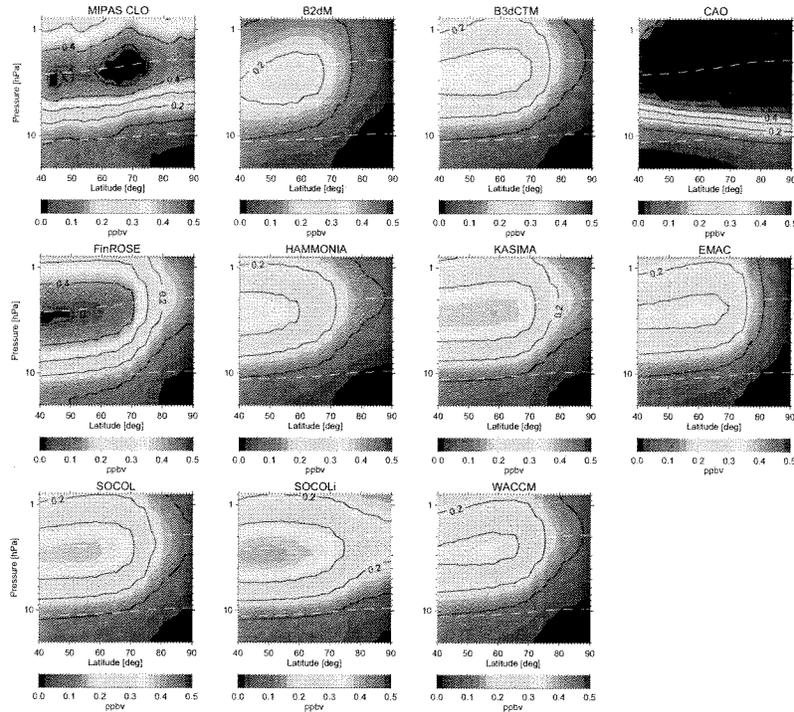


1840 The chemical lifetime of nighttime HOCl is very long below the stratopause. Above and at sunlit conditions, HOCl is removed by the reaction



and rapid photo-dissociation during daytime. Due to the high  $\text{HO}_2/\text{OH}$  ratio in the nighttime stratosphere under SPE conditions, active chlorine is expected to be mainly in the form of HOCl due to reaction R14. Hence, ambient ClO should be reduced in contrast to the results obtained by von Clarmann et al. (2005) from MIPAS observations during the Halloween SPE. On the other hand, OH is the dominant  $\text{HO}_x$  constituent during daytime and HOCl is quickly photolyzed even at high solar zenith angles. ClO enhancements might hence occur in the illuminated stratosphere, if SPE-related  $\text{HO}_x$  increases were well above the background concentration. In fact, the ClO enhancements observed by MIPAS on 29–30 October 2003 (von Clarmann et al., 2005) took place outside the polar night region.

The mid-term evolution of polar ambient ClO during the period of the Halloween event is characterized by a continuous decrease related to seasonal variations (see Fig. 3) which makes the analysis of SPE-induced changes on a longer timescale difficult. Therefore, we restrict our analysis to the period of the main proton event on 29–31 October. Figure 32 shows observed and modeled changes of the ClO zonal mean distribution, averaged over these days, with respect to 26–27 October. ClO increases of  $\sim 0.1$  ppbv are found in the MIPAS observations at latitudes around  $60^\circ\text{N}$  in qualitative agreement with the previous analysis of von Clarmann et al. (2005). These enhancements are reproduced by none of the models. Evidently, simulated daytime  $\text{HO}_x$  increases are too small compared to the ambient  $\text{HO}_x$  abundances to alter noticeably the ClO availability. Although the observed enhancements are significant at the  $2\sigma$ -level with respect to the average measurement precision (see Fig. 32, second panel), this important difference between the observations and the simulations should be carefully interpreted due to a possible systematic bias related to gain calibration errors in the measurements (see Section 2), particularly because the observed ClO change has been calculated from temporal aver-



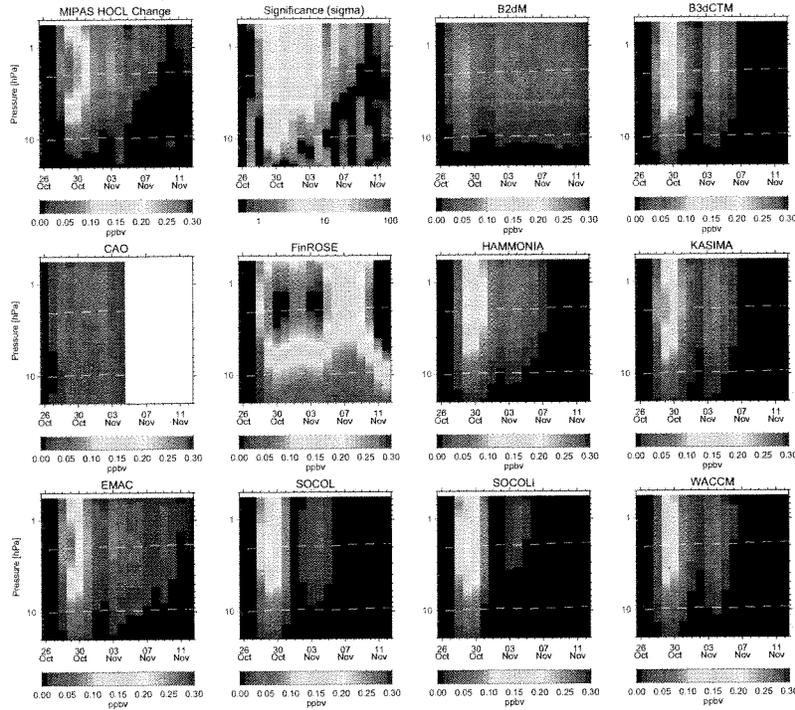
**Fig. 33.** Zonal mean ClO vmrs before the SPE 26–27 October from MIPAS observations and model simulations. Solid contour lines reflect 0.1 ppbv steps.

ages belonging to different gain calibration periods. In the polar night region, both, observations and models show a ClO decrease. The observed ClO reduction of up to 0.2 ppbv<sub>1905</sub> is considerably underestimated by the simulations, except for CAO. The latter model overestimates the ClO reduction by approximately a factor of 10. The unreasonably large ClO depletion in CAO is related to a high ClO availability before the SPE and goes along with a ClONO<sub>2</sub> buildup of a similar magnitude (see below). The reason for the higher background ClO concentrations in this particular model is still under investigation. In contrast to the observations, the ClO decreases obtained by B2dM, EMAC, and SOCOL are not pole-centered but shifted slightly to lower latitudes. The remaining models (except CAO) produce a very similar ClO<sub>1915</sub> signal.

The differences of observed and modeled ClO changes at latitudes poleward of 70°N are related to the background ClO abundances. Fig 33 shows the zonal mean distributions of ClO vmrs on 26–27 October prior to the onset of the proton forcing. ClO vmrs of more than 0.4 ppbv have been observed around 2 hPa in the entire NH with a slight decrease poleward of 70°N. Maximum abundances were found at 60–70°N, exactly at the same latitudes where the ClO in<sub>1925</sub>

creases during the following days occurred. Although we cannot exclude that the observed ClO in this latitude range is affected by gain calibration errors, this coincidence is somehow remarkable. In principle, the enhanced ClO abundances around 60–70°N can be related to differences in the latitudinal distributions of daytime OH and O, the first being responsible for ClO production and the latter for ClO removal.

Modeled ClO abundances do not show this enhancement around 60–70°N. Simulated ClO vmrs are also generally lower by 50% than those observed by MIPAS (except for FinROSE and CAO) and exhibit a pronounced decrease towards the polar night region. In some models (e.g., B2dM and EMAC) ClO has disappeared nearly completely at the pole. It is thus not surprising, that modeled ClO depletions at 70–90°N are less pronounced than in the observations in absolute terms. The much stronger modeled decrease of ClO towards the polar night region during pre-SPE conditions seems to be related to an overestimation of ClO losses. Since the sequestering into the Cl<sub>2</sub>O<sub>2</sub> dimer is inefficient around 2 hPa and simulated HOCl or ClONO<sub>2</sub> distributions before the SPE do not indicate a conversion of ClO to these species, it is most likely that ClO is more efficiently converted to HCl than indicated by the observations. The faster conversion in



**Fig. 34.** Temporal evolution of area-weighted averages of relative HOCl changes with respect to 26 October 2003 in MIPAS observations and model simulations at 70–90°N, as well as differences between modeled and observed averages. The significance of observed HOCl changes (in units of  $\sigma$ ) is shown in the upper second panel (from the left).

the models might be related to the reaction path  $\text{ClO} + \text{OH} \rightarrow \text{HCl} + \text{O}_2$  which has an uncertainty of its rate constant of several 100% (Sander et al., 2006). However, also dynamical reasons (i.e., differences in the magnitude of meridional mixing) cannot be excluded.

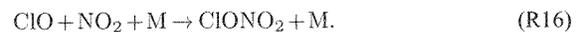
The temporal evolution of observed and modeled HOCl changes at 70–90°N until mid November is shown in Fig. 34. HOCl started to increase rapidly on 29 October, reaching values around 0.25 ppbv, and diminished after 1 November within a few days. A smaller second increase occurred on 3 November related to the second, weaker SPE. The simulations show generally smaller enhancements (approximately 30% less on average), except FinROSE. This model overestimates significantly the observed enhancements by nearly a factor of 2. There, HOCl abundances remain enhanced after the SPE for nearly one week and show a second, even more pronounced enhancement around 11 November.

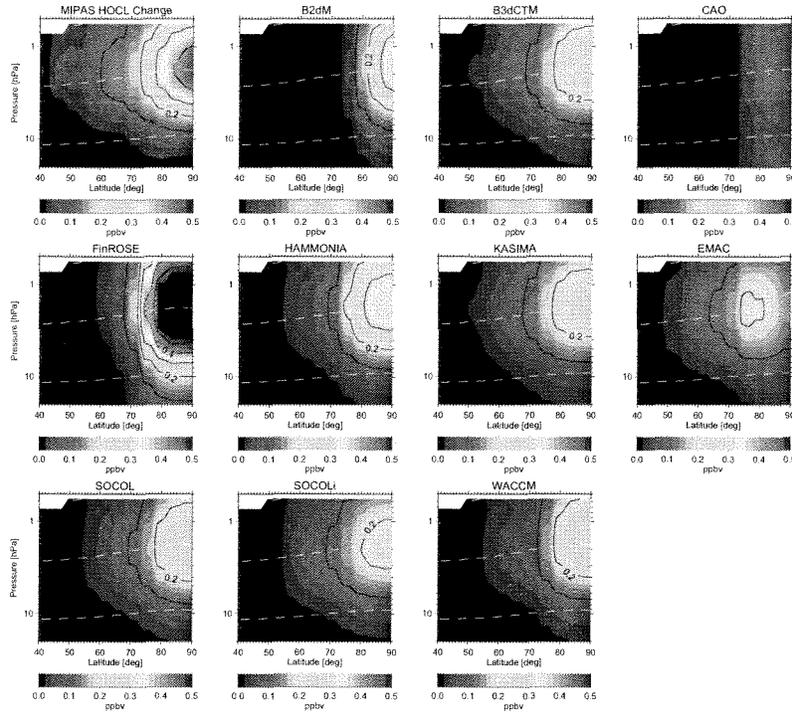
Figure 35 shows observed and modeled changes of the HOCl zonal mean distribution averaged 29–31 October with respect to 26–27 October. The pronounced anti-correlation of HOCl increases and ClO decreases (compare Figures 35 and 32) indicates that ambient ClO is quickly converted to

HOCl via reaction R14 during nighttime in the presence of proton forcing. However, HOCl increases are higher than the corresponding ClO losses, resulting in a net increase of active chlorine by approximately 2 ppbv in the observations and most of the models. This can be explained by SPE-related chlorine activation via reaction R12. FinROSE, however, overestimates the chlorine activation by a factor of 3.

The sharp decline of the HOCl enhancements after the proton forcing observed by MIPAS, and also reproduced by most models, must occur in the sunlit atmosphere close to the polar night terminator, since losses via reaction R15 are negligible in the polar night stratosphere after the SPE. This is also the reason for the relatively long lifetime of the HOCl enhancements in B2dM where meridional redistribution is weak. This is not the case in the FinROSE model. There, the long lifetime of the HOCl enhancements related to the SPE, as well as the second buildup around 11 November, seem to be caused by an underestimation of chemical losses of HOCl.

$\text{ClONO}_2$  increases, occurring approximately two days after the SPE, are attributed to the termolecular reaction





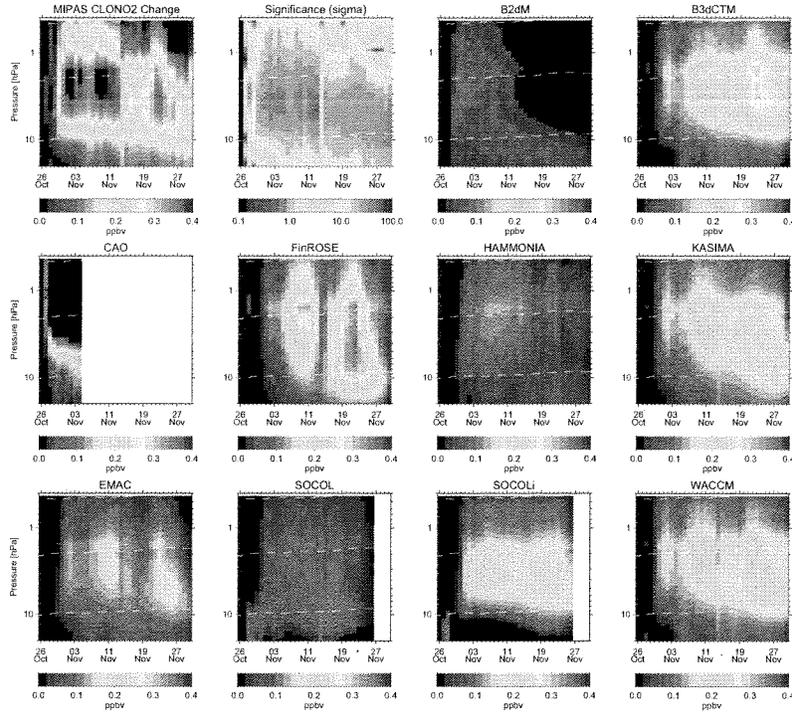
**Fig. 35.** Zonal mean HOCl changes during the main proton forcing (29–31 October) with respect to 26–27 October in MIPAS observations and model simulations. Solid contour lines reflect 0.1 ppbv steps.

1970 ClONO<sub>2</sub> is removed mainly by photolysis in the sunlit atmo-  
 sphere and, to a lesser extent, by reaction with atomic oxy-  
 gen. Due to its pressure dependence, ClONO<sub>2</sub> formation by  
 reaction R16 is more effective at lower altitudes. Enhanced  
 NO<sub>2</sub> availability related to the SPE, however, is increas-  
 1975 ing with altitude, leading to a peak height of the observed  
 ClONO<sub>2</sub> enhancements around 3 hPa (~36 km). This is  
 slightly higher than reported by López-Puertas et al. (2005a)  
 who based their analysis on an older MIPAS ClONO<sub>2</sub> data  
 version than used here.

1980 The temporal evolution of observed and modeled  
 ClONO<sub>2</sub> changes at 70–90°N until the end of November is  
 shown in Fig. 36. The observed enhancements of 0.4 ppbv  
 after the SPE remained in the stratosphere for about two  
 weeks. After a sudden decrease on 13 November, ClONO<sub>2</sub>  
 1985 abundances raised again on 19 November, reaching a second,  
 weaker maximum around 22 November. The modeled  
 ClONO<sub>2</sub> increases are generally smaller (except CAO, see  
 discussion above) and show a different temporal evolution.  
 The ClONO<sub>2</sub> underestimation in the simulations, particu-  
 1990 larly during the first enhancement starting on 1 November,  
 is related to the reduced ClO availability compared to the  
 observations. Figure 37 shows the corresponding zonal mean

distribution of the observed and modeled ClONO<sub>2</sub> enhance-  
 ments averaged over 1–5 November. From the observations,  
 it is clear that ClONO<sub>2</sub> is principally formed in the polar  
 night region where high NO<sub>2</sub> abundances are available and  
 no photochemical losses occur. Most of the model simula-  
 tions, except CAO, SOCOLi and WACCM, show negligi-  
 ble enhancements there. Instead, ClONO<sub>2</sub> formation occurs  
 around 70°N, where daytime losses are still small but ClO  
 is available, however, with a considerably smaller magni-  
 tude than observed. SOCOLi and WACCM simulations, which  
 have a similar latitudinal distribution of ClONO<sub>2</sub> changes as  
 observed, exhibit higher ClO abundances in the polar night  
 region than other models.

The observed temporal evolution of the ClONO<sub>2</sub> changes  
 in the second half of November is better captured by mod-  
 els based on ECMWF- and MERRA-driven meteorology up  
 to the stratosphere (i.e., B3dCTM, FinROSE, KASIMA, and  
 WACCM), which hints at a strong impact of vortex dynam-  
 ics on the ClONO<sub>2</sub> abundances. Wave-driven vortex ex-  
 cursions to illuminated latitudes, alternated by reformation  
 of a pole-centered vortex, are mainly responsible for the  
 ClONO<sub>2</sub> variability and particularly for the decrease around  
 16 November. The descending NO<sub>2</sub> layer, formed during the



**Fig. 36.** Temporal evolution of area-weighted averages of relative ClONO<sub>2</sub> changes with respect to 26 October 2003 in MIPAS observations and model simulations at 70–90° N, as well as differences between modeled and observed averages. Contour lines reflect 0.5 ppbv steps. The significance of observed ClONO<sub>2</sub> changes (in units of  $\sigma$ ) is shown in the upper second panel (from the left).

SPE, acts as a reservoir for continuous ClONO<sub>2</sub> formation in the following weeks after the SPE. Due to the reduced ClO availability in the polar stratosphere towards the end of November, additional ClONO<sub>2</sub> buildup is observed only around 60–70°N, in agreement with most of the model re-2040 sults (not shown). B2dM and HAMMONIA, however, show very small ClONO<sub>2</sub> increases in the second half of November. In the first model, this is related to the confinement of the NO<sub>2</sub> layer to high latitudes, where no ClO is available. In the latter model, strong meridional mixing led to a dilution of the SPE-generated NO<sub>2</sub> layer, such that insufficient NO<sub>2</sub> was available for additional ClONO<sub>2</sub> buildup. 2045

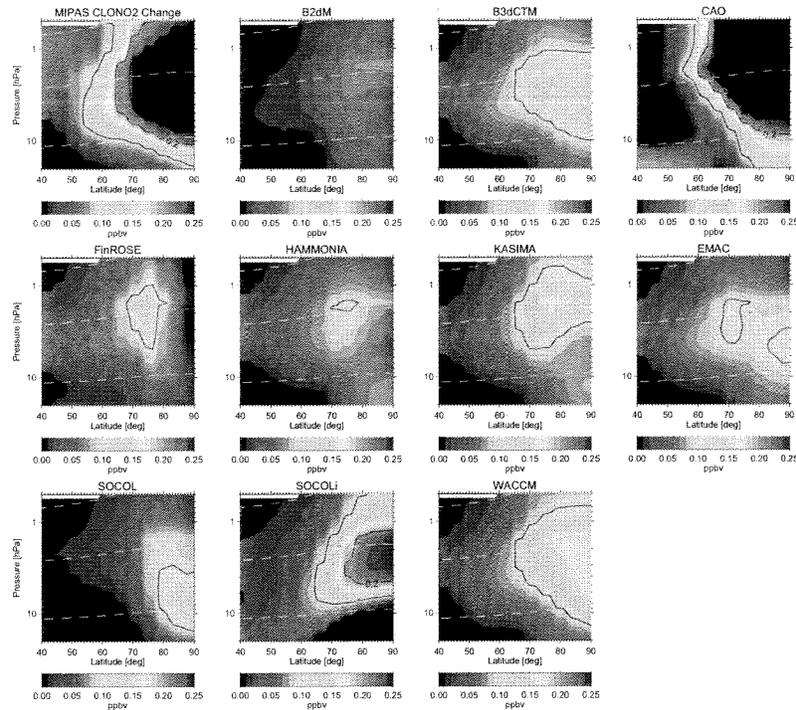
### 7 Conclusions

We have compared stratospheric and mesospheric composition changes observed by MIPAS in the NH during and after the Halloween proton event with simulations performed with state-of-the-art atmospheric GCM and CTM models. The large number of models participating in the intercomparison exercise allowed for an evaluation of the overall ability of atmospheric models to reproduce observed atmospheric 2050 2055 2056

perturbations generated by SPEs, particularly with respect to NO<sub>y</sub> and ozone changes. This model validation represents a mandatory first step towards an accurate implementation of particle precipitation effects in long-term climate simulations. It has also allowed to test and identify deficiencies in the chemical schemes, particularly with respect to nitrogen and chlorine chemistry, being relevant for stratospheric ozone.

Observed SPE-related short-time increases of the minor species HNO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> have been identified for the first time and are qualitatively reproduced by the simulations. The observed enhancements of 0.2 and 0.1 ppbv, respectively, are overestimated by the models on average. Both observations and simulations give further evidence for an SPE-induced CO depletion. A clear isolation of these chemical losses from dynamical variability, however, is difficult.

In general, atmospheric models are able to reproduce most of the observed composition changes. In particular, simulated SPE-induced ozone losses agree within 5% with the observations on average. This excellent agreement is found on a short-term scale (HO<sub>x</sub>-driven) in the mesosphere, as well as on a mid-term scale (NO<sub>x</sub>-driven) in the stratosphere. Sim-



**Fig. 37.** Zonal mean  $\text{ClONO}_2$  changes after the main proton forcing (1–5 November) with respect to 26–27 October in MIPAS observations and model simulations. Solid contour lines reflect 0.1 ppbv steps up to 0.6 ppbv and 0.2 ppbv steps above.

ulated  $\text{NO}_y$  enhancements around 1 hPa are on average 30% higher than indicated by the observations, while an underestimation of modeled  $\text{NO}_y$  of the same order was found in the mesosphere. The systematic behavior in the stratosphere suggests that these differences are related to the simulated ionization rate profile shape. WACCM simulations without inclusion of electron-induced ionization yield much better agreement with the observations around 1 hPa than the nominal model run including both electrons and protons throughout the period of interest. An upper stratospheric excess  $\text{NO}_y$  production by electron-induced ionization of 5–10 ppbv could be identified from these simulations, particularly after the minor second event around 4–5 November. The excess ozone loss related to electron-induced ionization has been estimated to be around 5%. Again, better agreement with the observations was achieved when excluding the electron contribution to ionization in the WACCM simulations. Our comparisons hence suggest that the modeled electron-induced ionization during the Halloween event is considerably overestimated. This might be related to the uncertainties in constraining the electron energy spectrum from available particle observations.

The impact of chemical NO losses due to reaction with

atomic nitrogen (R2) on the SPE-induced  $\text{NO}_y$  increases has been studied in detail. An important dependence of the net  $\text{NO}_y$  generation on temperature and background  $\text{NO}_x$  due to this mechanism has been identified. In the stratosphere, SPE-related  $\text{NO}_y$  increases are reduced (enhanced) by approximately 10% if temperatures were 10 K lower/higher. This behavior might be of relevance for future implications of SPE effects on climate when considering a stratospheric cooling trend related to climate change. The reduced  $\text{NO}_y$  production efficiency related to reaction R2 also implies limitations for models using family approaches in their chemical schemes, since this mechanism of  $\text{NO}_y$  destruction is not taken implicitly into account in these models.

The analysis of the observed and modeled  $\text{NO}_y$  partitioning in the aftermath of the Halloween SPE has clearly demonstrated the need to implement additional ion chemistry into the chemical schemes. Short-term  $\text{HNO}_3$  increases can only be reproduced by model calculations including ion-ion recombination between  $\text{NO}_3^-$  and  $\text{H}^+$  cluster ions (Veronen et al., 2008). The partitioning of  $\text{HNO}_3$  and  $\text{N}_2\text{O}_5$  in the following weeks after the SPE is significantly underestimated by the models that do not include  $\text{HNO}_3$  formation via water cluster ions (Böhlinger et al., 1983). However, fur-

ther work is required to tune the parameterizations of these mechanisms such that quantitative agreement with the observations can be achieved.

The overestimation of observed  $\text{H}_2\text{O}_2$  and  $\text{HNO}_4$  enhancements by the models hints at an underestimation of the OH/ $\text{HO}_2$  ratio in the upper polar stratosphere during the proton forcing. Further work is required to analyze in detail possible reasons for this behavior. The analysis of SPE-induced changes of the chlorine species ClO, HOCl and ClONO<sub>2</sub> has shown that the encountered differences between models and observations, particularly the underestimation of observed ClONO<sub>2</sub> enhancements, are related to a smaller availability of ClO in the polar region already before the SPE.

In general, the intercomparison has demonstrated that differences in the meteorology and/or initial state of the atmosphere in the simulations causes an important variability of the model results, even on a short timescale of only a few days. The model responses to the proton perturbation thus show a significant spread. On the other hand, this sensitivity of the simulated atmospheric responses to the background conditions, indicated by the spread in the model results, also implies that the real atmosphere response to proton events depends strongly on the actual conditions.

Future HEPPA model-data intercomparison activities will focus on the assessment of indirect effects of energetic particle precipitation related to polar winter descent of upper atmospheric NO<sub>x</sub> generated by electron precipitation. This is motivated, on one hand, by the higher potential of indirect effects to influence middle atmospheric composition on longer time scales compared to direct effects (i.e., SPEs) and, on the other hand, by its large variability related to dynamical modulations, making its representation in current atmospheric models challenging.

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